Multicomponent surface architectures with central perylenediimide stacks

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Abstract
The SOSIP and TSE methodologies were recently introduced to grow complex architectures on ITO surfaces. For the purpose of demonstrating these concepts, the use of NDI chromophores in the starting studies was justified. However, these materials are not in widespread use for organoelectronic applications. On the other hand, PDI chromophores are more common for this purpose. In the present work, we have designed, synthesized and evaluated PDI derivatives for the building of multicomponent architectures on surfaces.

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Multicomponent Surface Architectures with Central Perylenediimide Stacks

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La Faculté des sciences, sur le préavis de Monsieur S. MATILE, professeur ordinaire et directeur de thèse (Département de chimie organique), Monsieur C. MAZET, professeur associé (Département de chimie organique) et N. GIUSEPPONE, professeur (Institut Charles Sadron, Université de Strasbourg, France), autorise l'impression de la présente thèse, sans expirmer d'opinion sur les propositions qui y sont énoncées.

Genève, le 12 novembre 2014

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N.B. - La thèse doit porter la dédicace précédente et remplir les conditions énumérées dans les "Informations relatives aux thèses de doctorat à l'Université de Genève".
A ma famille.
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List of Publications


Summary

The SOSIP and TSE methodologies were recently introduced to grow complex architectures on ITO surfaces. For the purpose of demonstrating these concepts, the use of NDI chromophores in the starting studies was justified. However, these materials are not in widespread use for organoelectronic applications. On the other hand, PDI chromophores are more common for this purpose. In the present work, we have designed, synthesized and evaluated PDI derivatives for the building of multicomponent architectures on surfaces.

We have first prepared initiators \( S_1 \) and \( S_2 \) as well as propagators \( S_3 \) and \( S_4 \), then evaluated their ability to undergo SOSIP and finally studied the generation of photocurrent (Figure S1). Molecules \( S_1 \) and \( S_2 \) rapidly formed compact monolayers on ITO, due to the interaction between their bisphosphonic acid moieties and the metallic ions on the surface. Tert-butyl disulfide groups pointing outward of the monolayers were then converted to thiols upon treatment with dithiotheitol, and then to thiolate by deprotonation with a base. Propagator \( S_3 \), with twisted, dipyrridinly-PDI, was then polymerized on the monolayer containing \( S_1 \). In a similar fashion, propagator \( S_4 \) with a non-substituted, thus planar PDI (\( H,H \)-PDI), was polymerized on the monolayer containing \( S_2 \).
Propagators with strained disulfide rings readily underwent a ring-opening disulfide exchange polymerization, facilitated by preorganizing non-covalent interactions. In optimized conditions, polymerization occurred from thiol-covered surfaces exclusively and not from bare ITO surfaces used as negative control (Figure S2 A). Structural studies showed the formation of smooth films with long-range order that contained PDI chromophores assembled in H aggregates. Functional studies revealed that stacks made of S2 and S4, with planar PDIs, generated much more photocurrent than stacks made of S1 and S3, with twisted PDIs (Figure S2 B).
Figure S2. A) Absorption of architectures as a function of the concentration of propagator S3 (green) or S4 (red). Propagator spontaneously polymerized on monolayers of S1 (■) or S2 (○) but did not on clean ITO surfaces used as control (empty symbols). B) Normalized photocurrent generated by single stacks of S3 (green line) or S4 (red line).

Next, we focused on the installation of coaxial arrays of active materials along the PDI stacks by templated stack exchange (Figure S3). The quasi-planar, dicyano-PDI (CN$_2$-PDI) initiator S5 with lateral NDI “feet” as templates was bound to ITO (Figure S1) and used to initiate the polymerization of propagator S6 with a planar H,H-PDI and lateral benzylhydrazone templates. These already very active single stacks did not respond to ion gating after replacing the benzyl templates by charged peptides.
Figure S3. SOSIP architecture (left) with benzylhydrazone templates (marked as grey circles) is transformed into a double-channel architecture upon stack-exchange with aldehydes S7 to S9.

On the other hand, their exchange with terthiophene S7 or NDIs S8 and S9 yielded supramolecular heterojunctions displaying long-distance charge transport capabilities (Figure S4). In thin films less than 200 nm thick, single- or double-channel architectures showed identical photoactivities. Above a critical thickness \( d_c \) of 300 nm, the photocurrent from single-channel architectures decreased rapidly because charge carrier recombination rapidly increased with increasing distances. However, with coaxial alignment of terthiophenes (S7), the photocurrent increased up to \( d = 500 \) nm, reaching twice the value measured without terthiophenes. With coaxial arrays of NDI S8, the photocurrent increased up to \( d = 600 \) nm and reached three times the values measured without NDI. Finally, with a coaxial alignment of NDI S9, the photocurrent increased continuously up to more than \( d = 1000 \) nm of thickness, reaching almost six times the value measured without NDI.

Results obtained in this work revealed that thick architectures were mandatory in order to evaluate correctly the relevance of PDI chromophores for supramolecular heterojunctions (SHJs). As shown here, in thin systems the
behavior of all the tested architectures was dominated by the activity of the central \(H, H\)-PDI stacks.

![Figure S4](image)

**Figure S4.** Photocurrent as a function of thickness with single \(H, H\)-PDI stacks (empty squares) and double channel architectures with terthiophenes \(S7\) (filled squares), \(O, O\)-NDI \(S8\) (empty circles) and \(H, H\)-NDI \(S9\) (filled circles).

In thick systems however, the beneficial effects of SHJs for efficient generation and transport of charges became apparent. In addition, data evidenced the better charge separation when \(H, H\)-PDI were in contact with n-, rather than p-type semiconductors. This result, together with the gradually increasing activity of architectures with increasingly electron-deficient materials, from \(S7\) to \(S8\) and \(S9\), showed that in our systems, central \(H, H\)-PDI stacks worked better as hole acceptors and transporters, rather than electrons acceptors. \(H, H\)-PDIs are usually considered and used as n-type semiconductors; their activity as p-type material is poorly explored and documented by a few reports, now supported by our results.
Résumé

Les méthodologies SOSIP et TSE ont été récemment développées pour construire des architectures complexes sur des surfaces d’oxyde d’indium et d’étain (ITO). La démonstration de ces nouveaux concepts justifiait l’emploi de chromophores NDI pour les premières études, cependant l’emploi de ces matériaux est peu courant dans les systèmes optoélectroniques organiques. Les chromophores PDI en revanche se sont imposés pour ces applications. Dans ce travail, on a imaginé, synthétisé et évalué des dérivés de PDI pour le procédé SOSIP, puis ont les a employé pour la construction d’architectures à multiples composants sur des surfaces.

On a d’abord préparé les initiateurs $S_1$ et $S_2$ ainsi que les propagateurs $S_3$ et $S_4$ et évalué leur capacités pour le procédé SOSIP ainsi que le la génération de photo-courants (Figure S1). Les molécules $S_1$ et $S_2$ ont rapidement formé des monocouches compactes sur l’ITO, grâce aux interactions entre leurs acides bisphosphoniques et les ions métalliques de la surface. Les groupes disulfures de tert-butyl, dirigés vers l’extérieur de ces monocouches, ont ensuite été transformés en thiols par l’action du dithiothréitol, puis en thiolates par celle d’une base. Le propagateur $S_3$, contenant un PDI substitué par deux pyroles, et donc non-plan, a ensuite été polymérisé à partir de la monocouche faite de $S_1$. De même, le propagateur $S_4$, contenant un PDI non substitué, donc plan, a été polymérisé sur la monocouche contenant $S_2$. 
Les propagateurs ont rapidement subi une réaction de polymérisation par ouverture de leur cycles tendus et échange de disulfures, grâce à la pré-organisation par des interactions non covalentes. Dans des conditions optimisées, la polymérisation avait lieu exclusivement depuis des surfaces préalablement recouvertes de thiols, mais pas depuis l’ITO nu (Figure S2 A). Les études structurales ont montré la formation de films lisses, ordonnés sur de longues distances et contenant des chromophores PDI en agrégats de type H. Les études fonctionnelles ont révélé que les empilements de chromophores PDI
plans, provenant de S2 et S4, généraient bien plus de photo-courant que ceux de PDI non-plans, provenant de S1 et S3 (Figure S2 B).

![Figure S2](image)

**Figure S2.** A) Absorption des architectures en fonction de la concentration des propagateurs S3 (vert) ou S4 (rouge). Les propagateurs polymérisaient spontanément sur l’ITO recouvert d’initiateur S1 (■) or S2 (●) mais pas sur les surfaces d’ITO nu employées comme contrôles négatifs (symboles vides). B) Valeurs normalisées du photocourant généré par des emplacements simples de S3 (courbe verte) ou S4 (courbe rouge).

Dans la suite de ce travail, on s’est concentré sur l’installation, par modification post-SOSIP, d’alignements de matériaux le long des emplacements de PDI centraux (Figure S3). L’initiateur S5 contenant un di-cyano PDI, quasi-plan, avec des « pieds » faits de NDI en guise de gabarits sur ses flancs, a été lié à une surface d’ITO (Figure S1). On l’a employé pour déclencher la polymérisation du propagateur S6, contenant un PDI plan et portant des gabarits latéraux sous forme d’hydrazone de benzyle.
L'activité déjà élevée de ces empilements simples n’a guère été modifiée après remplacement des gabarits benzyles par des peptides chargés. En revanche, leur substitution par les terthiophenes S7 et les NDI S8 ou S9 a produit des hétérojonctions supramoléculaires capables de transporter des charges sur de longues distances (Figure S4). Pour des films de moins de 200 nm d’épaisseur, les configurations à simple ou double canaux ont montré des performances identiques. Au-dessus de la distance critique $d_c = 300$ nm, le photo-courant produit par les empilements simples de PDI a rapidement chuté, parce que la recombinaison des porteurs de charges augmentait rapidement avec l’épaisseur. Par contraste, en présence d’alignements coaxiaux de terthiophenes (S7), le photo-courant a augmenté jusqu’à une épaisseur de 500 nm, atteignant en ce point deux fois la valeur mesurée sans terthiophenes. Avec un alignement coaxial de NDI S8, le photo-courant a augmenté jusqu’à une épaisseur de 600 nm et en ce point atteignait trois fois la valeur mesurée sans NDI. Finalement, avec un alignement coaxial de NDI S9, le photo-courant a augmenté continuellement jusqu’à plus de 1000 nm d’épaisseur, atteignant en ce point près de six fois la valeur mesurée sans NDI.
Figure S4. Photocourant en fonction de l’épaisseur du film pour l’architecture à canal unique (□) et architecture à double canal avec le terthiophene S7 (■), le O,O-NDI S8 (○) et le H,H-NDI S9 (●).

Les résultats obtenus ont révélé que l’évaluation correcte de la performance des chromophores PDI dans des hétérojonctions supramoléculaires requérait l’examen d’architectures épaisses. En effet, dans des systèmes fins, l’activité de toutes les architectures était dominée par la contribution des empilements de PDI centraux. Plus généralement, ces résultats ont confirmé l’importance des hétérojonctions supramoléculaires pour la génération et le transport efficaces de charges dans les photosystèmes organiques. Les données expérimentales ont aussi mis en évidence une meilleure séparation des charges lorsque les PDI étaient en présence de semi-conducteurs de type n plutôt que p. Ce résultat, ainsi que l’augmentation graduelle de l’activité des architectures contenant des matériaux de plus en plus électro-attracteurs, de S7 à S8 et S9, ont montré que dans nos systèmes, les empiements centraux de PDI fonctionnaient mieux.
comme accepteurs et transporteurs de charges positives, plutôt que d’élèctrons. Habituellement, les PDI sont utilisés comme semi-conducteurs n ; leur activité comme matériaux p, peu explorée, est documentée par quelques rares rapports auxquels viennent maintenant se joindre nos résultats.
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Chapter 1

INTRODUCTION

In the last centuries, scientific discoveries and technical advances have made possible the fabrication of a growing variety of objects. By using mechanical machining and related processes, it is possible to shape very small pieces (~ 1 µm) from a macroscopic amount of material. This is the so-called top-down approach to structures of small size. On the other hand, synthetic chemistry allows the assembly of atoms into larger molecules which are objects with dimensions ranging from a few Ångstroms up to a few nanometers. This is the so called bottom-up strategy. However, our ability to construct objects of intermediate size (e.g., of the size of a protein, or a virus) using one or the other approach is still limited. Most importantly, the attainable complexity and precision of these man-made objects is incomparably lower than what biological organisms can do.

1.1. Organic Photosystems

The fabrication of organic photosystems is one representative field in which the discrepancy between biological and artificial synthesis capabilities is very apparent. The development of organic photovoltaics (OPVs) attracted a lot of research interest in academia and industry because it promises cheap, lightweight and flexible solar cells from easily processable materials.\[^{1-2}\] In those devices, two organic materials, one electron acceptor (A) and one electron donor (D), are brought into contact. Not only electron rich or deficient, these materials are also n- and p-type semiconductors, meaning that the electron acceptor displays high electron mobility \(\mu_e\) and the electron donor high hole mobility \(\mu_h\). Moreover, the materials have molar absorption coefficients (\(\varepsilon\)
as high as possible for efficient light collection. The generation of photocurrent in organic devices involves four basic steps (Figure 1)\(^3\).

**Figure 1.** Schematic representation of a heterojunctions between electron donor and acceptor materials sandwiched between cathode and anode electrodes. 1) Light absorption and formation of the electron-hole pair (exciton); 2) Diffusion of the exciton; 3) Charge separation; 4) Charge transport and collection at the respective electrodes. Adapted from ref. [2].

Firstly, an organic chromophore absorbs light and is excited with the simultaneous promotion of one electron from the HOMO to the LUMO of the molecule. One hole (a positive charge) is left behind in the HOMO. The obtained electron-hole pair is called an exciton and can’t dissociate at room temperature (RT): the coulombic attraction between the opposite charges is much higher than the average energy per exciton at RT \(k_B T\) (where \(k_B\) is the Boltzmann’s constant and \(T\) is the temperature) and the dielectric constant of organic materials is low. Excitons randomly diffuse in the layer and can be dissociated into free charge carriers when they reach the D-A interface because there, the driving force for the transfer of one hole from the HOMO of A into the HOMO of D, or one electron from the LUMO of D to the HOMO of A is sufficient to counterbalance the coulombic attraction between the charges. Finally, the free electrons and holes are conducted along the n- and p-type semiconductors and reach to the collecting electrodes.
Among several parameters that have to be considered in the development of photovoltaic devices, the power conversion efficiency (PCE, $\eta$) is crucial. PCE is defined as the ratio of maximum device output power density ($P_{\text{out}}$) to the irradiation intensity ($P_{\text{in}}$) as follows:

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}} \quad \text{(Equation 1)}$$

As it appeared, the PCE of a device is very much depends on the microstructures adopted by the selected organic materials. This is because the photogenerated excitons are short lived species with diffusion length limited to a few tens of nanometers only. If they don’t encounter a D-A interface within this range, they recombine unproductively and PCE is decreased. Therefore, the area of contact between the donor and acceptor materials has to be maximized while maintaining the integrity of continuous channels for the conduction of charges to the electrodes. To a large extend, the current strategies for the manufacturing of more efficient OPVs rely on top-down approaches and on complicated procedures to optimize the microorganisation of macroscopic quantities of materials.\textsuperscript{[4-5]}

**1.2. Natural Photosystems**

The situation is totally different in the case of natural photosystems. These are highly complex systems prepared from small components (amino acids, chromophores, small molecules) that assemble into larger architectures (40 kDa proteins, length of more than 100 Å). This is a typical case of bottom-up construction.

Structural, photophysical and electrochemical studies on the reaction centers of purple bacteria (Rhodopseudomonas viridis)\textsuperscript{[6]} and green plants (Photosystems I and II)\textsuperscript{[7]} have unraveled their mechanism of action. Solar light is absorbed by arrays of chromophores and funneled toward a cofacial, symmetric pair of chlorophylls ($a_1$ and $a_2$, Figure 2) by very efficient energy
transfer steps. This “special pair” then undergoes a symmetry-breaking charge separation, a process that separates one electron and one hole (or positive charge). Before these mutually attracted species recombine and dissipates their energy as heat, a charge transfer cascade of electron acceptors (chlorophylls $a_3$, pheophytin $a_4$ and quinones $a_5$ and $a_6$, Figure 2) and donors (tyrosine $d_1$ and manganese cluster $d_2$, Figure 2) rapidly transport the charges in opposite directions.

**Figure 2.** A) Architecture of biological photosystems, with electron and hole transfer cascades. $e^-$ = electron; $h^+$ = hole; $a$ = electron acceptors; $d$ = electron donors = hole acceptors; $a_4/a_5$ = chlorophyll special pair; $a_6/a_6$ = quinones. B) Corresponding energetic levels of HOMO (solid) and LUMO (dashed). Dashed arrow = electronic transition. Adapted from ref. [8].

The high performance of natural photosystems is directly related to the precise organization of their multiple components. Firstly, efficient light collection is ensured by the efficient energy transfer between multiple chromophores maintained in precise orientations. Secondly, charge separation is efficient because the chlorophylls in the special pair are maintained in appropriate position. Thirdly, losses from electron and holes recombination are prevented by donor-acceptor transfer cascades and unidirectional charge transport. All this guarantees the high quantum yield of photosynthetic processes, which is the ratio of the number of electrons produced to the number of photons absorbed by the photosystems. In photosystem II, this yield is already impressive at 85% whereas in photosystem I, it is even quantitative.\(^7\)
1.3. Bioinspired Photosystems

As it was explained above, in natural photosystems excitons don’t need to diffuse before they dissociate because the site where they form is also the one where they dissociate. In a bioinspired photosystems, each donor (D) would be positioned next to an acceptor (A) so that photoexcitation of any component would yield separated charges with a high probability (Figure 3 A and B). However, as in natural photosystem, continuous pathways should be preserved for efficient charge collection. This architecture is called here a p/n-supramolecular heterojunction (SHJ). In practice, preparation of p/n-SHJ is hampered by the spontaneous tendency of D and A materials to form D-A charge-transfer complexes, rather than to segregate into distinct aggregates. In D-A complexes, charge separation is optimal but charge mobility is hampered because no transport pathway exist (Figure 3 C).

![Figure 3](image)

**Figure 3.** Supramolecular organization of donor and acceptor materials. A) Schematic representation of a p/n-SHJ. $e^-$ = electron; $h^+$ = hole; $a^-$ = electron acceptors; $d^+$ = electron donors = hole acceptors. B) Corresponding energetic levels of HOMO (solid) and LUMO (dashed). Dashed arrow = electronic transition. Electrons and holes are transferred to the final acceptors (electrodes, gray dots). C) Donor-acceptor complex. Adapted from ref. [8].

In SHJ architectures, charge separation and mobility are optimized, however the photogenerated holes and electrons then diffuse non-directionally along the charge-transporting channels and can therefore recombine. In natural photosystems, random diffusion of charge carriers and recombination is prevented by antiparallel redox gradients. To reproduce this mechanism in
artificial photosystems, p/n-SHJ with antiparallel redox gradients are requested. Additionally, broad absorption in the solar spectrum is achieved only by using multicolored, thus multichromophoric systems. Finally, orientation of the photosystem toward an electrode, for example would mimic the orientation of natural photosystems in lipid bilayers. Therefore a fully bioinspired artificial photosystem would be an p/n-SHJ with oriented, multicomponent antiparallel redox gradients (OMARG SHJ) (Figure 4 A and B).

![Figure 4. OMARG SHJ. A) Schematic representation of an OMARG SHJ. e⁻ = electron; h⁺ = hole; a = electron acceptors; d = electron donors = hole acceptors. The gray horizontal bar at the bottom stands for a supporting surface. B) Corresponding energetic levels of HOMO (solid) and LUMO (dashed). Dashed arrow = electronic transition. Adapted from ref. [8].](image)

Construction of artificial p/n-SHJs and OMARG architectures remains very challenging today because the methods needed for their synthesis and characterization are still underdeveloped. The assembly of nanoarchitectures from a bottom-up approach starts indeed with the preparation of small building blocks for which classical organic synthetic and analytical methods are perfectly suited. However, assembly of larger architectures cannot rely only on classical covalent and step-by-step synthesis because of the tedious synthetic routes and the rapidly dropping yields. Rather, the approaches proposed up to now have combined covalent synthesis with supramolecular chemistry, self-
recognition and dynamic, reversible interactions to assemble multiple small building blocks into larger structures.[10]

1.4. Characterization of Photosystems

The characterization of (photoactive) nanoarchitectures is complicated by their size and multicomponent nature. It requires the combination of a variety of analytical, structural and functional studies. Spectroscopic methods, such as electronic absorption and fluorescence as well as vibrational spectroscopy, can be applied to characterize the interaction between the materials in the assemblies, and morphology can be studied by optical and atomic force microscopy (AFM). Diffusion-ordered (DOSY) or nuclear Overhauser effect (NOESY) spectroscopies are NMR techniques suited for the determination of structures in solutions, as is also osmometry. Size of nanoobjects in liquid suspension was probed by dynamic light scattering. Structural details in the solid phase, in crystals or powders are best revealed by X-ray diffraction techniques. From a functional point of view, electron and energy transfer mechanisms in photosystems can be studied by steady-state or time-resolved spectroscopic methods. However, probing the photovoltaic activity of these functional architectures, by the measurement of photogenerated electrical currents, is the most informative way to understand their microscopic organization.[11]

When a photosystem is irradiated with light, it absorbs the wavelengths that overlap with its absorption spectrum. Charges are generated according to the mechanism described above and can be collected in an external circuit by appropriate electrodes. Immobilization of photosystems on transparent conducting materials, such as indium-tin oxide (ITO), is common since they can be used then for implementation in engineered devices, such as solar panels or screens. However, for routine testing, these functionalized electrodes are conveniently implemented in robust electrochemical setups inspired from the
dye-sensitized solar cells (Figure 5 A).\textsuperscript{112} The photosystem itself is linked to a measurement apparatus by one solid electrode (e. g., ITO) and one wet electrode constituted by a platinum wire and a solution of a mobile charge carrier. This carrier is either an electron donor (such as electron-rich triethanolamine, TEOA) or acceptor (such as electron-poor methylviologen, MV), that undergoes electron transfer reactions with the photosystem and the wire. Photocurrent $I$ arises when the photosystem is irradiated with light (Figure 5 B). Photocurrent density $J$ is a normalized value derived from $I$ and is useful in order to compare several photosystems (Equation 2).

$$J = \frac{I}{A_c}$$  \hspace{1cm} (Equation 2)

Where $A_c$ is the area of the photosystem simultaneously irradiated with light and in contact with the solution of charge carrier.

\textbf{Figure 5.} Functional evaluation of photosystems. A) Electrochemical cell for anodic photocurrent measurements with soluble electron donor X. The photosystem (red surface) is assembled on a conducting electrode (grey surface) and connected to a potentiostat through metallic connectors (black lines). The setup is dipped in a solution of X (blue) in a glass cell (cylinder) and irradiated with light (yellow). $e^-$ = electron; X = charge carrier, neutral form; $X^+$ = charge carrier, radical cation; $h\nu$ = incident photons. B) Typical photocurrent density $J$ as a function of time $t$. On this example, anodic photocurrent (positive $J$) arises when light is turned on (white stripes) and vanishes when irradiation is turned off (grey stripes). C) Typical $J$-$V$ curve recorded from a photosystem irradiated with light and indication of $J_{SC}$, $V_{OC}$, $J_{max}$ and $V_{max}$ (see text for details). The red rectangle represent the maximal power generated by the photosystem in operating conditions.
The photocurrent density $J$ produced by a photosystem under irradiation with light is dependent on the voltage $V$ applied at the electrodes (Figure 5 C). From the obtained $J$-$V$ curves, the open-circuit voltage $V_{OC}$, the short-circuit current density $J_{SC}$ and the fill factor FF are obtained. In principle, $V_{OC}$ is related to the energy difference between the HOMO of the donor material and the LUMO of the acceptor material. It increases with increasing energy gap. $J_{SC}$ depends on the driving force for charge separation and increases with the energy difference between the LUMOs (the HOMOs respectively) of the donor and acceptor in the case of electron injection (hole injection, respectively). FF is defined as the quotient of the maximum power produced by the photosystem under operational conditions, with current density $J_{max}$ and voltage $V_{max}$, and the theoretical power obtained by the multiplication of $V_{OC}$ and $J_{SC}$ (under conditions where the system produces no actual power) (Equation 3).

$$\text{FF} = \left( \frac{J_{max} \cdot V_{max} \cdot 100}{J_{SC} \cdot V_{OC}} \right) \quad \text{(Equation 3)}$$

From a graphical point of view, FF is the ratio of the area of the largest rectangle that fits under the $J$-$V$ curve to the rectangle constructed with $J_{SC}$ and $V_{OC}$. From a physical point of view, FF describes how similar the photosystem to an ideal diode. Values varying from 25% for a linear, “ohmic” $J$-$V$ curve, to 100% for a square, on-off dependence of $J$ on $V$.

$J_{SC}$, $V_{OC}$ and FF are important parameters that primarily define the efficiency $\eta$ of the system (Equation 4).

$$\eta = \frac{V_{OC} \cdot J_{SC} \cdot \text{FF}}{P_{in}} \quad \text{(Equation 4)}$$

Apart from directly quantifying the efficiency of a photosystem, measurement of these parameters for a series of differently organized architectures allows to draw conclusion on the relative performance of each structure and to establish structure-property relationships.
The incident photon-to-current efficiency IPCE is the ratio of the number of electrons produced by the system \( N_e \) to the number of incident photons \( N_\nu \) at a given wavelength \( \lambda \) and is related to \( J_{SC} \) and \( P_{in,\lambda} \) at \( \lambda \) (Equation 5).

\[
\text{IPCE} = \frac{N_e}{N_\nu} = 100 \cdot \frac{1240 \cdot J_{SC}}{\lambda \cdot P_{in,\lambda}} \quad \text{ (Equation 5)}
\]

The IPCE reflects the efficiency with which charges are generated and transported in a photosystem. In addition, plotting IPCE as a function of \( \lambda \) yields the action spectrum, and reveals which parts of the irradiation spectrum are most efficiently converted into charges.

Charge recombination in a photosystem is the destructive mechanism by which the energy of light that has been collected and stored into separated charges is lost.[13-15] The proportion of photogenerated holes and electrons that recombine is an important parameter to evaluate the relevance of a given architecture. It also allows comparing the performances of different systems and drawing conclusion on the way each of them work. Charge recombination can be of mono- or bimolecular type. Bimolecular recombination occurs when two free charge carriers meet at the boundary between n- and p-type materials. The bimolecular recombination efficiency \( (\eta_{BR}) \) is related to the dependence of current density \( J_{SC} \) on \( P_{in} \) through factor \( \alpha \) (Equations 6 and 7).[15]

\[
\eta_{BR} = \alpha^{-1} - 1 \quad \text{ (Equation 6)}
\]
\[
J_{SC} \propto P_{in}^\alpha \quad \text{ (Equation 7)}
\]

It is considered that bimolecular charge recombination is quantitative for \( \alpha = 2 \) (exponential increase of \( J_{SC} \) with \( P_{in} \)) and negligible for \( \alpha = 1 \) (linear increase of \( J_{SC} \) with \( P_{in} \)).

During monomolecular recombination, mobile charges recombine with immobile species of opposite sign that stay blocked in shallow energy traps. Those traps originate from the presence of defect or impurities in the active semiconducting layer.[16] The trapping process is independent from temperature, but de-trapping is a thermally activated event that re-injects the
trapped electrons (or holes) into the conduction (or the valence) band of the material (Figure 6 A).\textsuperscript{[13]} Therefore, de-trapping events are more frequent at high, rather than low temperature and the current concomitantly increases. The signature of monomolecular recombination is an exponential dependence of $J_{SC}$ on the temperature $T$ at which the photosystem is operated (Equation 8).\textsuperscript{[13]}

$$J_{SC}(T, P_{in}) = J_{SC,00} \cdot \exp (-E_a/k_B T) \quad \text{(Equation 8)}$$

Where $J_{SC,00}$ is a factor independent from the temperature, $E_a$ is the trap depth and $k_B$ is the Boltzmann constant. Determination of trap depth $E_a$ gives information on the ease of charge transport and on the integrity of the charge transporting channels.

Figure 6. A) Mechanism of electron (black dot) and hole (circle) trapping in shallow traps. The charge carrier diffuses in the conduction (top, electron) or valence (bottom, hole) band (1) and falls in energy traps (2). The de-trapping process (3) is thermally activated. B) Dependence of the photocurrent density $J$ on the thickness $d$ of a photosystem with indication of the critical thickness $d_C$.

Another important aspect in the perspective of building photosystem is the dependence of the photocurrent density $J$ on the thickness of the system $d$ (Figure 6 B). Typically, $J$-$d$ profiles show an initial linear increase of $J$ with $d$, because the more light is absorbed, the more charges are generated and the highest is the current. However, at a critical thickness $d_C$, $J$ reaches a maximum and then stays constant or even decreases. The reason for this saturation of $J$ comes from increased charge recombination in thick systems, where the probability for a charge to encounter a species with opposite sign increases with
the distance to reach the collecting electrodes. In relationship with the structure of photosystems, $d_C$ is expected to depend on the microorganization of the architectures. Structures that allow the separated transport of holes and electrons along distinct channels, for example, should have higher critical thickness than disorganized architectures with discontinuous channels or photosystems composed of one unique material. Comparing $d_C$ for various systems may indicate their relative level of organization.

1.5. Organic Semiconductors

Research on organic photovoltaics and related electronic devices has led to the discovery, development and characterization of a variety of organic semiconducting materials. These species are conjugated oligo- or polymeric species with conductivities between those of metals and of insulators, and in which the main carriers are electrons or holes in $\pi$ orbitals. Electrical conductivity ($\sigma$) in a material is defined as (Equation 9):[^17]

$$\sigma = n \cdot e \cdot \mu$$  \hspace{1cm} (Equation 9)

where $n$ is the number density of the charge carriers, $e$ is the electronic charge, and $\mu$ represents the charge carrier mobility. For a given charge carrier, $\mu$ (in cm$^2$ V$^{-1}$ s$^{-1}$) is defined as (Equation 10):

$$\mu = \frac{v}{E}$$ \hspace{1cm} (Equation 10)

Where $v$ (in cm s$^{-1}$) is the drift velocity of the charge carriers and $E$ (in V cm$^{-1}$) is the applied electrical field. Charge-carrier mobility is of primary importance in the development of organic photosystems because it limits the photocurrent that can be extracted from a device and numerous techniques have been described in the literature for the determination of $\mu$ in organic semiconductors.[^17]
The electrical properties of these materials are governed by parameters related both to their molecular and structural features and to the arrangement of the materials in the solid state, presence of impurities and defects, etc., on the other hand. Since charge carriers are located in $\pi$ orbitals, all organic semiconductors contain double bonds in their molecular structure. However, charge mobility $\mu$ depends also on the intermolecular overlap between these $\pi$ orbitals, a parameter mainly governed by the molecular packing of the molecules in the solid state. One other important parameter that influences on the transport in a semiconductor is the reorganization energy associated with the charge transfer. In principle, more rigid molecules have lower reorganization energy and thus they transport charges more efficiently. Synthetic organic semiconductors often contain aromatic rings since aromaticity increases both the chemical stability and the rigidity. In addition, extended conjugation yields strong molar absorption coefficients, necessary for photovoltaic applications. However, due to the complex interplay of molecular and bulk parameters influencing the performance of organic semiconductors, so far it has been difficult to draw clear structure-property relationships in this field.

1.5.1. p-Type Semiconductors

p-type, hole-transporting organic semiconductors are electron-rich molecules that undergo facile, reversible oxidation and have high hole mobility ($\mu_h$) (Figure 7). A number of small molecules or polymers have been reported that fulfill these requirements, such as pentacenes (1), phtalocyanines (2), -oligo- and polythiophenes (3), oligo- and poly-phenylenevinlylenes (4), squaraines (5), tri- and polyarylamines (such as 6), and hexabenzocoronenes (7). The record hole mobility of $\mu_h = 43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been recently reported for 2,7-dioctylbenzothienobenzothiophene (C8-BTBT). Among them, oligothiophenes show interesting properties due to their high polarizability and hole mobility, as well as the advantage of small
molecules, namely structural definition, reproducibility and well-developed synthetic routes.\cite{29-30} Hole mobility up to $\mu_h = 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been reported for functionalized oligothiophenes.


1.5.2. n-Type Semiconductors

Fewer are the available n-type organic semiconductors (Figure 8). Fullerene C$_{60}$ (8) and its soluble derivatives, such as the well-known phenyl C$_{61}$ butyric acid methyl ester (PCBM, 9)\cite{31} have been largely used because of their high electron affinity and mobility.\cite{32} These materials have been very successful for the fabrication of organic photovoltaic devices, especially in combination with oligo- or polythiophenes.\cite{33-35} The highest electron mobility reported so far was
\[ \mu_e = 11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \] measured on C\textsubscript{60} crystalline needles.\textsuperscript{[36]} For non-crystalline films of C\textsubscript{60} \textbf{8}, electron mobility as high as \( \mu_e = 6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) have been obtained.\textsuperscript{[32]} However, fullerenes present some drawbacks as well, such as low molar absorption coefficient in the visible range, difficulties to tune their HOMO and LUMO levels and relatively high costs.

![Schematic of molecules](image)

**Figure 8.** Organic n-type semiconductors. A) C\textsubscript{60}, B) PDI, C) PCBM, D) NDI.

To avoid these shortcomings, alternative n-type organic semiconductors were successfully proposed, such as perylenediimides (PDI, \textbf{10}) and naphtalenediimides (NDI, \textbf{11}) (Figure 8).\textsuperscript{[18, 37-42]} These planar, aromatic molecules displayed electron mobility up to \( \mu_e = 7.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for the former\textsuperscript{[43]} and \( \mu_e = 2.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for the latter in OFETs.\textsuperscript{[44]} As a general remark, electron transport capabilities of n-type semiconductors still lag behind those of their p-type counterpart. Moreover, achieving stable electron transport under ambient conditions is still challenging since negative charge carriers are easily trapped by oxygen or water. Materials with very low LUMO levels or containing perfluorinated alkyl chains are needed for successful practical applications.\textsuperscript{[45]}
Beside of n- and p-type semiconductors, materials with ambipolar characteristics have been reported as well. They display both high hole and electron mobilities, depending on the conditions applied. To date, the most successful examples were halogenated or N-containing pentacene derivatives\cite{47} or rubrenes. However, recent experimental and theoretical reports have documented the ambipolar activity of PDI as well. Sariciftci et al. reported balanced electron and hole mobilities of $\mu_e = 7 \cdot 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $\mu_h = 8 \cdot 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively, for organic field-effect transistors (OFETs) assembled from compound 12 (Figure 9).\cite{46} Wasielewski et al. examined the hole and electron transporting properties of a series of PDI by density functional theory (DFT) calculation and identified several molecules with potential ambipolar transport capabilities.\cite{48}

1.6. Perylenediimides

Among the n-type organic semiconductors, the PDI family has attracted much attention due to a collection of attractive features. PDI chromophores have been known since the beginning of the 1910s\cite{49} and recognized for their high chemical and photostability. Structurally speaking, they are constituted by two adjacent naphthalene rings forming a perylene moiety that bears two imide groups on the sides, linked to the 3,4 and 9,10 carbon atoms of the perylene 13 (Figure 10), respectively.
Perylene diimides are usually synthesized from a common starting material, perylene dianhydride (PDA) 14 which can be functionalized at various positions with a broad range of methodologies (Scheme 1). Initially (from the 1910s to 1985), functionalization at the imide positions only, by straightforward nucleophilic reactions of PDA 14 with a variety of aliphatic and aromatic amines, yielded a collection of unsubstituted PDI (H,H-PDI). Nevertheless, the materials exhibited poor solubility and monotonous absorption features. Therefore, the main application of PDI remained the synthesis of dye particles for which low solubility is beneficial. Noteworthy, color tuning was possible in the solid state because modifications at the imide substituents induced variations in the packing of the molecules with concomitant changes in the absorption of excitonically coupled chromophores.
Scheme 1. Synthetic modifications of PDIs at imide, bay and ortho positions.

Poor solubility of \( H,H \)-PDI results from their large, planar perylene core. Strong hydrophobic interaction as well as electrostatic interactions induced by the carbonyl groups and extended coupling of the \( \pi \) orbitals facilitate the formation of aggregates.\(^{\text{[51]}}\) A first progress to make \( H,H \)-PDI more versatile was the introduction of solubilizing groups at the imide nitrogen by Langhals et
Long alkyl chains or aryl groups were effective, especially when parts of them are forced out-of-the-plane with respect to the planar H,H-PDI core. In this regard, the so-called “swallowtail” substituents - long alkyl chains attached to the imide nitrogen atom through their central positions, such as 10-nonadecyl groups - and o-substituted N-aryl groups were most effective. However, all had very comparable absorption properties in diluted solution. This observation was explained by the presence of nodes located at the imide position in both HOMO and LUMO that prevent electronic coupling across the nitrogen atom.

In addition, H,H-PDI exhibited strong fluorescence with quantum yields generally close to unity in diluted solutions, also independently from the substituents. Noteworthy, Würthner et al. discovered exceptions to this rule. Fluorescence of compound 16 is efficiently quenched by photoinduced electron transfer between the electron-rich 3,4,5-tridodecyloxyaryl and the electron-poor H,H-PDI (Figure 11).

1.6.1. Synthesis

To overcome the limitation of H,H-PDI in terms of absorption and emission properties, methodologies were developed to further substitute PDI at the positions 1, 6, 7 and 12 (so-called bay positions, Figure 10). From 1985, various procedures have been reported for the halogenation of PDA 14 that can be then converted to various core-substituted PDIs (c-PDIs) by successive...
reactions with nucleophiles, either on the halogenated core, or on the imide positions (Scheme 1). The initially proposed chlorination procedures could afford 1,6,7,12-tetrachloro PDA 17, however with contamination from tri- and pentachloro PDI impurities. This halogenated compound was then successively reacted with amines, that attacked the anhydride groups, and with phenolates that replaced chlorine at the bay positions, to yield tetraphenoxy PDI 18. Later on, more user-friendly bromination procedures replaced chlorinations and gave access to mono-, di- and tetrabrominated PDIs. An inherent difficulty of these routes was the initial, poorly selective bromination of PDA 14 that yielded a mixture of insoluble products halogenated to various degrees. An additional difficulty layed in the fact that disubstituted PDA might exist as 1,6 or 1,7 isomers (19). The protocols proposed so far for the preparation of mono-,[58-59] di-,[60] and tetra-brominated[61] c-PDI relied on the conversion of the crude mixture of halogenated PDA 19 into more soluble species 20 and their subsequent purification by column chromatography. However, the preparation of tribrominated c-PDI is reportedly difficult.[60, 62] In addition, the successful separation of 1,6- and 1,7-dibromo PDI involved a mandatory recrystallization procedure that yielded the pure 1,7 isomer only, while its 1,6 counterpart still contained traces of 1,7-dibromo PDI, as described by Würthner et al.[60]

Replacement of the bromine atoms in c-PDI 20 by aromatic nucleophilic substitution occured readily. The use of phenols in basic conditions or secondary amines such as piperidine, morpholine or pyrrolidine successfully gave a collection of c-PDI 21.[63-64] Cyan groups were readily introduced as well by Pd(0)-catalyzed coupling using CuCN or Zn(CN)₂ as reagent.[65-66] Finally, 1,7-di- and 1,6,7,12-tetrafluoro PDI were obtained upon exchange of bromine for fluorine.[67] Moreover, C-C bond forming transition-metal catalyzed reactions, such as Sonogashira,[68] Stille[69] and Suzuki[61] cross-
couplings, have been applied for the further replacement of bromine with aryl or alkyne groups.

More recently, positions 2, 5, 8 and 11 (so-called ortho positions) of PDI have been functionalized by transition metal-catalyzed reactions. Direct reaction of H,H-PDI with arylboronates or terminal alkenes using a ruthenium catalyst were first reported, yielding the corresponding 2,5,8,11-tetrasubstituted PDI (22). Later on, procedures for the ruthenium- or iridium catalyzed tetraborylation of PDI were reported as well, yielding a useful key intermediate 23 for the synthesis of ortho-tetrasubstituted PDI (24).

1.6.2. Molecular Structure

On the structural point of view, core substitution of PDI at the 1, 6, 7 and / or 12 (bay) positions causes a deplanarization of the molecule as compared to the planar H,H-PDI counterparts. The value of this torsional angle (θ, Figure 12) depends on the number of substituents and on their steric bulk.

![Figure 12. Tetrachloro-PDI 25 and torsional angle θ associated with the bay carbon atoms C12-C13-C14-C1, as measured from single-crystal X-ray diffraction. From ref. [74].](image)

For example, torsional angle of 1,6,7,12-tetrachloro PDI 25 was determined from X-ray crystallography at θ = 36.7° (Figure 12)[37, 75], whereas in tetrafluoro PDI with less bulky substituents, θ varied between 19 and 25° (due to crystal packing effects).[76] Disubstituted PDIs have smaller θ. For 1,7-dibromo PDI, θ = 24°,[60] for 1,7-difluoro PDI, θ = 4°,[76] whereas for CN2-PDI, θ = 5°.[40] These to last derivatives are almost planar since fluorine is quasi-isosteric with hydrogen, and cyano groups are also sterically benign. For
a number of compounds, the value of \( \Theta \) could not be determined because crystals needed for X-ray diffraction experiments were not obtained. However, semiempirical AM1 calculations have been performed to determine the missing values. Calculated torsional angle for 1,7-dipyrrrolidinyl PDI was \( \Theta = 25^\circ \), whereas for 1,7-diphenoxyl, \( \Theta = 18^\circ \).\(^{64}\)

No distortion of the molecule’s core was observed in the case of substitution at the 2, 5, 8 and 11 (ortho) positions. As confirmed by X-ray diffraction analysis, 2,5,8,11-tetraborylated PDI \(^{23}\) is a perfectly planar molecule.\(^{73}\) The ortho-substitution pattern does not generate the same steric constraints on the PDI core since in that case each substituent is far apart from the others and points to a different direction.

1.6.3. Optical Properties

Apart from its structural effects, core-substitution also modifies the optical properties of PDI. For example, diluted solutions of \( H,H \)-PDI \(^{26}\) (Figure 13) display a strong, main absorption band corresponding to the electronic \( S_0-S_1 \) transition. It is located at \( 400 < \lambda < 550 \) nm with a maximum at \( \lambda_{\text{max}} = 521 \) nm and a high molar absorption coefficient of \( \epsilon_{\text{MAX}} > 80'000 \) M\(^{-1}\) cm\(^{-1}\).\(^{77}\) This absorption band exhibits a clearly apparent fine structure, arising from the coupling between the vibrational breathing of the core and the electronic transition. It is noteworthy that the optical properties of \( H,H \)-PDIs are not much affected by solvatochromism and thus these chromophores were widely used as a reference for the determination of fluorescence quantum yields.

\( Ortho \)-tetrachloro PDI \(^{27}\) has clearly ipsochromically shifted absorption as compared to \( H,H \)-PDI \(^{26}\), at \( \lambda_{\text{max}} = 505 \) nm.\(^{72}\) Substitution of the four chlorine atoms with cyano groups yields \(^{28}\) (Figure 13) but with little optical effect since the absorption maximum is blue-shifted by only 3 nm. Other substitution patterns such as 1,7-dicyano, 1,7-dibromo and 1,6,7,12-tetrachloro \(^{29, 30}\) and
31, respectively), have almost no incidence on the position of the absorption maxima which remain comparable to the case of H,H-PDI 26.

![Graph showing energy (E) in eV against vacuum and maximal absorption in nm indicated for different compounds.]

Figure 13. H,H-PDI 26, c-PDI 27-34 and PCBM 9, with indication of HOMO (bold) and LUMO (dashed) energies in eV against vacuum and maximal absorption in nm indicated in the middle. Dashed arrows represent electronic transitions. Data from ref. [72], [65], [63], [74], [55].

However, the molar absorption coefficients tend to decrease. For example $\varepsilon_{MAX} = 47'000 \text{ M}^{-1} \text{ cm}^{-1}$ for 1,7-dicyano-PDI 29 is much lower than $\varepsilon_{MAX} > 80'000 \text{ M}^{-1} \text{ cm}^{-1}$ for 26. On the other hand, some patterns cause a bathochromic shift of the absorption maximum. With two phenoxy groups at positions 1 and 7, such as in 32 (Figure 13), the absorption maximum shifts by 20 nm to the
red as compared to \(H,H\text{-PDI}\) \(^{[57]}\). Tetrasubstitution with four phenoxy groups, such as in \(33\) further shifts the absorption maximum by 30 nm to the red, at \(\lambda_{\text{max}} = 575\) nm.\(^{[78]}\) The 1,7-substitution with pyrrolidinyl (\(N,N\text{-PDI}\)), such as in \(34\), substituents has a more dramatic effect since the absorption maximum is shifted up to \(\lambda_{\text{max}} = 700\) nm in CHCl\(_3\) and the corresponding molar absorption coefficient decreases to \(\delta_{\text{MAX}} = 46'000\) M\(^{-1}\) cm\(^{-1}\).\(^{[63, 79]}\) As a consequence and in contrast to the other c-PDI that mostly appears as red materials, \(N,N\text{-PDI} 34\) has a green color. In contrast to other c-PDI, \(N,N\text{-PDI}\) is subject to significant solvatochromism since its main absorption band has a strong charge-transfer character.

1.6.4. Redox Properties

In addition to its effect on optical properties, core substitution also modifies the electrochemical characteristics of PDI. Unsurprisingly, substitution with electron-withdrawing groups lowers both the reduction and the oxidation potentials of the corresponding PDI derivatives. Table 1 summarizes electrochemically determined redox potentials recorded for compounds 26-34.

Table 1. Redox properties of PDI dyes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cpd (^a)</th>
<th>(E_{1/2}(\text{PDI}/\text{PDI}^-))(^b) (V)</th>
<th>(E_{1/2}(\text{PDI}^+/\text{PDI}))(^b) (V)</th>
<th>(E_{1/2}(\text{PDI}^+/\text{PDI}^+)^{\text{c}}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28(^{[72]})</td>
<td>-0.75</td>
<td>-0.38</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>29(^{[65]})</td>
<td>-0.92</td>
<td>-0.59</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>27(^{[72]})</td>
<td>-1.06</td>
<td>-0.83</td>
<td>---</td>
</tr>
<tr>
<td>4</td>
<td>30(^{[63]})</td>
<td>---</td>
<td>-0.97</td>
<td>&gt;+1.48</td>
</tr>
<tr>
<td>5</td>
<td>31(^{[74]})</td>
<td>-1.07</td>
<td>-0.87</td>
<td>&gt;+1.20</td>
</tr>
<tr>
<td>6</td>
<td>26(^{[72]})</td>
<td>-1.21</td>
<td>-0.98</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>32(^{[55]})</td>
<td>-1.29</td>
<td>-1.11</td>
<td>+1.05</td>
</tr>
<tr>
<td>8</td>
<td>33(^{[55]})</td>
<td>-1.30</td>
<td>-1.10</td>
<td>+0.89</td>
</tr>
<tr>
<td>9</td>
<td>34(^{[63]})</td>
<td>-1.46</td>
<td>-1.28</td>
<td>+0.16</td>
</tr>
</tbody>
</table>

\(^a\) Coupounds, see Figure 13. \(^b\) Half-wave potential, vs. Fc/Fc\(^+\). The oxidation potential for Fc/Fc\(^+\) is taken as +0.52 V vs. SCE.\(^{[37]}\)
It is worth to note that in the recent years, there has been controversy about the numerical values used for the determination of redox potentials vs. Fe/Fe$^+$ from data recorded with the standard calomel electrode (SCE).\cite{80} For the sake of consistency, values reported here are calculated in accordance with Würthner et al. who took the oxidation potential for Fe/Fe$^+$ as $+0.52$ V vs. SCE.\cite{37}

From the first reduction potential, the energy (in eV) of the LUMO level of PDI derivative can be reported relative to $-5.1$ eV in a vacuum for the ferrocenium/ferrocene couple (Fc$^+$/Fc) (Equation 11).\cite{80}

$$E_{\text{LUMO}} = -5.1 \text{ eV} - E_{1/2}(\text{PDI/PDI})$$

(Equation 11)

Figure 13 represents the frontier molecular orbital (FMO) energy levels for a series of core substituted PDI derivatives 27 to 34, together with $H,H$-PDI 26 and PCBM 9, the classical electron acceptor in bulk heterojunctions solar cells. As it appears, core substitution is a valuable strategy to tune the HOMO and LUMO energies of PDI derivative. The optical bandgap $\Delta E_g$ (in eV) is calculated from the onset wavelength ($\lambda_{on}$, in nm) of the most red-shifted absorption band for each derivative (Equation 12).

$$\Delta E_g = 1240 / \lambda_{on}$$

(Equation 12)

$\Delta E_g$ slightly increases with decreasing LUMO levels (Figure 13), which makes possible the construction of charge transfer cascades using c-PDI for the transfer of holes and electrons in opposite directions.\cite{8,38}

1.6.5. Supramolecular Chemistry

The supramolecular chemistry of PDIs is dominated by the propensity of these compounds to undergo self-assembly by strong $\pi$-stacking interactions. These interactions are responsible for the low solubility of PDI and formation of insoluble dye particles, useful for painting applications. To promote the self-assembly of PDI but avoid their crystallization in macroscopic grains, chemical modifications are needed so that the attractive interactions are still possible in
one or two dimensions but prevented in the third one. According to this principle, PDI derivatives capable of self-assembly into well-defined 1D or 2D aggregates have been reported.

![Energy diagram for a dimeric aggregate with coplanar transition dipoles.](image)

**Figure 14.** Energy diagram for a dimeric aggregate with coplanar transition dipoles. Energy ($E$) is represented as a function of the the slip angle ($\theta$). $\Delta E_{vdW} =$ difference in van der Waals interaction energies between ground and excited states. $\Delta \varepsilon =$ Davydov splitting. Figure adapted from ref. [51].

Aggregation of PDIs was conveniently monitored by $^1$H NMR and electronic absorption in several studies reported by Würthner and coworkers. The latter technique is particularly well suited since the optical properties of molecularly dissolved PDIs are markedly different from those of aggregates. Alteration of the absorption properties of PDIs upon the formation of aggregates has been explained by the excitonic coupling theory of Kasha and coworkers (Figure 14). In a dimer formed by two chromophores with parallel alignment, exciton coupling splits the $S_0$-$S_1$ optical transition in two excitons separated by an energy gap, called the Davydov splitting ($\Delta \varepsilon$ on Figure 14). For such a parallel conformation, the optical excitation is only allowed from the ground state $S_0$ to one of the two excitonic states depending on the slip angle ($\theta$ on Figure 14). For $\theta < 54.78$, transition to the lower-energy state is allowed, leading to a bathochromically shifted J band, while for $\theta > 54.78$
transition to the upper energy state is allowed, leading to a hypsochromically shifted H-band. These changes are easily monitored by UV-Vis spectroscopy.

![Graph showing UV-Vis absorption spectra](image)

**Figure 15.** Concentration-dependent UV-Vis absorption spectra of PDI 35 (2.0 · 10⁻⁷ M to 2.0 · 10⁻⁶ M) in methylcyclohexane. Arrows indicate spectral changes upon increasing the concentration. Figure adapted from ref. [83].

Examples reported in the literature showed that H,H-PDIs easily form H aggregates because their geometry favors a perfect cofacial alignment (θ = 90°). As inferred from absorption spectroscopy in solution (Figure 15), compound 35 readily self-assembled upon gradually increasing the concentration of the dye in non-polar methylcyclohexane. Upon aggregation, the absorption maximum located initially at λ = 520 nm was blue shifted by ca. 30 nm. Simultaneously, the molar absorption coefficient of 35 decreased from ca. 100 down to ca. 40 mM⁻¹ cm⁻¹. These indications are characteristic for the formation of H aggregates. However, a bathochromically shifted broad band with low intensity aroused at λ = 540 nm and beside that, the authors reported the strong, excimer-type emission of the aggregates. These
observations were incompatible with the formation of perfectly cofacial H aggregates because in that case, the transition from the electronic ground state $S_0$ to the lower exciton would be forbidden. The authors explained this apparent discrepancy by a 70-80° rotational displacement of each dye with respect to its neighbors around the main axis of the columnar architecture. In this way, transition into the lowest exciton became partially allowed. The rotational displacement was also in accordance with the observed excimer-type emission of the aggregate, otherwise forbidden. Additional structural studies by AFM in the solid state revealed that 35 formed one-dimensional rod-like aggregates, 3.9 nm in diameter.

Interestingly, Würthner et al. also reported successful attempts to design PDI derivative that spontaneously formed J aggregates. In one example, J- was forced over H-aggregation by encoding the preferential formation of slipped π-stacked architectures in the structure of molecule 36 (Figure 16). A donor-acceptor pattern of hydrogen bonds was used to promote the assembly of monomers 36 into a linear, cable-like aggregate. Additionally, the formation of columnar aggregates was prevented by the strong twisting of the PDI core induced by four bay substituents. As a result, temperature or solvent-induced aggregation yielded soluble supramolecular architectures that exhibited the characteristic absorption features of J aggregates. Molecularly dissolved 36 showed a characteristic $S_0$-$S_1$ band with $\lambda_{\text{max}} = 570$ nm, which shifted bathochromically upon aggregation, at $\lambda_{\text{max}} = 642$ nm. Also consistent with the formation of J aggregates, the architecture was highly fluorescent, with a quantum yield of 0.96.
Figure 16. Self-assembly of c-PDI 36 into J type aggregates. A) Molecular structures and schematic representation of 36. B) Schematic representation of an aggregate of 36. Green lines represent hydrogen bonds, only the left-handed helical structure is shown for simplicity. C) Temperature-dependent UV-Vis spectra of 36 in MCH (1.5 $\cdot$ 10$^{-5}$ M) at 20–90°C; arrows indicate the spectroscopic changes upon increasing the temperature (deaggregation). Figure adapted from ref. [85].

In an independent study, Frauenrath et al. prepared the $H,H$-PDI derivative 37 functionalized at imide positions with an oligopeptide – soft polymers conjugate, and demonstrated its spontaneous, hierarchical self-assembly in tetrachloroethane (TCE) (Figure 17 A).[87-88]
Figure 17. A) Molecular structure of 37. B) Model of the supramolecular self-assembly of 37 showing the superposition of π surfaces. C) Changes in UV-Vis and CD spectra upon TFA-promoted deaggregation of 37. D) Model showing the helical structure and the dimensions (E) of nanofibrils formed by 37. F) AFM images of nanofibrils. Arrows points to periodic structural motives. Figure adapted from ref. [87].

Using a variety of characterization methods, among them IR, UV-Vis and CD spectroscopies together with optical microscopy and AFM, they could precisely describe the self-assembled architectures (Figure 17 B). In this
hydrophobic environment, hydrogen bonding between the peptide side-chains was promoted and gave β-sheet-like structures, while the poly(isobutylene) external segments were well-dissolved. UV-Vis spectra showed both H- and J-type bands that were explained by the formation of cofacial aggregates of chromophores with both lateral and rotational displacement (Figure 17 C). Therefore the authors postulated that monomer 37 self-assembled into extended, soluble nanofibrils of 7 to 8 nm in diameter with a constant helical twist (Figure 17 D and E). This twisting presumably prevented further direct contact between \( H,H \)-PDI chromophores from distinct nanofibrils. AFM images revealed a regular, periodic structure (Figure 17 F). However, in the solid state, hydrophobic interactions among the external soft polymeric envelopes of each nanofibril promoted their further assembly into nanowires and microfibers up to 20 µm in diameter and several centimeters in length.

The possibility to achieve artificial architectures similar to natural photosystems depends on our ability to assemble a variety of dyes in a precisely controlled fashion. Beside the self-assembly of PDIs, many other examples involving different chromophores have been reported.

1.7. Aggregates of Other Dyes

Recently, Giuseppone et al. have reported the light-triggered self-assembly of triarylamines into columnar aggregates (Figure 18).\(^{89-90}\) Compound 38 underwent aggregation in the presence of both light and a chlorinated solvent. Mechanistically speaking, self-assembly proceeded through the initial formation of a small amount of triarylamine radical cations that then promoted the aggregation of a multiple neutral monomers 38 (Figure 18 A). Electron paramagnetic resonance (EPR) measurements showed that one radical cation could stabilize up to 160 adjacent monomers. Aggregation resulted thus from a combination of charge-transfer, \( \pi \)-stacking and hydrogen bonding interactions. High resolution AFM images revealed the formation of corn-like, fibrilar
aggregates (10–50 nm in width and 50–1000 nm in length) constituted from bundles of triarylamine stacks (Figure 18 B and C). Further studies revealed that the direction of self-assembly could be controlled by the application of an electric field during the process. Supramolecular organic nanowires were installed between two metallic electrodes (Figure 18 D and E) and their electrical characteristics determined, revealing a very high conductivity and metallic behavior at low temperatures (1.5 K).

![Figure 18.](image)

**Figure 18.** Hierarchical self-assembly of triarylamine 38. A) Following irradiation of 38 with light, planar radical cations are generated by electron transfer to chloroform and self-assemble into 1D supramolecular polymers. B) High-resolution AFM image and (C) model showing the combination of 1D polymers, forming larger 3D fibers. D) AFM phase image and (E) model showing the self-assembly of 38 in the gap between two metallic electrodes. Figure adapted from ref. [89, 91].
Frauenrath et al. reported the self-assembly of quaterthiophenes functionalized with oligopeptide-polymer substituents into 1D nanowires, in a similar approach than with the PDI derivative 37. The aggregation of the chromophores was driven by the interplay of π–stacking and hydrogen bonding. These wires further assembled into fibrils of several micrometers in length.\textsuperscript{[92]}

1.8. Supramolecular Heterojunctions

More relevant for the synthesis of artificial photosystem, the simultaneous assembly of more than one chromophore into organized architectures has attracted considerable interest in the past years.

Aida et al. have reported the assembly of amphiphilic H,H-PDI-quaterthiophene dyad 39 into bicontinuous, segregated donor/acceptor stacks with long-range organization (Figure 19).\textsuperscript{[93]} A hot solution of 39 in THF was cooled down from 60°C to 25°C and nanofibers spontaneously formed. Incompatibility between hydrophilic triethyleneglycol and hydrophobic alkyl side-chains was used to orient the dyad in the aggregates and to avoid the formation of D/A complexes between the electron-rich quaterthiophene and the electron-poor H,H-PDI. Nanofibers with a tape-like morphology, 13–15 nm in width were observed by scanning electron microscopy. Efficient electron transfer from the oligothiophene donor to the H,H-PDI acceptor was confirmed by complete quenching of emission for both chromophores. High photoinduced conductivity measured on fibers obtained from 39 confirmed the presence of continuous, segregated n- and p-type charge-conducting channels.
Recently, Würthner et al. have reported on the synthesis of n-type c-PDI derivative 40 and p-type, chiral oligo(p-phenylene vinylenes) (OpV) 41 to 43 (Figure 20 A).\cite{94} Complementary hydrogen bonding motives readily promoted the assembly of both building blocks together into triads 41-40-41 to 43-40-43. Moreover, data from UV-Vis and CD spectroscopy in solution evidenced both temperature and concentration-triggered self-assembly of the triads into helical aggregates (Figure 20 B and C) with left-handed conformation (M helicity). Formation of J aggregates was evident from the absorption spectra. Aggregation strength increased steadily with the increasing number n of p-phenylene-vinylene units. AFM images revealed the presence of nanofibers ca. 4 nm in width corresponding to single helices, together with thicker, rod-like
fibers, presumably resulting from the aggregation of several nanofibers into bundles in the solid-state (Figure 20 D).

**Figure 20.** Self-assembly of c-PDI-OpV triads into p/n-SHJ. A) Structure of triads 41-40-41 to 43-40-43. B) Schematic representation of aggregates with left-handed, M helicity. Blue blocks = OpV, red blocks = c-PDI. C) UV-Vis absorption spectra of 42-40-42 in MCH, typical for J aggregation (concentration from 1.0 · 10⁻⁷ M to 5.0 · 10⁻⁵ M). Arrows indicate changes upon increasing concentration. D) AFM height image of fibrils obtained from self-assembly of 42-40-42. Figure adapted from ref. [94].

Strong aggregation-induced quenching of emission despite the J-type aggregation suggested an efficient electron transfer from the OpV donor to the c-PDI acceptor. This was then confirmed by transient absorption measurements. However, photovoltaic devices based on triad 42-40-42 gave poor photocurrent, presumably because the parallel orientation of the fibers with respect to the collecting electrodes was unsuited for the efficient collection of charge carriers. Recently, a comparable system based on a similar design was reported by Braunschweig and coworkers. [95-96]
Recently, Wasielewski et al. reported an even more complex multichromophoric system based on the covalent dyad 44 with four lateral 1,7-diaryloxy-PDI and one central 1,7-dipyrrolidinyl PDI (Figure 21 A).\textsuperscript{[97]}

![Figure 21](image)

**Figure 21.** An artificial mimic of the natural photosynthetic reaction center. A) Molecular structure of covalent dyad 44. B) Schematic representation of the aggregate obtained upon cofacial dimerization of 44 with direction of energy (blue arrow) and symmetry-breaking electron (yellow arrow) transfers. Figure adapted from ref. [97].

Dyads spontaneously assembled into cofacial dimers in toluene, as confirmed by $^1$H NMR, gel permeation chromatography (GPC), UV-Vis spectroscopy and small-angle X-ray scattering (SAXS). Transient absorption measurement evidenced rapid Förster resonant energy transfer (FRET) from the external diaryloxy-PDI donors to the central N,N-PDI acceptor when solution of the cofacial dimers were excited with 550 nm laser pulses (Figure 21 B). Moreover, subsequent symmetry-breaking charge transfer between the central cofacial pair of N,N-PDI was evident from transient absorption and time-resolved fluorescence spectroscopy. This elegant example was able to reproduce the sequence of light absorption, energy and electron transfers that occur in the natural photosynthetic reaction center. Moreover, it evidenced the propensity of N,N-PDI cofacial dimers to undergo symmetry-breaking charge
transfer and thus to mimic the activity of the cofacial porphyrin pairs found in biological photosystem.

1.9. Heterojunctions on Surfaces

As explained earlier, one of the key features of natural photosystems is their precise orientation in lipid membranes. This is an essential point for the conversion of light into chemical energy, for example by creating a proton gradient across the lipid bilayer. Recently, Matile et al. reported the successful design of a synthetic rigid-rod β-barrel for the biomimetic photoproduction of proton gradient across the membrane of artificial large unilamellar vesicles.[98] However, for practical use, oriented photosystems built on conducting surfaces that convert light into electric current are more promising. In the recent years, several groups explored the synthesis of surface-immobilized nanoarchitectures by bottom-up approaches. [12, 99-103]

1.9.1. Layer-by-Layer Assemblies

Martinson et al. have used the known affinity of phosphonate groups for Zr⁴⁺ ions to grow interdigitated networks of porphyrins electron donors and PDI acceptors on transparent and conductive ITO surfaces (Figure 22).[100] Molecular square 45 was designed to accommodate diphosphonate PDI 46 in its central void. Porous multilayer architecture 47 was first grown by alternating zirconation-chelation steps, successively using solutions of Zr⁴⁺ and 45. Absorption spectroscopy showed the linear increase of film thickness up to at least ten elongation steps. Next, a network of PDI 46 and Zr⁴⁺ was infiltrated in the porous scaffold of porphyrins by alternatively soaking the film in solutions of cations and of 46 to yield architecture 48. Electrochemical measurements showed that PDI were really interdigitated with porphyrins in architecture 48 and did not just accumulate on top of film 47.
Figure 22. p/n-SHJ architecture 48 with porphyrin squares 45 and PDI 46 assembled by Zr\(^{4+}\)-phosphonate chemistry on ITO or glass surfaces. a) Incubation in a solution of Zr\(^{4+}\). b) Incubation in a solution of 45. c) Repetition of steps a) and b). d) Successive incubations in solutions of Zr\(^{4+}\) and 46. Adapted from ref. [100].
Further evidences came from film photoluminescence measurements, as the emission of porphyrins was quenched by PDI in p/n-SHJ architecture 48. Control experiments indeed indicated that quenching occurred only if chromophores were interdigitated at the molecular-scale. Finally, photocurrent measurements on the resulting photosystem 48 showed that $V_{OC}$, $J_{SC}$ and IPCE all compared favorably with those measured on control bilayer architecture without p/n-SHJ structure.

Imahori et al. have used metal-ligand interactions to grow interdigitated networks of porphyrins electron donors and fullerenes acceptors on transparent conductive tin oxide (SnO$_2$) surfaces (Figure 23). The oxide surface was first modified with monoacid-monopyridyl porphyrin 49 and fullerene-acid 50 to form the mixed, self-assembled monolayer (SAM) 51. Then Pd$^{2+}$ ions and diphenyl-dipyridyl zinc porphyrin 52 were assembled stepwise by successive metallation-coordination cycles to give porous architecture 53. Up to 8 porphyrin layers could be assembled in total. Structural investigations revealed that the linear arrays were tilted by an angle of 28° with respect to the SnO$_2$ surface. Thereafter, pyridylfullerene 54 were infiltrated in the porous network 53 and coordinated to the central Zn$^{2+}$ ion of porphyrins to give the p/n-SHJ architecture 55. Photocurrent in interdigitated photosystem 55 increased linearly up to 5 porphyrin layers, whereas it saturated at lower distance (3 layers) in single-component architecture 53. Moreover, IPCE in p/n-SHJ 55 was found to be twice as high as for control system 53. These results evidenced the more improved charge generation and transport in coaxial arrays of electron donors and acceptors organized at the molecular scale.
Figure 23. p/n-SHJ with zinc porphyrins and fullerenes assembled through metal-ligand interactions. a) Incubation of an SnO₂ surface with acids 49 and 50 to prepare SAM 51. b) Repeated, sequential treatments with Pd²⁺ and ligand 52 to assemble up to 8 layers of porphyrins into architecture 53. c) Treatment with a solution of 54 to yield p/n-SHJ 55. Adapted from ref. [104].
1.9.2. Zipper Assembly

More recently, Matile et al. have reported the self-assembly of multicomponent photoactive architectures by using the zipper assembly methodology.\(^{112, 105-114}\) In the most elaborated example, an OMARG SHJ architecture was assembled from the five components 56, 57, 58, 59, 60 (Figure 24 and 25).

![Building blocks](image)

**Figure 24.** Building blocks 56 to 60 for the preparation of OMARG SHJ zipper architectures Au-56-(57-58)_n-57-(59-60)_m (see Figure 25). Adapted from ref. [111].

A gold surface (Au) was modified with anionic, \(p\)-quaterphenyl initiator 56 and yielded self-assembled monolayer Au-56. \(p\)-octyphenyl (POP) functionalized with yellow diethoxy-NDI (O,O-NDI) as cationic (57) or anionic
derivatives were then assembled by successive cycles to build interdigitating architectures \( \text{Au-56-(57-58)_{n}} \cdot 57 \) with terminal cationic “sticky ends”

\[
\begin{align*}
\text{Au-56} & \quad \text{Au-56-(57-58)_{n}} \cdot 57 & \quad \text{Au-56-(57-58)_{n}} \cdot 57-(59-60)_{m}
\end{align*}
\]

Figure 25. OMARG SHJ zipper assembly. A) Assembly formation. B) HOMO (solid) and LUMO (dashed) energy diagram of the various components. C) Photocurrent response as a function of the number of deposited layers for OMARG-SHG \( \text{Au-56-(57-58)_{n}} \cdot 57-(59-60)_{m} \) (●) with \( n = 4 \) and anti-OMARG SHJ with redox gradients in the opposite direction (○). Adapted from ref. \([111]\).

Zippers spontaneously assembled through interdigitating \( \pi-\pi \) interactions assisted by ion pairing and hydrogen bonds. In a subsequent step, \( p \)-oligophenylethynyl (OPE) chromophores functionalized with red amino-bromo
NDI (N,Br-NDI) as anionic (59) or cationic (60) derivatives were assembled on top of architecture Au-56-(57-58)_{n-57} to yield OMARG SHJ architecture Au-56-(57-58)_{n-57}-(59-60)_{n}. Coaxial electron and hole transporting channels were constituted by the NDI stacks and POP/OPE scaffolds, respectively. Additionally, the HOMO and LUMO of the components constituted redox gradients in both the electron and hole conducting channels. Photocurrent measurements showed that with the OMARG SHJ architecture, the photocurrent steadily increased up to 40 layers. However in control experiments involving so-called anti-OMARG SHJ architectures with inverted redox gradients, photocurrent already saturated at only 10 layers, pointing out the importance of oriented redox gradients for long-distance charge transport.

Zipper assembly was the first approach that allowed the building of complex architectures needed to evaluate the relevance of OMARG SHJ for long distance charge transport. However, despite its conceptual relevance, zipper assembly suffered from drawbacks. The preparation of the eight requested building blocks involved long and low-yielding covalent synthetic routes. In addition, the multiple cycles needed for the supramolecular synthesis of the large OMARG and anti-OMARG architectures were highly time-demanding because the kinetics of self-assembly were slow.

1.9.3. Surface-Initiated Polymerization

On the other hand, surface-initiated polymerization (SIP) has been introduced recently as a way to prepare oriented organic architectures on solid surfaces. SIP has been used to prepare the so-called polymer brushes, which are densely grafted polymer chains attached to a surface, stretching away from it to minimize interactions with their neighbors. SIP compares favorably with attachment of preformed polymers to surfaces because it gives access to much higher grafting densities. A variety of polymerization techniques have been explored to achieve such structures, among them ring-opening polymerizations.
(ROPs) or a recently proposed light-mediated living radical polymerization reaction.\textsuperscript{[117]}

Huck et al. have used SIP to prepare hole-transporting polymer brushes.\textsuperscript{[118]} Initiator 61 was attached on ITO, yielding monolayer ITO-61 (Figure 26).

![Image](image_url)

**Figure 26.** Synthesis of oriented p/n-SH ITO-61-(62)\textsubscript{n}•63 by atom-transfer radical polymerization of monomer 62 on SAM ITO-61 and subsequent infiltration of CdSe quantum dots (CdSe-QDs) 63. Adapted from ref. [8].

Acrylate monomer 62 with triarylamine side groups was then polymerized from the surface via atom-transfer radical polymerization, yielding brush architecture ITO-61-(62)\textsubscript{n} with amorphous p-type polymer and vertical orientation on ITO. The current density normal to the surface was 3 orders of magnitude higher with ITO-61-(62)\textsubscript{n}, as compared to non-oriented, spin-coated
films of the same material. In a subsequent study, they infiltrated CdSe quantum dots (CdSe-QDs) \(63\), which are n-type semiconductor, in the poly(triphenylamine acrylate) film and obtained three-component architecture ITO-61-(62)\(_n\)•63\(^{[102]}\) CdSe-QDs \(63\) and the brushes were mutually attracted by the interaction of nitrogen atoms from triarylamines with the surface of CdSe, thus infiltration of CdSe-QDs \(63\) in the brushes was spontaneous. The successful of the infiltration was very dependent on the size of the crystal, which is consistent with the actual penetration of the solid material into the compact network of the polymer brushes. From these data and others, the authors concluded that architecture ITO-61-(62)\(_n\)•63 had continuous, coaxial electron and hole conduction channels, vertically orientated with respect to ITO over the entire thickness of the film (Figure 26). AFM measurements in phase-contrast mode evidenced long-range order, together with the regular alternation of hard and soft materials. Typical separation length between the two phases was 10 nm, compatible with the length of exciton diffusion. These structural data pointed to the formation of p/n-SHJ architectures. Moreover, photocurrent measurements on ITO-61-(62)\(_n\)•63 obtained after infiltration of the nanocrystals showed an increase of current density by three orders of magnitude as compared to the pristine polymer film ITO-61-(62)\(_n\).

Improved performance after installation of the crystals was thus explained again by the formation of a SHJ photosystem. It reflected the ability of the composite system to transport electrons in the CdSe-QDs phase, in addition to holes in the polymer phase. Also, control experiments showed that this interdigitated architecture generated much higher current densities than a macroscopic bilayer structure assembled from the same materials. This was expected since p/n-SHJ architecture ITO-61-(62)\(_n\)•63 offers a much larger contact for electron transfer between the triarylamine donor and CdSe acceptor materials, as compared to bilayer architecture. This example demonstrated how SIP could be used for the straightforward preparation of oriented, charge-
transporting polymer brushes and the stepwise construction of multicomponent photosystems.

1.10. Self-Organizing Surface-Initiated Polymerization

Recently, Sakai et al. have introduced self-organizing surface-initiated polymerization (SOSIP) as a versatile approach toward the synthesis of complex organic architectures on ITO surfaces.\textsuperscript{[103]} SOSIP combines the ability of supramolecular chemistry to organize materials in three-dimensions with the simplicity of SIP for the rapid preparation of oriented architectures on surfaces, starting from small building blocks.

In their first study, Sakai et al. have used unsubstituted NDI (H,H-NDI) as a structural and functional element in initiator \textsuperscript{64} (Figure 27). This flat, rigid core supported the two lateral peptide side chains in opposite directions that contained bisphosphonic acids for anchoring to ITO, protected cysteines for subsequent initiation of SOSIP and hydrogen bonds donor and acceptor groups for preorganization with propagator \textsuperscript{65}. Firmly attached to the oxide surface by the four phosphonic acid anchoring groups, initiator \textsuperscript{64} formed a monolayer \textsuperscript{66} with tert-butyl (t-Bu) disulfide groups pointing out. The affinity of phosphonic acids for ITO has been known for some time and used mainly for the modification of oxide surfaces with concomitant tuning of their work function in the development of electronic devices.\textsuperscript{[119-122]} Additionally, phosphonic acids have been used for the grafting of organic materials on ITO, such as polythiophene\textsuperscript{[123]} and ferrocene polymetacrylate\textsuperscript{[124]} brushes, formation of electroactive phtalocyanine monolayers\textsuperscript{[125]} or attachment of whole biological photosystems with orientation.\textsuperscript{[126]} Data from cyclic voltammetry (CV) and UV-Vis spectroscopy pointed to a dense coverage of the ITO surface by a defect-free monolayer \textsuperscript{66}. 

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Figure 27. Preparation of monolayer 66 and SOSIP architecture 67. a) 64. b) 1. DTT; 2. 65, iPr$_2$NEt. The grey surface stands for ITO. Dotted lines stand for preorganizing, non-covalent interactions. Adapted from ref. [103].

For SOSIP, t-Bu disulfide groups in 64 were converted to thiols with the reducing agent DL-dithiothreitol (DTT), and then to thiolates with an organic base. Subsequently, this activated, nucleophilic monolayer was immersed in a solution of propagator 65 in CHCl$_3$/MeOH 1:1, v/v with 100 mM iPr$_2$NEt as a catalyst. 65 was built around a planar, aromatic O,O-NDI core, which has a similar shape as H,H-NDI and can interact with it through non-covalent π-
stacking. In addition, 65 bore lateral peptide side chains with hydrogen bond donors and acceptors topologically matching with those from initiator 64. Thus SOSIP was envisioned to take place in two phases, first by the formation of a supramolecular complex between the mutually-recognizing initiator 64 and propagator 65, and then by the covalent capture of the complex in a macrocycle to yield SOSIP architecture 67. In SOSIP, disulfide-exchange ROP gave the best results for covalent capture.\textsuperscript{[127-130]}

The polymerization of cyclic disulfide by ring-opening reactions has been known since chemists have tried to synthesize these materials, at least because this is a major decomposition pathway of these products (!) This reaction is initiated by a nucleophilic catalyst, generally a thiolate which attacks a strained cyclic disulfide. The cyclic S-S bond is broken, a new, acyclic S-S bond is formed and a thiolate is regenerated to continue the reaction (Figure 28 A). For SOSIP, the natural product asparagusic acid 68 with a five-membered disulfide ring showed optimal reactivity.

\textbf{Figure 28.} A) Ring-opening disulfide-exchange polymerization of a five-membered, cyclic disulfide derived from asparagusic acid. B) Dihedral angle $\theta$ in a linear disulfide C-S-S-C, in lipoic acid 69 (C) and in asparagusic acid 68 (D). Adapted from ref. [131].
Studies on their reactivity have shown that indeed five-membered cyclic disulfides readily polymerize, underlining their propensity to undergo ring-opening reactions, whereas six-membered cyclic disulfides are much more stable.\textsuperscript{132-134} This is due to the much higher conformational strain in five-membered, as compared to six-membered cyclic disulfides, in clear contrast to their cycloalkane counterparts. In a linear disulfide (C-S-S-C) virtually without strain, the dihedral angle around the S-S bond is $\theta = 90^\circ$, whereas in a five-membered ring it is forced down to $\theta = 35^\circ$ (in lipoic acid 69), and to $\theta = 27^\circ$ (in asparagusic acid 68\textsuperscript{135}) (Figure 28 B C and D). By comparison, six-membered 1,2-dithianes have $\theta = 58-66^\circ$, resulting in much lower conformational strain.\textsuperscript{133} The S-S bond length increases in parallel with the increased cyclic strain, from 2.02 Å in linear disulfides to 2.05 Å in lipoic acid 69 and to 2.10 Å in asparagusic acid 68 (Figure 28).\textsuperscript{131} Therefore, these two natural products have been used for disulfide exchange ROP. The slightly less reactive lipoic acid was best suited for the preparation of cell-penetrating poly(disulfides) in solution phase,\textsuperscript{136-138} whereas the more reactive asparagusic acid performed ideally for SOSIP. From a general perspective, the preparation and use of poly(disulfides) from cyclic starting materials by ring-opening polymerization has been recently reviewed.\textsuperscript{139}

Sakai et al. developed optimized conditions where polymerization of propagator 65 was exclusively initiated from the monolayer of initiator 64 on ITO. Selective initiation from the surface was proved by microcontact printing experiments and AFM imaging. Polymer brushes visualized on height images reproduced accurately the microprinted pattern of initiator 64, showing that SOSIP took place exclusively where 64 had been previously printed on the ITO surface (Figure 29 A). Both the concentration of propagator and the nature of the solvent were critical for selective surface-initiated polymerization. In the range of concentration $c_{\text{SOSIP}} = 7 - 11$ mM, polymerization occurred exclusively on the SAM of initiator 64 (Figure 29 B, filled circles). If $c > c_{\text{SOSIP}}$,
polymerization was not selectively initiated from the surface and occurred also in solution, in the presence of bare ITO electrodes used as control (Figure 29 B empty circles). Solution-initiated polymers were not oriented with respect to the ITO surface. Accordingly, photocurrent produced by SOSIP architecture 67 was much higher than with non-oriented, solution-initiated polymers coated on ITO (Figure 29 C).

**Figure 29.** A) AFM height image of an ITO surface with SOSIP pattern obtained from microcontact printing with initiator 64 and polymerization with propagator 65. Z axis = 0 (black) – 100 nm (white). SOSIP took place exclusively where initiator was printed. B) Dose-response curve corresponding to SOSIP with initiator 64 and propagator 65. Absorbance of ITO electrodes without (open circles) and with DTT-activated initiator 64 (filled circles) after 24 h of incubation with varied propagator concentrations at constant concentration of iPr2NEt (100 mM) in CHCl3 / methanol 1:1. C) Transmittance-normalized photocurrent generated by SOSIP architecture 67 (solid line) and by solution-initiated polymer coated on ITO (dotted line). D) AFM phase-contrast image of SOSIP architecture 67. Adapted from ref. [103].

Finally, AFM imaging of architecture 67 in phase-contrast mode evidenced long-range order with smooth surface (Figure 29 D, roughness $R_s = 5.1$ nm,
comparable with the bare ITO electrode), while solution-initiated polymers with random orientation were clearly rougher \((R_s = 87 \text{ nm})\).

Sakai et al. prepared the panchromatic architecture 70 by successive SOSIP steps with the yellow, red and blue propagators 65, 71 and 72 (Figure 30 A).

**Figure 30.** A) Panchromatic architecture 70 built from propagators 65, 71 and 72. B) HOMO and LUMO levels of \(H_2H\)-NDI in 64, \(O,O\)-NDI in 65, \(O,N\)-NDI in 71 and \(N,N\)-NDI in 72 with indication of the electron (e\(^{-}\)) and holes (h\(^{+}\)) transfers.\[^{[103]}\)

A redox gradient was installed along the NDI stacks since electron density gradually increased in \(O,O\)-NDI 65, \(O,N\)-NDI 71 and \(N,N\)-NDI 72 (Figure 29 B). IPCE was much higher with panchromatic architecture 70 than with single
component photosystem 67, evidencing that the presence of one redox gradient is already sufficient to activate the generation of charges.

1.11. Templated Stack Exchange

For access to p/n-SHJ having interdigitated n- and p-transporting channels by SOSIP, two main strategies were explored. The first one relied on surface-templated lateral self sorting and the specific recognition of initiators in a mixed monolayer by complementary propagators.\textsuperscript{[140-143]} The second one relied on templated stack exchange (TSE)\textsuperscript{[142]} and used dynamic covalent bonds to replace inert templates with optoelectronically active components along a central stack installed by SOSIP (Figure 31).\textsuperscript{[144-151]} The SOSIP-TSE approach toward p/n-SHJ is based on the confirmed orthogonality of disulfide chemistry and hydrazone exchange.\textsuperscript{[152-155]}

**Figure 31.** Post-SOSIP stack exchange. A) SOSIP architecture with central stack (yellow boxes) and lateral hydrazone templates (gray circles). B) Upon treatment with excess hydroxylamine NH\textsubscript{2}OH, templates are cleaved and hydrazide-rich pores are drilled through the SOSIP architecture. C) Covalent capture of aldehydes stack exchangers (red boxes) yields an interdigitated, SHJ-type architecture.\textsuperscript{[144]}
For SOSIP-TSE, an ITO surface was first modified with a monolayer of phosphonate-containing initiator, having lateral templates to reserve space around each starting site for SOSIP (Figure 31). On propagators, lateral acylhydrazones with inert templates also reserved space along the growing stacks. After polymerization, templates were removed along the stacks by hydrazone-oxime exchange and then replaced by so-called stack exchangers with aldehyde “handles”. Slightly acidic conditions were used for template removal and replacement. This is essential for reversible hydrazide-hydrazone conversion and ensured the easy diffusion of stack-exchanger aldehydes over the full length of the central stacks.

Sakai et al. prepared multicomponent architectures made of NDI derivatives by SOSIP and TSE (Figure 32 A to D).\textsuperscript{[144]} To test the relevance of OMARG SHJ, they prepared a series of architectures and evaluated their functional capabilities. Photosystem 73 was a simple double-channel p/n-SHJ without redox gradient that contained $O,O$-NDI 74 in the central stacks and $N,Br$-NDI 75 in the lateral stacks (Figure 32 A). Architecture 76 was a [2+2] OMARG SHJ with correctly aligned antiparallel redox gradients, that contained $O,O$- and $H,H$-NDI 74 and 77 in the central stacks and $N,O$- and $N,Br$-NDI 78 and 75 in the lateral stacks (Figure 32 B). Architecture 79 was a [1+2] OMARG SHJ with one single gradient that contained $O,O$-NDI 74 in the central stacks and $N,O$- and $N,Br$-NDI 78 and 75 in the lateral stacks (Figure 32 C). Finally, architecture 80 was a [1+2] anti-OMARG SHJ with one misaligned redox gradients that contained $O,O$-NDI 74 in the central stacks and $H,H$- and $N,Br$-NDI 77 and 75 in the lateral stacks (Figure 32 D). The precise positioning of each component in the architectures resulted in different alignment of HOMO and LUMO levels and directional flow of electrons and holes toward the ITO and TEOA (Figure 32 E).
Figure 32. Multicomponent photosystems obtained by SOSIP and TSE. A) p/n-SHJ 73 with central O,O- and lateral N,Br-NDI stacks. B) [2+2] OMARG SHJ 76 with central mixed O,O- and H,H-NDI stacks and lateral mixed N,O- and N,Br-NDI stacks. C) [1+2] OMARG SHJ 79 with central pure O,O-NDI stacks and lateral mixed N,Br- and H,H-NDI stacks. D) [1+2] anti-OMARG SHJ 80 with central pure O,O-NDI stacks and lateral mixed N,Br- and H,H-NDI stacks. E) HOMO (solid) and LUMO (dashed) energy diagram of NDIs 74-75 and 77-78 together with work function of ITO and HOMO of TEOA. F) Dependence of the short-circuit current density ($J_{SC}$) on the irradiation intensity ($P_{in}$) for 73 (○), 76 (●), 79 (▲), and 80 (△). Bimolecular charge recombination efficiencies $\eta_{BR}$ are also shown.\[144\]
The benefits of [2+2] OMARG SHJ became apparent when bimolecular charge recombination efficiencies $\eta_{\text{BR}}$ were quantified for each system (Figure 32 F). In [2+2] OMARG SHJ $\eta_{\text{BR}} = 22\%$ was minimal, whereas in [2+1] anti-OMARG SHJ $\eta_{\text{BR}} = 76\%$ was maximal. Interestingly, $\eta_{\text{BR}} = 53\%$ with [1+2] OMARG SHJ was identical to $\eta_{\text{BR}} = 50\%$ with SHJ, showing that double-channel redox gradients were needed to minimize loss of charges.

1.12. Ion-Gated Photosystems

The generation and transport of charges is primordial in biological systems. According to a hopping model, electrons are sequentially transferred from site to site.\cite{156-157} In DNA scaffolds, the redox-active sites are easily oxidized bases\cite{156, 158-159} whereas in peptides, the hopping sites are oxidizable residues.\cite{157, 160-162} Charge transfer is also influenced by the environment of the redox active sites, e. g. by the presence of ions\cite{163} or dipole moments,\cite{164} and by proton transfer in proton-coupled electron transfer.\cite{165} For example, studies on DNA scaffold revealed the critical importance of the phosphate counteranions for electron transfer over long distances.\cite{166} Other studies showed that the presence of ions in the vicinity of electroactive species, and the resulting charge repulsion or attraction, influenced the redox properties as well as the rate of charge separation and recombination.\cite{163, 167-171}

Sakai et al. have explored the influence of charges on the photoactivity of single NDI stacks grown on ITO by SOSIP.\cite{150} For that purpose, they exchanged the lateral benzyl templates in SOSIP architecture \textbf{81} with anionic (\textbf{82}), cationic (\textbf{83}) or neutral (\textbf{84}) aldehydes and obtained the ion-gated photosystems \textbf{85}, \textbf{86} and \textbf{87} (Figure 33). Symmetry-breaking charge separation in the central $O,O$-NDI stacks was maximal with anionic photosystem \textbf{85} at pH $\sim$ 7.5 as compared to cationic \textbf{86} and neutral \textbf{87} (Figure 34 A). At this pH, the simultaneous presence of protonated and deprotonated carboxylic acids in \textbf{85} was likely because of charge repulsion.
Figure 33. Ion-gated photosystems 85, 86 and 87.\textsuperscript{[150]}

Meanwhile, the presence or absence of negative charges close to the NDI has been shown to influence the HOMO and LUMO levels of these chromophores.\textsuperscript{[172]} Therefore, the significantly higher photocurrent generation at pH $\sim$ 7.5 by photosystem 85, compared with 86 or 87 was explained by the facilitated charge separation between NDIs with and without anion (Figure 34 B). In addition, the presence of partially deprotonated carboxylates along the
central $O,O$-NDI stacks was found to promote long-distance transport of photogenerated charges (Figure 35).

**Figure 34.** A) pH dependence of photocurrent $I$ by 85 (●) and 86 (○) relative to 87 ($I_0$). B) Expected HOMO (bold) and LUMO (dashed) energy levels of NDIs with/without cations/anions and electron or hole transfer. Energies in eV against a vacuum, normalized for $-5.1$ eV for Fc$^+/$/Fc. $e^-$ = electron, $h^+$ = hole.$^{[150]}$

In a control experiment, templates in SOSIP architecture 81 were replaced by a mixture of anionic 82 and neutral 84. However, at pH ~ 9 with fully deprotonated carboxylates and half of the $O,O$-NDI bearing a negative charge, the same long-distance charge transfer was not observed. In this system, protons could not flow together with electrons and stabilize them because neutral amides (from 84) were intercalated between the carboxylates (from 82).

These results suggested that the presence of mobile protons along partially protonated carboxylic acids was essential to stabilize the separated electrons and holes over long distances. The same effect was expected with photosystem 86 at pH values where amines would be partially protonated, however no long-distance charge transport was observed in that case. This suggested that hole, rather than electron stabilization was critical in this system.
Figure 35. Dependence of photocurrent generation on the thickness of films for 85 (●), 86 (○), and 87 (■). [156]
Chapter 2

OBJECTIVES

The first objective of this work is to evaluate PDI chromophores for SOSIP and synthesize single PDI stacks. Thus we envision combining the advantages of SOSIP with the appealing properties of a class of well-studied organic semiconductors that have already been engineered in many electronic devices.

We want first to demonstrate that SOSIP with PDI is successful and prepare single stacks on ITO. We start with 1,7-dipyrrolidinyl PDI (N,N-PDI) because this well-soluble molecule is more easily modified synthetically, and its processing is less troublesome than with less soluble unsubstituted PDI (H,H-PDI). We then prepare H,H-PDI derivatives for SOSIP as well. Experimental evidence for the formation of SOSIP architectures and structural information are gained from, e.g., exciton coupling that occurs in PDI stacks or AFM imaging of the surface of the films. On the functional point of view, we want to compare N,N-PDI and H,H-PDI stacks for the generation of photocurrent. Since PDIs that stack better should perform best for charge transport, SOSIP architectures with H,H-PDI stacks should give more current than with N,N-PDI stacks. We want also to establish the performance of ambipolar N,N-PDI in the presence of the recognized n-type semiconductor H,H-NDI to see if the performance of N,N-PDI stacks can be still improved.

The second part of the project concerns the preparation of multicomponent architectures on ITO surfaces with central PDI stacks. To fulfill this goal, we use templated stack exchange and thus prepare initiators and propagators with H,H-PDI and templates suited for hydrazone-oxime exchange. We then focus on the processing of these materials by SOSIP to install H,H-PDI stacks on ITO. We next explore the replacement of lateral templates with charged
peptides to prepare ion-gated H,H-PDI stacks. The photoactivity of ion-gated systems should depend on external factors such as pH and temperature, and the possible antiport transfer of electrons and protons could have an influence on the long-distance transport of charges.

In a next development, we want to prepare double-channel architectures with central H,H-PDI stacks and lateral p-type, electron-donating terthiophene stacks. We want also to explore the inverted configuration, where central, hole-transporting H,H-PDI stacks stand next to lateral, weakly or strongly electron-accepting O,O-NDI or H,H-NDI stacks, respectively. These configurations are interesting because the ambipolar activity of H,H-PDI has been reported. It is expected that charge separation in double-channel systems will be higher than in single H,H-PDI stacks because of the increased area of contact between n- and p-type materials. In double-channel systems, charge recombination should also be lower than in single channel since holes and electrons move along separate paths. Especially, we want to explore the possibility to obtain long-distance charge transport with double-channel architectures. Finally, we will know the relative performance of central H,H-PDI stacks with electron-donating or accepting lateral stacks.

Finally, we prepare dyad-type stack exchangers with ter- and quaterthiophenes and install them along central H,H-PDI stacks to obtain triple-channel systems. The central, electron-accepting H,H-PDI channel and the external hole-accepting terthiophene domain are separated by a quaterthiophene unit in the middle. Performances of these architectures are expected to excel, because electron-accepting and -donating moieties are remote, a configuration which minimizes charge recombination and increase the number of charge carriers. Also electron and hole-transporting paths are more clearly isolated, like wires, which support long-distance charge-transport. However, shortcomings could be expected if disorganized structures with poorly defined charge-transporting paths are formed, instead of the desired architectures
featuring three parallel channels. To overcome this issue we propose to use the incompatibility of shape to segregate the three components and promote the formation of the well-defined triple-channel architecture. The use of propeller-shaped triarylamines instead of planarizable terthiophene as the ultimate electron acceptor would be considered at this point.
Chapter 3

RESULTS AND DISCUSSION

As outlined in the Introduction, SOSIP is an innovative approach, developed for the user-friendly synthesis of ordered and oriented organic architectures on ITO surfaces. A very careful design of building blocks with encoded structures, reactivity and functionality is the fundamental basis of this methodology. Guidelines for the design of initiators and propagators will be briefly summarized here.

At first the self-recognition, self-assembly and preorganization of molecules is essential for the purpose of constructing ordered and oriented regular structures. Therefore supramolecular recognition motives have to be integrated in the design. Moreover, the process of building photosystems from SOSIP relies on a set of orthogonal chemical reactions. For that reason, a set of selected reactive groups have to be implemented in the structures of target compounds. Finally, protecting groups have to be placed on reactive sites. They play an important role, during the synthesis of the building blocks, and later allow precise transformations on the architectures by the mean of chemical stimuli. Here also, chemical orthogonality is essential. Finally, elements that are essential for function have to be implemented.

Before the beginning of the present work, the above-presented characteristics had already been implemented in the design and synthesis of NDI initiators and propagators for SOSIP, as described in the introduction. At first glance, our initial goal consisted in the replacement of NDI by PDI as the central aromatic moiety, while keeping structural motives and reactivity already successfully developed.
To start with, we prepared an initiator and a propagator containing core-substituted 1,7-dipyrrolidinyl PDI \(N,N\)-PDI. This chromophore was selected as the candidate of choice to demonstrate the applicability of PDIs for SOSIP.

First, the pyrrolidinyl-substituents on the \(N,N\)-PDI core induce a twisting from the planar conformation, increasing the solubility of this species as compared to its \(H,H\)-PDI counterpart. This feature simplifies the synthesis and purification of both initiator and propagator, shortening the time needed to obtain the first proof-of-principle results.

Second, and functionally speaking, cofacial dimeric aggregates of \(N,N\)-PDI have been shown to undergo symmetry-breaking charge separation. This means that disproportionation of photoinduced electrons and holes spontaneously occur after photoexcitation. This is favorable in terms of photoactivity because excitation of the architecture with single \(N,N\)-PDI stacks with light will generate free holes and electrons and produce a measurable photocurrent.

Third, and in spite of their distorted core, \(N,N\)-PDI form aggregates both in solution and in the solid state. This is desirable for the preorganization of initiator-propagator and propagator-propagator pairs prior to polymerization. Moreover, the coupling of excitons arising from aggregation gives a characteristic signature in UV-Vis absorption spectroscopy, making of this simple tool a structural probe for the structural study of the resulting architectures.

### 3.1. Single-Channel Photosystems

#### 3.1.1. Green Perylenediimides

##### 3.1.1.1. Synthesis

Initiator 88 constructed around a \(N,N\)-PDI chromophore was synthesized as outlined in Scheme 2. The synthesis started with molecule 89, which was
prepared according to reported procedures from the commercially available perylene tetracarboxylic dianhydride (PDA, 14).

Scheme 2. a) Ref [60]; b) H-Lys(Cbz)-NH₂, pyridine, reflux (55%); c) 1. HBr / AcOH, thioanisole, pentamethylbenzene, TFA. 2. Boc-Cys(S-t-Bu)-OH, TBTU, HOBr, 2,4,6-collidine, DMF (2 steps, 60%); d) 1. TFA, DCM. 2. 80, TBTU, 2,4,6-collidine, DCM/DMF (2 steps, 50%); e) 1. TMSBr. 2. MeOH (quant).

As previously outlined by Würthner et al. in the original procedure, both 1,6- and 1,7-isomers of the dissubstituted PDI are likely to form during the initial step of the synthetic route. We took care to isolate isomerically pure 1,7-
disubstituted PDI exclusively, according to the original paper. Analytical data obtained with 89 proved that the pure 1,7-dipyrrolidino isomer had been successfully obtained. Anhydride 90 was obtained from diimide 89 upon saponification with KOH and subsequent treatment with acetic acid to close the anhydride. This poorly soluble material could be slowly reacted with the amine H-Lys(Cbz)-NH₂ by heating it at reflux in pyridine for 18h to give the corresponding symmetric diimide 91 in 55% yield. This material showed a good solubility in dichloromethane and also, more surprisingly, in ethyl acetate. 91 is a key intermediate here because it is involved in the preparation of both initiator 88 and propagator 92. From there, deprotection of the two carboxybenzyl (Cbz) groups of 92 with acid yielded an amine, which was linked to a protected cysteine Boc-Cys(S-t-Bu)-OH in standard peptide coupling conditions using O-(Benzotriazole-1-yl)-N,N,N',N'-tetramethyluronium tetrafluoroborate (TBTU) and hydroxybenzotriazole (HOBt). Diamide 93 was obtained in good yield and, after deprotection of two Boc groups with trifluoroacetic acid (TFA) to release amines, was coupled to the carboxylic acid 94, again in standard peptide coupling conditions, to give the fully protected intermediate 95. Owing to its eight benzyl and two t-Bu groups, this latter molecule was found to be highly soluble in pure chloroform.

In the last step, the benzyl protecting groups in precursor 95 were removed to yield initiator 88. To do so, phosphonate ester were attacked with oxophilic trimethylsilyl bromide (TMSBr) to generate a silylated species, which was subsequently decomposed into free phosphonic acid groups by the action of methanol. 88 was very poorly soluble in common organic solvents and couldn’t be purified by column chromatography because of the high affinity of the phosphonic acid groups for silica gel. Therefore, the crude material obtained after deprotection was repeatedly washed with diethylether and dichloromethane (DCM) (solid-liquid extraction) to remove the non-polar impurities and yield pure 88. Complete removal of the benzyl groups was assessed by ¹H NMR run in CD₃OD.
The synthesis of the \(N,N\)-PDI propagator 92 is outlined in Scheme 3. The procedure is straightforward because the starting material 91 is a common intermediate in the synthesis of initiator 88. In brief, the Cbz protecting groups in 91 were removed as described above to give amines that were reacted with the activated ester 96. This latter compound was prepared according to literature procedures from asparagusic acid and N-hydroxysuccinimide. Presence of strained disulfide rings in 96 and in the product 92 made these species prone to polymerization. Therefore, reaction conditions for the preparation of amide 92 were carefully optimized in order to avoid undesired polymerization during the process. The main parameter was the pH of the medium, which was regularly checked and maintained at 8 upon addition of triethylamine (TEA). Below that value, the reactivity of the amine was too low to attack the activated ester 96 and conversion remained low. Above that value, the probability that a nucleophile (e. g. amine, thiolate) could initiate the polymerization of the precursor 96 or of the already formed propagator 92 became too high. The concentration of 91 also played an important role because it influenced the concentration of 92 at the end of the reaction. It had to be high...
enough to ensure the rapid conversion of the species but not at the point that the concentration of 92 reached a level where undesired polymerization side-reactions occurred at a significant rate. In the optimized conditions, concentration of 91 was set at 20 mM. Moreover, the solvent mixture DCM/N,N-dimethylformamide (DMF) 2:1, v/v was found to be ideal to solubilize both the amine starting material and the product 92. Precipitation of 92 during the reaction would result in its immediate decomposition.

It has to be mentioned as well that 92 readily polymerized in the solid state. For purification of the crude material by column chromatography, crude 92 was absorbed on small amounts of silica gel that were then loaded on the column, avoiding the use of unstable, concentrated solutions. The favorable effect of solid deposit was likely due to both the acidic character of silica that deactivated nucleophiles before they could initiate polymerization and its large specific surface, which dispersed 92 and limited intermolecular contacts. With rare contacts between molecules, the occurrence of polymerization decreased significantly. Accordingly, purified 92 was never kept dry for a long time, but stored as a dilute solution in a mixture of CHCl₃/MeOH 1:1, v/v.

3.1.1.2. Self-Assembled Monolayers

With both the initiator and propagator with N,N-PDI core successfully prepared, the next step was the formation and characterization of self-assembled monolayers (SAM) on ITO surfaces. Numerous reports exist in the literature on the functionalization of ITO with phosphonic acids. For that purpose, initiator 88 was dissolved in a mixture of DMSO/MeOH at a concentration of 1 mM. The ITO electrodes were prepared and treated with the initiator solution as described in the experimental part to assemble monolayer 97 (Figure 36).
A sensitive electrochemical method was used to assess the integrity of the formed monolayer, and particularly the absence of defects or pinholes that would otherwise compromise the growth of an organized, regular polymeric film afterward. It has been shown in the case of alkylthiol monolayers assembled on gold surface that ferricyanide Fe(CN)₆³⁻ is a sensitive probe to detect the presence of defects in the organic layer. In our case, we used this technique to monitor the formation of SAM 97 on ITO, which was used as working electrode (Figure 37 A). With clean ITO, a characteristic redox wave arising from a reversible single-electron transfer between ITO and Fe(CN)₆³⁻ was recorded (Figure 37 A, dotted line). After incubation of ITO in a solution of 88 for 4h, the peak current decreased by one order of magnitude already (Figure 37 A, chopp line and B). After 24h of incubation, the peak current decreased again by one order of magnitude (Figure 37 B).
Figure 37. A) Cyclic voltammograms of aqueous ferricyanide measured with an ITO surface as a working electrode (a) before the deposition of initiator 88, (b) after 4h, and (c) 24h of incubation in the solution of the initiator 88. B) Peak current (absolute values) of the ferricyanide reduction wave as a function of the incubation time.

The voltammogram recorded at this time point showed essentially a capacitive current between 0 and 0.3 V vs. Ag/AgCl (Figure 37 A, solid line), indicating that the diffusion of Fe(CN$_6$)$_3^-$ to the ITO electrode was blocked by the presence of a compact SAM of 88.

Once the assembly process of 88 on ITO had reached to equilibrium, we heated up the resulting monolayer 97 in an oven at 120 °C for 1h. According to literature reports, this procedure strengthened the bonding between phosphonic acid groups and ITO. IR studies revealed that surface-adsorbed phosphonic acids were converted into surface-bound phosphonates at this temperature. The effect of thermal treatment on the packing of monolayer 97 was evidenced by a further decrease of the ferricyanide wave after heating (Figure 38).
Figure 38. Cyclic voltammograms of aqueous ferricyanide measured with monolayer 97 on ITO as a working electrode before (chopped line) and after (solid line) heating at 120 °C for 1h. Increased packing of the monolayer is evidenced by a decrease in the peak current at 0.4 V vs. Ag/AgCl.

Cyclic voltammetry allowed also for the recording of the characteristic reduction waves of \( N,N \)-PDI when 97 was used as a working electrode without ferricyanide (Figure 39 A). As the peak currents were linearly dependent on the scan rate, a typical feature for redox processes that take place on surfaces, the presence of initiator molecules bound to the oxide was confirmed. (Figure 39 B).\(^{[178]}\) A surface coverage \( \Gamma = 0.12 \text{ nmol cm}^{-2} \) (0.7 molecule nm\(^{-2} \)) was estimated from the charge of the reduction waves, assuming a single-electron transfer process.
Figure 39. A) Cyclic voltammograms of (a) N,N-PDI 89 (0.25 mM) in DCM, and (b) ITO electrode coated with 88 (monolayer 97, scan rate = 0.05, 0.1, 0.2, 0.4, 0.8 V/s). B) Peak current of the second reduction (filled arrow in Figure 4A) and the second oxidation (hollow arrow in Figure 4A) as a function of scan rates.

Noteworthy, the presence of N,N-PDI 88 on ITO was evidenced by UV-Vis spectroscopy as well (Figure 40). Therefore another estimate of surface coverage $\Gamma$ was obtained on the basis of the absorption of N,N-PDI at 700 nm, as explained in the experimental part. This time $\Gamma$ was found to be 0.18 nmol cm$^{-2}$ (1.1 molecule nm$^{-2}$). The two values obtained from CV and UV-Vis spectroscopy globally correlate and were consistent with molecular models that
considered the anchoring of 88 with four phosphonic groups to the oxide surface.

Figure 40. Absorption spectrum of 97 bound to an ITO electrode. Background absorption of a clean ITO surface has been subtracted from the raw data.

With compact monolayers in hand, we next reduced the $t$-Bu disulfide group sticking out of the surface of monolayer 97 with dithiothreitol (DTT). This dithiol rapidly reduces linear disulfides into thiols due to its strong tendency to form a six-membered disulfide ring.\textsuperscript{133, 179} Our procedure consisted in dipping 97 in a solution of DTT in aqueous NH$_4$HCO$_3$ (pH 8) for 1 hour at RT. Solutions of DTT in the reduced form are stable for extended periods of time under ambient condition, nevertheless the vial containing the reducing mixture was purged with Ar to avoid reoxydation of thiols by air. The obtained monolayers 98 with thiol groups pointing out were immediately used to optimize the polymerization conditions of propagator 92.

3.1.1.3. Self-Organizing Surface-Initiated Polymerization

Monolayer 98 with thiols pointing out of the surface was expected to be deprotonated in the presence of a base to give 99 (Figure 41). This deprotonation was expected to be easily obtained using tertiary amines for example, since the $pK_a$ of the thiol in free L-cysteine is reported to be 8.3.\textsuperscript{180}
while in peptides and protein values between 8-11 have been found for this  \(-\text{SH}\) group.  

Preorganized by the recognition pattern encoded in its structure (Figure 41, dotted lines), propagator 92 was then expected to form a supramolecular complex with monolayer 99, where the thiolate nucleophiles would be in close proximity with the strained five-membered disulfide rings. Disulfide-exchange ring-opening polymerization would then occur, forming new disulfide bonds between initiator and propagator and regenerating active thiolates on the surface of architecture 100 for covalent capture of a next propagator. The polymerization mechanism and polymer structures that are shown on figure 41 are best considered as speculative. However they were derived from substantial experiment data obtained with NDIs and are consistent with molecular models. In the case of NDIs, formation of a regular ladderphane was helped by a self-
repair mechanism, for which experimental support exists, that could correct structural errors during SOSIP.\[^{140}\]

From a practical point of view, the next task to address was the development of conditions that could make SOSIP to happen with \(N,N\)-PDI. At the beginning of this optimization, extensive experience gained from previous works with SOSIP of NDI existed in the group. It was shown that successful surface initiated polymerization of disulfide imposed the following requirements:

- A base is needed to deprotonate the thiols that are present at the surface of monolayer 98. Studies on NDI had revealed that Hüning base (\(i\)PrNEt) was the most suited for that task. Its good performance likely arouse from the non-nucleophilicity of this sterically encumbered amine.

- The solvent (or mixture of solvents) used should preserve the non-covalent interactions involved in the recognition and preorganization of building blocks during the SOSIP process. At the same time, it has to solubilize the propagator well enough to reach a concentration where SOSIP takes place. The right balance between solubilization and aggregation has to be found. In the case of NDI, chloroform mixed with various amounts of methanol generally performed well.

- For NDIs, it existed a concentration of the propagator, \(c_{\text{SOSIP}}\), where polymerization occurs exclusively from the surface. Below that value, no reaction took place because of dilution. Above that, polymerization from the solution started, and solid material precipitated on the walls of the reaction vial and on the electrode. This in turn disturbed or even blocked the course of SOSIP.

These lessons were applied to the case of \(N,N\)-PDI propagator 92. A three steps strategy was followed to find conditions suited for successful SOSIP.
First, solvents and mixtures of solvents were screened to rapidly eliminate those in which 92 was not soluble.

Second, polymerization trials on 98 and clean ITO were done in parallel with the selected solvents. A fixed concentration of 100 mM iPr₂NEt and of 20 mM 92 was used. The purpose of these experiments was to eliminate the solvent systems which would give either no polymerization at all on 98 or precipitation on the clean ITO control. Already at this stage, a mixture of chloroform and methanol (CHCl₃: MeOH 1:1) showed satisfying results.

Third, \( c_{\text{SOSIP}} \) was determined from a series of experiments where 98 and control clean ITO were incubated together with increasing concentrations of 92 in CHCl₃/MeOH 1:1, v/v and 100 mM iPr₂NEt, resulting in increasingly thicker SOSIP architectures 100 (Figure 42 A). The resulting dose response curve gave best results with a propagator concentration \( c_{\text{SOSIP}} \sim 20 \) mM (Figure 42 B). At lower concentration, polymerization did not take place. Above the critical

\[ \text{Figure 42. A) UV-Vis spectra of 100 with increasing thicknesses. The arrow shows the spectral changes with increasing concentration of propagator 92 from 10 to 30 mM. B) Absorption of SOSIP architecture 100 at } \lambda_{\text{max}} = 737 \text{ nm as a function of the concentration of propagator 92 in CHCl₃/MeOH 1:1, v/v, 100 mM iPr₂NEt during incubation of ITO without (□) and with (■) activated monolayer 98.} \]
SOSIP concentration, polymerization occurred also in solution and precipitates accumulated on the clean ITO surface. Contrary to the situation that had been previously reported with NDIs, polymers obtained by this competing process did not stick to the clean ITO surface and could be detached from the control electrode by stirring it in DMSO.

3.1.4. Structural Characterization

To gain insight in the structure of architecture 100, the UV-Vis spectra obtained from the films polymerized on ITO were compared to those of diluted solutions of 92 in CHCl₃/MeOH 1:1, v/v (Figure 43).

![Normalized absorption spectra of propagator 92 in diluted solution (10⁻⁵ M in CHCl₃/MeOH 1:1, v/v, dotted line) and of SOSIP architecture 100 (solid line).](image)

In a dilute solution, propagator 92 showed a strong absorption band arising between 600 and 800 nm. This was the signature of the S0-S1 optical transition. A vibronic progression was apparent in this band, with the absorption maximum at 717 nm corresponding to the v0,0 transition and the shoulder at 680 nm to the v0,1 transition. The ratio of intensity of the maximum to the shoulder was 1.95. On the other hand, the UV-Vis spectrum recorded with SOSIP architecture 100 showed a slightly broader band, between 580 and 650 nm. Compared to the diluted solution, the absorption maximum was red-shifted by
20 nm, to 737 nm. A shoulder appeared at higher energy, around 680 nm. Interestingly, the intensity ratio of the maximum to the shoulder was lower than in solution, at 1.25.

In the aggregated state, the absorption spectrum of N,N-PDI is explained by the theory of exciton coupling. In perfect cofacially stacked N,N-PDIs, the exciton coupling model predicts that the optical transition in the \( v = 0 \) vibronic level of the upper exciton is the only allowed. In SOSIP architecture 100, it was at the origin of the band observed at 680 nm.\(^{[184]}\) To explain the additional red-shifted band that appeared at \( \lambda = 737 \) nm, vibrational coupling was taken into account. According to the exciton model, it permitted the transition in the \( v = 1 \) level of the lower exciton as well, corresponding to the band at \( \lambda = 737 \) nm. Wasielewski et al. reported that for N,N-PDI perfectly cofacial aggregates, the band at 680 nm should be more intense than the one at 737 nm.\(^{[184]}\) In the case of SOSIP architecture 100, the situation was inverted and resembled more the case of diluted propagator 92, suggesting that the face-to-face stacking was not very good (Figure 43).

Attempts to quantify the thickness of the film and the corresponding number of stacked N,N-PDI chromophores was done on the basis of UV-Vis measurements. The related equations are described in the experimental part. For these calculation, we used the surface coverage \( \Gamma = 0.12 \) nmol cm\(^{-2} \) found for the monolayer 97 (vide supra) and assumed an molar absorption coefficient \( \varepsilon_{\text{MAX}} = 39500 \) M\(^{-1} \) cm\(^{-1} \) for the N,N-PDI chromophore. By using these values, architecture 100 with an absorption \( A_{\text{MAX}} = 0.1 \) at \( \lambda_{\text{MAX}} = 737 \) nm resulted in a thickness \( d = 7.4 \) nm. With a constant distance of 3.5 Å between each chromophore in the stack, the number of N,N-PDI involved was 21. It has to be stressed that the calculations involved the molar absorption coefficient \( \varepsilon_{\text{MAX}} \) of the diluted propagator 92 under the assumption that it did not change much upon aggregation of the N,N-PDI chromophores in SOSIP architecture 100.
This was of course an approximation but is justified here by the fact that the coupling of \(N,N\)-PDIs was not very strong (see Figure 43).

The superficial morphology of SOSIP architecture 100 was probed by AFM. In phase-contrast mode, low-defect organization over very long distances was evident (Figure 44 A). These phase-contrast images were nearly identical to those obtained by Sakai et al. with NDI SOSIP architectures.\(^{[103]}\)

Topographic data revealed a smooth surface with monotonous height profile \((R_a \sim 4 \text{ nm}, \text{Figure 44 B})\). Optical imaging supported the formation of a smooth film as well (Figure 44 C).

\[ \text{Figure 44. Images recorded from SOSIP architecture 100. A) AFM phase contrast image (Phase range: 70°); B) AFM height image (Z range: black 0 nm – white 50 nm) with (bottom) height profile; C) Optical image.} \]
3.1.1.5. Functional Characterization

Structural studies confirmed that 100 was a smooth film with long-range organization, which contained N,N-PDI chromophores in cofacial aggregates. The next step was to probe the functionality of the system and correlate it with the structural features pointed out. We hypothesized that the architecture 100 would generate photocurrent by separation of holes and electrons in the stack upon illumination with a light source. Figure 45 shows the HOMO and LUMO energy levels of N,N-PDI, together with the work function of ITO and the HOMO of TEOA.[63]

\[
E / \text{eV}
\]

![Figure 45. Energy levels of the partners involved in the photocurrent generation upon irradiation of 100. HOMO (bold) and LUMO (dashed) of N,N-PDI together with HOMO of TEOA and work function of ITO, reported relative to -5.1 eV for Fc'/Fc. Full arrow denotes electronic transition resulting from photoexcitation, half arrows illustrate subsequent electrons (e^-) and holes (h^+) transfer.](image)

The oxidation potential of TEOA was found to be \( E_{\text{ox}}(\text{TEOA}/\text{TEOA}^+) = +0.140 \text{ V vs. Ag/AgCl in 0.1 M aqueous Na}_2\text{SO}_4 \)[185] The HOMO level of TEOA was calculated from the redox potential of Fc'/Fc, \( E_{\text{red}}(\text{Fc}^+/\text{Fc}) = +0.440 \text{ V vs. Ag/AgCl and reported relative to } -5.1 \text{ eV vs. vacuum for Fc}^+/\text{Fc}.[186]

Upon excitation by light, one electron would be promoted from the HOMO to
the LUMO of \(N,N\)-PDI. Then electron transfer to the ITO electrode would occur. The hole left behind in the HOMO of \(N,N\)-PDI would be filled with an electron provided by TEOA.

SOSIP architecture 100 was submitted to the illumination of a solar simulator in the presence of a sacrificial electron donor (TEOA) and the resulting photocurrent recorded (Figure 46 A, see Experimental Section for details).

![Figure 46. A) Transmittance-normalized photocurrent generated by photosystem 100 (\(A = 0.255\) at \(\lambda_{\text{MAX}} = 737\) nm); B) Short-circuit densities as a function of the thickness of the film \(d\). Gray line added as visual guide. Film thickness \(d\) was estimated from \(N,N\)-PDI absorption using \(A_{737} = 0.1\) a. u. \(~7.4\) nm. Conditions were: TEOA concentration 50 mM, \(P_{\text{in}} = 67\) mW cm\(^{-2}\).](image)

Photocurrent was recorded upon switching the light source on and off. Anodic photocurrent rose rapidly upon illumination and could be repeated several times without alteration of the kinetic profile (Figure 46 A). Photosystem 100 was therefore stable under the illumination condition used and the initial photocurrent decay resulted from saturation of the charge transport mechanism rather than from instability of the materials. The ability of photosystem 100 to generate a measurable current confirmed the ability of \(N,N\)-
PDI to undergo symmetry-breaking charge separation between electrons and holes in cofacial aggregates, in the absence of a second electroactive material.

The photocurrent produced by photosystem 100 was strongly dependent on the thickness $d$ of the architecture (Figure 46 B). Photocurrent density $J_{SC}$ initially increased until the absorption of the film reached critical $d_C \sim 30$ nm. This was expected because the absorbance of architecture 100 increased with $d$ and thus an increasing number of photons were absorbed. In turn, they were converted into an increasing number of charge carriers, resulting in an increasing photocurrent $J_{SC}$. Above $d_C \sim 30$ nm, the current strongly decreased, most probably because photogenerated holes and electrons recombined in the thick architecture before they could reach the electrodes. Additionally, the electric resistance of the film increased with $d$, contributing to the decrease in photocurrent.

The transmittance-normalized current obtained with SOSIP architecture 100 could be compared to what had been obtained with NDI SOSIP. Clearly, the photocurrent generated by $N,N$-PDI-containing 100 was lower in spite of the larger aromatic core of $N,N$-PDI as compared to NDI and the resulting (expected) better aggregation and charge-transport properties. Efficient photoinduced electron transfer in perfect cofacial $N,N$-PDI dimers has been evidenced in the literature. However, we found that the coupling between $N,N$-PDI chromophores in photosystem 100 was somehow limited. Therefore the low current obtained with SOSIP architecture 100 resulted probably from poor charge mobility, because of the limited aggregation. Indeed, rapidly saturating and soon slightly decreasing photocurrents in thicker photosystems were in support of poor charge mobility because of poor $\pi$ stacking.

### 3.1.1.6. Co-Polymerization

The poor performance of single $N,N$-PDI stacks in architecture 100 prompted us to prepare the potentially more active, two-component architecture
with \( N,N\)-PDI and \( H,H\)-NDI. With its HOMO and LUMO lying 2.01 and 0.49 eV under the ones of \( N,N\)-PDI, respectively, \( H,H\)-NDI appeared as the ideal electron-accepting partner for \( N,N\)-PDI (Figure 47).

![Energy levels diagram](https://via.placeholder.com/150)

**Figure 47.** Energy levels of the partners involved in the photocurrent generation upon irradiation of photosystem 101. HOMO (bold) and LUMO (dashed) of \( N,N\)-PDI 74 and \( H,H\)-NDI 77 together with HOMO of TEOA and work function of ITO, reported relative to -5.1 eV for Fc+/Fc. Full arrows denote electronic transitions resulting from photoexcitation, half arrows illustrate subsequent electrons (e\(^-\)) and holes (h\(^+\)) transfer.

Upon excitation of \( N,N\)-PDI by light at 737 nm, one electron from its HOMO would get promoted to the LUMO. From there, it was hypothesized that electron transfer to the LUMO of the electron accepting \( H,H\)-NDI could occur, leaving a hole in the HOMO of \( N,N\)-PDI. This hole would then be refilled by an electron from TEOA and the electron located in the LUMO of \( H,H\)-NDI would be transferred to the ITO anode.
To test this hypothesis, target molecule 102, equipped with two strained five-membered disulfide ring, was designed as a propagator that could be co-polymerized with propagator 92 (Scheme 4).

**Scheme 4.** a) 1. HBr / AcOH, thioanisole, pentamethylbenzene, TFA. 2. 96, DCM/DMF, TEA, pH 8, 80 min (2 steps, 60%).

Synthesis of 102 was a simple two-step procedure from the Cbz-protected precursor 103. Removal of the Cbz protecting groups with acid, followed by coupling of the resulting amines with activated ester 96 yielded 102 in 60% yield. This material was prone to polymerization and therefore stored as a diluted solution in CH2Cl2/MeOH 1/1.

In a simple, co-polymerization (co-SOSIP) experiment, activated monolayer 98 (vide supra) was incubated in a solution of 92 (20 mM) and 102 (15 mM) in CHCl3/MeOH 1:1, v/v with 100 mM iPr2NEt as a base catalyst. The mixture was stirred at RT and kept protected from light and oxygen. After 24h of reaction, the ITO electrode was covered with a green film that did not dissolve upon rinsing with CHCl3/MeOH 1:1, v/v or DMSO. UV-Vis spectrum of the film was measured and showed the characteristic signatures of the N,N-PDI chromophore at 737 nm together with the absorption band of H,H-NDI at 380 nm (Figure 48 A).
Figure 48. A) Absorption spectra of propagator 102 in diluted solution (dotted) and of photosystem 101 (solid). B) Transmittance-normalized photocurrent generated by photosystem 100 (dotted) and by photosystem 101. Conditions were: concentration of TEOA 50 mM, $P_{in} = 67$ mW cm$^{-2}$. Film thicknesses were comparable and below $A_{737} = 0.4$. C) Action spectrum of photosystem 101 (IPCE normalized to unity at 360 nm).

On the functional point of view, this system was probed by photocurrent measurement using a solar simulator. Transmittance-normalized photocurrent with co-SOSIP architecture 101 was indeed higher than with single-component SOSIP 100, as expected from the addition of the second chromophore $H,H$-NDI (Figure 48 B). However, the action spectrum of co-SOSIP 101 revealed that the main contribution to the photocurrent arouse from a high energy band located below 400 nm and thus attributable to the $H,H$-NDI component of the system (Figure 48 C). On the other hand, the activity of $N,N$-PDI in the presence of the
confirmed electron transporting material \( H,H\text{-NDI} \) remained very limited, as testified by the very low IPCE measured between 600 and 800 nm.

Although other explanations remained possible, poor charge mobility in poorly organized stacks could conceivably account for the inactivity of SOSIP architectures with \( N,N\text{-PDI} \). Efficient photoinduced charge separation has been demonstrated previously in cofacial dimers\(^{79}\) and in the present work, the absorption spectra provided direct experimental support that the stacking was insufficient (Figure 43). Moreover, rapidly saturating and soon slightly decreasing photocurrents in thicker photosystems were in support of poor charge mobility because of poor \( \pi \)-stacking (Figure 46 B).

### 3.1.2. Unsubstituted Perylenediimides

At this point of the work, it was demonstrated that the preparation of initiator and propagator for SOSIP based on the \( N,N\text{-PDI} \) core was addressable synthetically. Moreover, the formation of a SAM on ITO was demonstrated, with results comparable to what had been obtained with NDIs. Suited conditions could be found for SOSIP to occur. On the structural point of view, formation of a smooth film with long-range organization was evident from AFM. However, UV-Vis spectroscopy supported poor \( N,N\text{-PDI} \) stacking, and from a functional point of view, photocurrent measurements had shown that single \( N,N\text{-PDI} \) stacks performed poorly. We concluded that PDIs that stack better should give active photosystems.

As outlined above, the dipyrrolidinyl substituents at the 1 and 7 positions of the \( N,N\text{-PDI} \) core induced a twisting of the polycyclic moiety. In the case of unsubstituted PDI (\( H,H\text{-PDI} \)) on the other hand, the small hydrogen atoms are compatible with a total planarization of the system. This structural feature is responsible for the poor solubility of \( H,H\text{-PDI} \) derivatives and the facile formation of aggregates. This in turn affects the optical properties of the
corresponding materials and give rise to interesting charge-transporting properties.

3.1.2.1. Synthesis

In our case the strongly aggregating \(H, H\)-PDI core was an appealing motif around which initiator and propagator could be constructed using the methodology developed with \(N, N\)-PDI. Initiator 104 and propagator 105 were prepared for that purpose (Scheme 5). Indeed their preparation was carried out following the procedures developed with the \(N, N\)-PDI counterparts, with minor modification concerning the purification.

![Scheme 5](image)

**Scheme 5.** a) H-Lys(Cbz)-NH\(_2\), pyridine, reflux (74%); b) 1. HBr / AcOH, thioanisole, pentamethylbenzene, TFA. 2. Boc-Cys(S-t-Bu)-OH, TBTU, HOBt, 2,4,6-collidine, DMF (2 steps, 55%); c) 1. TFA, DCM. 2. 94, TBTU, 2,4,6-collidine, DCM/DMF (2 steps, 71%); d) 1. TMSBr. 2. MeOH (quant); e) 1. HBr / AcOH, thioanisole, pentamethylbenzene, TFA. 2. 96, DCM/DMF, TEA, pH 8, 80 min (2 steps, 62%).
The common starting material for both 104 and 105 was the commercially available perylene dianhydride (PDA) 14. It was transformed in the key diimide 106 in good yield by refluxing in pyridine with H-Lys(Cbz)-NH₂. For 104 then, the side chain of lysine was elongated with successive deprotection / coupling procedures using classical peptide chemistry to give intermediates 107 and then 108. This fully protected intermediate displayed a good solubility in mixtures of chloroform and methanol but the deprotected target 104 on the other hand was poorly soluble in common organic solvents. Solubility in DMSO amounted to 0.5-1 mM as measured from UV-Vis spectroscopy, using reported molar absorption coefficients.

For 105, removal of the Cbz protecting group with acid, followed by the coupling of resulting amines with the activated ester 96 yielded the target compound in approximately the same yield as for the N,N-PDI counterpart 92 (Scheme 5). Contrary to the latter, and as expected from the planarity of H,H-PDI core, the solubility of 105 in CH₂Cl₂/MeOH 1:1 and CHCl₃/MeOH 1:1, v/v was very poor and remained under 1 mM. Soon it was discovered that the replacement of methanol by the halogenated alcohol 2,2,2-trifluoroethan-1-ol (trifluoroethanol, TFE) greatly improved the solubility of 105. Therefore this compound was stored as diluted solutions (5 mM) in CHCl₃/TFE 1:1. In comparison, the propensity of N,N-PDI propagator 92 to undergo irreversible decomposition (most probably by polymerization) when kept dry was seemingly increased. Although they represented challenges that had to be addressed for the synthesis, these features were also encouraging because they indicated better aggregation properties, in the line of what was expected, and promised improved performances for the resulting photosystem.

3.1.2.2. Self-Assembled Monolayers

The formation of SAM 109 on ITO using solutions of initiator 104 at 0.5 mM in DMSO (Figure 49). The detailed procedure is described in the
experimental part and is very similar to what had been done with the $N,N$-PDI initiator.

Figure 49. Hypothesized formation of SAM 109 by the assembly of 104 on ITO surface through phosphonic acid-metal interactions. The grey background represents an ITO surface. Red color evidence structural elements for binding to the surface, orange shows amide bonds involved in the preorganizing interactions with propagator 105 (not shown), blue is for the protected disulfide sticking out of the surface, that are used subsequently used to initiate the polymerization. Violet color covers the aromatic core of $H,H$-PDI.

In brief, cleaned ITO surface were dipped in the diluted solution of 104 at RT and the coverage process monitored by the inhibition of the ferricyanide redox wave. From these measurements (Figure 50 A), the formation of a compact monolayer was evident after one day of incubation. After completion of the process, the resulting monolayer 109 was stirred in DMSO for 0.5 h to dissolve initiator molecules that remained physically adsorbed on the surface, and then heated at 120 °C for 1 h to achieve complete chemical binding of the phosphonates to the oxide surface.
Figure 50. A) Cyclic voltammograms of aqueous ferricyanide measured with an ITO electrode (a) before the deposition of initiator 104, (b) after 4h, and (c) 24h in the solution of the initiator as a working electrode. B) Cyclic voltammograms of (a) 106 (0.25 mM) in DCM, and (b) the initiator coated ITO electrode (monolayer 109, scan rate = 0.0125, 0.025, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.8 V/s). C) Peak current of the second reduction (●) and the second oxidation (■) as a function of scan rates.

Structural studies that aimed at determining the coverage $\Gamma$ (in molecules per surface area) of the ITO achieved with initiator 104 were then carried out. Using ITO with monolayer 109 as a working electrode in a cyclic voltammetry setup, two reduction waves appearing at -0.5 and -0.75 V were observed (Figure 50 B solid lines). The position of these signals corresponded to those observed with a diluted solution of 106 (Figure 50 B dotted line) used for comparison, suggesting that they originated from the redox activity of the $H,H-$
PDI core in 104. On the basis of reports from the literature, these waves were assigned to the first (PDI/PDI) and second (PDI/PDI\(^2\)) reduction reactions of the \(H,H\)-PDI chromophores bound to the surface. The peak current of these waves showed a linear dependence on the scan rate, confirming that the redox-active species were bound to the electrode (Figure 50 C). Under the applied conditions, no oxidation peaks could be recorded. As it is the case with the \(N,N\)-PDI initiator, \(\Gamma\) was determined by CV from the charge of these reduction waves. Assuming that each of the waves corresponded to a single-electron transfer process, a value of \(\Gamma = 0.15 \text{ nmol cm}^{-2} \) (0.9 molecule \(\text{nm}^{-2}\)) was obtained. This value was in accordance with molecular models and supported the anchoring of initiator 104 bound to the ITO surface with all four phosphonates. It is additionally consistent with the value previously found with initiator 88 (0.12 nmol cm\(^{-2}\), 0.7 molecules \(\text{nm}^{-2}\)). Monolayer 109 was transformed into 110 upon treatment with DTT at RT for 1h and reduction of the disulfide groups pointing out of the monolayer to thiols by using DTT (Figure 49).

3.1.2.3. Self-Organizing Surface-Initiated Polymerization

Polymerization of propagator 105 was envisioned to occur after deprotonation of thiol-rich monolayer 110 to 111 (Figure 51). In the previous case of \(N,N\)-PDI initiator and propagator, SOSIP occurred at a \(c_{\text{SOSIP}} = 20 \text{ mM in CHCl}_3/\text{MeOH 1:1, v/v with 100 mM iPr}_2\text{NEt as a base catalyst. However, with this solvent mixture and in the case of 105, the upper limit of solubility remained below 1mM. Moreover, such solutions, once basified with 100 mM iPr}_2\text{NEt and incubated with 110 for 24 h at RT did not give rise to polymerization of 105, neither on the ITO surface nor in solution.}
Figure 51. Hypothesized mechanism for the polymerization of propagator 105 on activated monolayer 111 by ring-opening disulfide-exchange. The grey background represents an ITO surface. Dotted lines denote preorganizing interactions between initiator and propagator.

On the other hand, 105 was much more soluble in a mixture of CHCl₃/2,2,2-trifluoroethanol (TFE) 1:1 and concentrations up to 30 mM could be reached. In these conditions and using 100 mM iPr₃NEt as a base catalyst, SOSIP occurred at \( c_{\text{SOSIP}} \sim 13 \) mM (Figure 52 A, filled circles). After 2 h of reaction, SOSIP architecture 112 was formed on the surface and could not be dissolved upon rinsing with CHCl₃/TFE 1:1 or DMSO. Increasing concentration of propagator 105 resulted in increasingly thicker films, as revealed by UV-Vis spectroscopy (Figure 52 B). Below the critical concentration \( c_{\text{SOSIP}} \), no polymer could form on monolayer 97. On the other hand, clean ITO surfaces used as control and incubated in the same conditions did not give rise to any polymerization (Figure 52 A, empty circles).
Figure 52. A) Absorption of SOSIP architecture 112 as a function of the concentration of propagator 105 in CHCl3/MeOH 1:1, v/v, 100 mM iPr2NEt during incubation of ITO without (○) and with (●) activated monolayer 110. B) UV-Vis spectra of 112 with increasing thicknesses obtained with increasing concentration of propagator 105 (2 (dotted line), 10 (chopped line) and 20 mM (solid line)).

During SOSIP experiments performed with concentration between $10 < c$(105) $< 20$ mM, the initial clear solution of initiator and iPr2NEt was transformed into a suspension of red solid material, most likely oligomeric and polymeric species. However, these materials did not stick to the surface of either SOSIP architecture 112 nor on clean ITO and could be removed by rinsing with CHCl3/TFE 1:1 and DMSO, combined with short sonication procedures.

The UV-Vis spectra of 112 and of a diluted solution of propagator 105 (1.5 $\mu$M in CHCl3: MeOH 1:1) were compared (Figure 53). In the diluted solution, a strong absorption band corresponding to the $S_0$-$S_1$ electronic transition appeared between 400 and 550 nm with $\lambda_{max}$ = 528 nm. This band is featured by a very distinct progression, with vibrational transition $v_{0,0}$ at 528 nm, $v_{0,1}$ at 491 nm and $v_{0,3}$ at 455 nm. This progression has been ascribed to the breathing vibration of the perylene skeleton, which is strongly coupled with the $S_0$-$S_1$ transition.$[84]$ Indeed, such a fine-structured absorption band is characteristic for monomeric, molecularly-dissolved PDI molecules. The spectra obtained from
SOSIP architecture 112 on the other hand was featured by an absorption band located between 450 and 600 nm with $\lambda_{\text{max}} = 508 \text{ nm}$, blue-shifted by 20 nm as compared to monomeric 105. Here, the band was broader and vibronic progression less resolved, characterized by shoulders at 545 and 475 nm.

**Figure 53.** Normalized absorption spectra of propagator 105 in solution at a concentration of 1.5 $\mu$M in CHCl$_3$/MeOH 1:1, v/v (dotted line) and of SOSIP architecture 112 (solid line).

### 3.1.2.4. Structural Characterization

The shape of these spectra is very characteristic for $H,H$-PDI in face-to-face H aggregates.$^{[83-84, 187]}$ In the general case of H aggregates, the model predicts that the optical transition in the upper exciton is the only allowed, giving rise to a typical blue shift of the absorption maximum upon aggregation.$^{[81]}$ In the particular case of $H,H$-PDI, the additional bathochromic band appearing at 545 nm corresponds to a transition in the lower energy exciton state that becomes allowed by the rotational displacement of molecules around the main axis of the stack.$^{[51]}$ In addition to that, electronic coupling between molecules also broadens the band (Figure 53, solid line) and decreases the molar absorption coefficient by a factor of 2, down to $\varepsilon_{\text{MAX}} \sim 40'000 \text{ M}^{-1} \text{ cm}^{-1}$ (Figure 54).$^{[84]}$ These characteristic elements were observed on the spectrum of architecture 112 and thus confirmed the strong $\pi$-stacking of the $H,H$-PDI. H aggregates with columnar structures was consistent with the design of SOSIP architecture.
Figure 54. Typical concentration-dependent UV-Vis absorption spectra of H,H-PDI (2.1·10⁻⁷ to 1.1·10⁻³ M) forming H aggregates in methylcyclohexane at RT. Arrows indicate the changes upon increasing the concentration. Adapted from ref. [84].

Attempt to quantify the thickness of the film and the corresponding number of stacked H,H-PDI chromophores \( n_l \) was done on the basis of light absorption. The related equations are described in the experimental part. For this estimation, we used the surface coverage \( \Gamma = 0.15 \) nmol cm⁻² found for the monolayer 109 (vide supra) and the molar absorption coefficient \( \varepsilon_{\text{MAX}} \approx 40'000 \) M⁻¹ cm⁻¹ reported by Würthner et al for H aggregates of H,H-PDI.⁸⁴ With these values, SOSIP architecture 112 with an absorption \( A_{\text{MAX}} = 0.1 \) resulted in a thickness \( d = 5.8 \) nm. With a constant distance of 3.5 Å between each chromophore in the stack, the number of H,H-PDI was to \( n_l = 17 \). The values obtained with architecture 112 were very similar to those obtained with the N,N-PDI system 100 since the molar absorption coefficients \( \varepsilon_{\text{MAX}} \) and surface coverages \( \Gamma \) were comparable in both cases. It has to be stressed out that the estimation of \( d \) and \( n_l \) performed here were very qualitative because light absorption in architecture 112 with H,H-PDI will be strongly affected by preferential orientation of the chromophores with respect to the ITO surface. Assuming that \( \varepsilon_{\text{MAX}} \) is the same for aggregates in solution with random
orientation vs. incident light as for SOSIP architecture \textbf{112} is correct in a first approximation only.

\textbf{3.1.2.5. Functional Characterization}

Photocurrent generation with \textit{H,H}-PDI photosystem \textbf{112} was examined next. Figure 55 shows the energy levels for HOMO and LUMO of the \textit{H,H}-PDI chromophore (from ref. [37]) together with the HOMO level of TEOA and the work function of the ITO surface.

![Energy levels of the partners involved in the photocurrent generation upon irradiation of photosystem 112. HOMO (bold) and LUMO (dashed) of H,H-PDI 26 (from ref. [188]) together with HOMO of TEOA and work function of ITO (from ref. [189]), reported relative to -5.1 eV for Fe\(^+\)/Fe. Full arrow denotes electronic transition resulting from photoexcitation, half arrows illustrate subsequent e\(^-\) and h\(^+\) transfer.](image)

We hypothesized that, upon photoexcitation of the \textit{H,H}-PDI chromophore, one electron would get promoted from the HOMO to the LUMO. This electron placed in an excited state then would be transferred to the ITO anode, leaving behind a hole in the HOMO that then would be filled with an electron coming from the sacrificial electron donor TEOA. Alternatively, the hole in the HOMO of \textit{H,H}-PDI could be filled with an electron of TEOA first and then the excited electron located in the LUMO would be transferred to ITO. Whatever the order
of the process is, a net anodic current is expected to be generated upon light excitation because the energetic levels of TEOA and ITO are asymmetric.

To test this hypothesis, photosystem 112 was used as a working electrode in an electrochemical setup as previously described (see Experimental Part for details), and irradiated with a solar simulator. To close the circuit, a 50 mM aqueous solution of the sacrificial electron donor TEOA in 0.1 M Na$_2$SO$_4$ was used. Photocurrent was recorded upon switching the solar simulator on and off. An anodic photocurrent appeared rapidly upon illumination and was repeatable without alteration of the kinetic profile (Figure 56 A). Photosystem 98 was therefore stable under the applied illumination conditions, in the presence of TEOA.

![Figure 56. A) Photocurrent generated from photosystem 112 (A = 0.31 at $\lambda_{MAX} = 508$ nm); B) Photocurrent generated by 112 as a function of the thickness of the film $d$. Film thickness $d$ was estimated from $H, H$-PDI absorption using $A_{508}$ = 0.1 ~ 5.8 nm. Conditions were: TEOA concentration = 50 mM, $P_{in} = 67$ mW cm$^{-2}$.](image)

Photocurrent generation with $H, H$-PDI architecture 112 was found to depend on the thickness $d$ of the photosystem (Figure 56 B). With $0 < d < 20$ nm, the photocurrent density $J_{SC}$ increased linearly with increasing thickness. With $d > 20$ nm, the increase was markedly lower and the photocurrent

96
seemingly saturated. However, the actual critical thickness $d_C$ was not determined as a result of missing datapoints for higher thickness. A comparison between the thickness dependence observed in the case of $N,N$-PDI photosystem 100 (Figure 46 B) and $H,H$-PDI photosystem 112 (Figure 56 B) showed that the photocurrent remained very low ($J_{SC} < 0.2 \, \mu A \, cm^{-2}$) and strongly decreased with $d > d_C \sim 20 \, nm$ in the former case, whereas $J_{SC}$ reached to much higher values ($J_{SC} \sim 10 \, \mu A \, cm^{-2}$) and did not decrease even with $d > 60 \, nm$ in the latter case.

To further assess the superiority of architecture 112 with $H,H$-PDI chromophores for photocurrent generation, a comparison was performed between photosystem 112 with single $H,H$-PDI stacks, photosystem 100 with single $N,N$-PDI stacks and photosystem 101 with copolymerized $N,N$-PDI and $H,H$-NDI stacks. In the three cases, the photocurrent was measured in the same conditions. Thickness of the film was kept at $d < 30 \, nm < d_C$, that is in the linear range of the $J_{SC} = f(d)$ curves for 100 ($A_{737} = 0.25$, $d = 18 \, nm$) and 112 ($A_{508} = 0.11$, $d = 6 \, nm$). Therefore, it was possible to normalize the photocurrents produced with each of the architectures on the basis of their transmittance $T_{MAX}$ at $\lambda_{MAX}$ (see Experimental Part for details) without distortion of the data (Figure 57 A). The normalized photocurrent produced by $H,H$-PDI SOSIP 112 in this range of thickness was 25 times higher than with co-SOSIP 101 and 50 times higher than with $N,N$-PDI SOSIP 100.
Figure 57. A) Transmittance-normalized photocurrent generated by \textit{N,N}-PDI photosystem 100 (green solid), co-SOSIP photosystem 101 (blue dotted) and \textit{H,H}-PDI photosystem 112. Conditions were: TEOA concentration = 50 mM, $P_{\text{in}} = 67$ mW cm$^{-2}$; B) Action spectra of \textit{H,H}-PDI photosystem 112 (●) and co-SOSIP photosystem 101 (○) measured with TEOA concentration = 50 mM (all IPCE values were normalized with respect to activity of architecture 112 at 500 nm, for which IPCE was set at unity).

To better understand of the high activity of photosystem 112, we measured its action spectrum of in the presence of TEOA as a sacrificial electron donor (Figure 57 B, black solid line). Overall, IPCE and absorption values matched with the absorption spectrum of photosystem 112 (Figure 53, solid line). Specifically, the dependence of IPCE on illumination wavelength clearly evidenced a strong contribution to the photocurrent in the range $\lambda = 480 – 540$ nm. This region of the spectrum corresponds to the absorption band generated by the \textit{H,H}-PDI H aggregates (see Figure 53). This feature suggested that the
charge carrier generation and transport was best along the ordered face-to-face $H,H$-PDI stacks in photosystem 112. Direct comparison between the IPCE from $H,H$-PDI SOSIP architecture 112 and co-polymerized architecture 101 showed again the superiority of $H,H$-PDI chromophores concerning the generation and transport of charge carriers. The maximal IPCE value measured at 500 nm for the photosystem 112 was more than 10 times higher than the maximal IPCE of 101. In addition, 112 displayed high photon-to-current conversion efficiency over a broad spectral range ($\lambda = 480 – 540$ nm) while architecture 101 showed photocurrent generation abilities over a limited range only, located at short wavelengths (Figure 57 B).

$I$-$V$ curves were measured for systems 100 and 112 by systematic measurement of the evolution of the current $I$ extracted from the architectures upon variation of the applied voltage $V$ (Figure 58 A and B). It can be seen that the open-circuit voltages $V_{OC}$ is similar in both cases, but that the shapes of the $I$-$V$ curves are markedly different. Using these data, the Fill Factor (FF) was calculated for each of the two systems (see Introduction). With FF = 0.47, the value obtained with $H,H$-PDI architecture 112 was clearly higher than FF = 0.28 obtained for photosystem 100 with $N,N$-PDI. In the latter case, FF = 0.28 is almost equal to FF = 0.25 obtained for linear $I$-$V$ curves.
Figure 58. Current-voltage profiles of photosystem 112 (A) \( (P_{in} = 67 \text{ mW cm}^{-2} \) and photosystem 100 (B) \( (P_{in} = 200 \text{ mW cm}^{-2} \) in 50 mM TEOA, 100 mM Na2SO4, with indication of short circuit current \( (I_{SC}) \), open circuit voltage \( (V_{OC}) \), maximum power rectangle (gray surface), maximum power point \( (P_{max}, \text{gray dot}) \) and fill factor FF.

3.1.3. General Considerations on Single-Channel Photosystems

In summary, this study showed that the whole process of constructing architectures from SOSIP worked with PDI chromophores on ITO surfaces. Monolayer formation was assessed. Concentration-dependent polymerization on those monolayers as well as control experiments with clean ITO surfaces confirmed a surface-initiated covalent capture process. Structural analysis by light absorption and morphologies observed by AFM reflected the formation of smooth films with long-range order that contained stacked chromophores.

Interestingly, UV-Vis measurement revealed that the \( \pi \)-stacking interaction between \( H,H \)-PDI chromophores in architecture 112 was tighter than between the \( N,N \)-PDI chromophores in architecture 100. Photocurrent measurements correlated well with these observations. On the one hand, the highly ordered stacks obtained with the planar and more \( \pi \)-acidic \( H,H \)-PDI chromophores gave a comparatively very high photocurrent. On the other hand, the poor photoactivity found with core substituted, non-planar and less \( \pi \)-acidic \( N,N-\)
PDI coincided with weaker π–stacking interactions and presumably less ordered structures.

It has to be stressed out that the facts presented here, in spite of their coherent appearance, can’t rule out the possibility of simple coincidences. Therefore, they remain insufficient to prove a direct correlation between activity and organization of SOSIP architecture. Although the key external parameters, such as illumination intensity, concentration of the sacrificial electron donor and volume of electrolyte, have been conserved throughout the different measurements, several factors other than π–stacking could have affected the function. The energies of the frontier molecular orbitals of H,H- and N,N-PDI differ by 0.3 eV (LUMO) or 1.0 eV (HOMO) (~4.1/~6.3 eV for H,H-PDI, ~3.8/~5.3 eV for N,N-PDI).[37, 63] This difference is likely to influence charge injection in many ways. Charge injection from an organic semiconductor into electrodes, for example, has been shown to depend strongly on the work function of the latter and on the energetic levels of the former. Electron transfer from the sacrificial electron donor TEOA to the organic semiconductor could be also influenced by the position of the involved molecular orbitals. Finally, the detrimental process of electron trapping by residual oxygen is likely to be influenced by the level of the HOMO and LUMO of N,N- and H,H-PDI.

Overall, the results collected in the first part of this work were significant because they introduced a new class of dyes in the library of compounds that can be used to build complex photosystems from SOSIP. Especially, the very high activity observed with single H,H-PDI stacks in photosystem 112 opened perspectives. In this context, it is worth noting that Li et al. recently reported the surface-grafting of tetrachloro-PDI on silicon wafers by using a surface-initiated ring-opening polymerization process.[193] Although conceptually very similar to SOSIP, this approach used the ring-opening of a strained anhydride by an amine as key capturing process instead of disulfide exchange.
Polymerization was initiated by a SAM of 3-aminopropylsiloxane grafted on a silicon surface. However, in contrast to our work, no functional studies concerning the generation of photocurrent were reported.

At this point, two directions could be explored. In the first one, the already very active $H,H$-PDI chromophores would be combined with other optoelectronically-active organic materials to build architectures with improved function. In the second one, the high activity of $H,H$-PDI would be used to generate a powerful, easily measurable signal that would be then modulated by the influence of optoelectronically-inactive components. In both cases, the possibility to further functionalize the single $H,H$-PDI stacks in architecture 112 and build more complex, multicomponent architectures was needed. At this point, the templated stack exchange strategy had already been developed and demonstrated with NDI and oligothiophene chromophores.$^{144,145}$ It still remained to prove that this approach could be applied for the construction of multicomponent architectures with central $H,H$-PDI stacks.

### 3.2. Single Stacks for Templated Stack-Exchange

Templated stack exchange (TSE) was developed as a way to functionalize the central chromophore stacks produced by SOSIP on ITO surfaces with lateral stacks or strings of functional materials. Exchangeable templates are used to reserve functionalizable space in the compact film obtained by SOSIP. In a subsequent step, these templates are removed, leaving holes in the structure that is backfilled with a material of interest (Figure 59).
Figure 59. Conceptual representation of a bicomponent architecture assembled on a solid surface by SOSIP and TSE. The free surface (A, grey rectangle) is functionalized by SOSIP (B) with π-stacked chromophores (red rectangles) and templates (blue rectangles) on the side. Templates are removed (C) and the holes drilled in the structure are filled (D) with the second component (yellow rectangles).

Such a succession of steps imposes several requirements:

- During the SOSIP step, the functional groups and the chemistry used for ring-opening disulfide exchange polymerization shouldn’t be perturbed by the chemistry needed for TSE.

- The templates used to functionalize the initiator on the monolayer and the propagators along the stacks should preserve sufficient space for further exchange with a variety of molecules. At the same time, the templates should not interfere with the process of SOSIP, for example by imposing too much steric hindrance that would prevent the preorganization of propagators by π-stacking interactions and hydrogen bonding. Since solubility of the propagator is a key factor for the success of SOSIP together with the nature of the organic solvent used to solubilize the propagators, choice of the template is critical to obtain a right balance between solubility and aggregation.
Finally, the chemistry used to remove the templates and to reinstall the next molecules should not degrade, nor modify the disulfide bond network that maintains the integrity of the central ladderphane scaffold.

Dynamic covalent chemistry appeared well suited to address these challenges. Extensive studies published in the literature had demonstrated that the dynamic chemistry of disulfides used for SOSIP is orthogonal to dynamic hydrazone exchange. In basic medium, the disulfide bond is labile, whereas hydrazone exchange is simultaneously blocked. In acidic conditions, hydrazone exchange occurs rapidly while the dynamic exchange of disulfide bonds is inhibited.

3.2.1. Design

This idea had already been applied to SOSIP and TSE with success when we arrived at this point of our work. Multicomponent architectures that contained either NDI or oligothiophene in the central stack had been assembled on ITO surfaces. NDIs on the side of the initiators were used as templates to save the space needed for stack exchange already on the surface. Benzaldehyde templates on the propagators ensured both the successful SOSIP and exchange with a variety of aldehyde chromophores, such as NDI and core-substituted derivatives, PDI, porphyrins, phtallocyanines, squaraines, thiophenes and fullerenes. These reported successes prompted us to design initiator 113 and propagator 114 with PDIs as key structural and functional moieties, suited for both SOSIP and TSE (Figure 60).
Structures of initiator 113 and propagator 114 for SOSIP and TSE with PDIs. Structural elements involved in the anchoring of initiator to the ITO surface are in blue, functional groups used for SIP are in green and templates for stack exchange are in gray.

In initiator 113, the central 1,7-dicyano PDI (CN$_2$-PDI) core is functionalized at the imide position with modified L-lysines amino acids attached by their $\alpha$-amino groups. Their $\epsilon$-amino groups at the other end are linked to $t$-Bu-protected L-cysteins and continue with $gem$-bisphosphonic acids.
The carboxylic acids of the L-lysines are linked to H,H-NDIs bearing gem-bisphosphonic acids through hydrazone linkages.

Propagator 114 on the other hand was designed around a H,H-PDI chromophore, functionalized at both imide positions with L-Lysine attached by their α-amino groups. Both remaining ε-amines pointing out of this structure were linked to strained five-membered disulfide rings from asparagusic acid by peptidic bonds. The carboxylates of the L-Lysines were functionalized with benzylhydrazone templates, used as handles for stack exchange.

In initiator 113, the strongly electroattracting 1-7-dicyano substitution motif was chosen to decrease the electron density on the PDI core. In that way, the frontier molecular orbitals of CN₂-PDI (HOMO: ≈ -4.63 eV; LUMO: ≈ -6.93 eV) lay under the ones of H,H-PDI (HOMO: ≈ -4.12 eV; LUMO: ≈ -6.31 eV). Therefore, it was expected that the monolayer of initiator would favor the injection of electrons in the ITO electrode and simultaneously hinder the injection of holes. In addition, it has been shown by X-ray crystallography that core-cyanation of PDI only slightly distorted the planarity of the perylene core, with torsion angles of about 5° in crystals. The quasi planarity of CN₂-PDI retains the π-stacking ability of the molecule, as needed for SOSIP. The low-lying frontier molecular orbitals of the electron-accepting H,H-NDI (HOMO: ≈ -4.31 eV; LUMO: ≈ -7.31 eV) further favor electron injection from the organic film into the ITO electrode.

3.2.2. Synthesis

The synthetic route toward initiator 113 is depicted on Scheme 6. Starting material 115 is the pure 1,7-regioisomer of dibromoperylenedianhydride and was prepared according to reported procedures. The anhydride moieties were first reacted with the α-amino groups of ε-Cbz-protected L-lysines to give intermediate 116.
Scheme 6. a) H-Lys(Cbz)-OH, AcOH, NMP, 75 °C, 2h (87%); b) dppe, Zn(CN)₂, Pd₂dba₃, 1,4-dioxane, reflux, 12h (53%); c) Boc-NHNH₂, EDCI, DCM, 0°C, 2h (91%); d) 1. H₂, Pd/C, AcOH, MeOH, 4h, RT, quantitative, 2. Fmoc-Cys(S-t-Bu)-OH, HBTU, collidine, HOBT, DMF, RT, Ar, 1h (2 steps 52%); e) 1. TBAF, DMF, RT, 2. 94, HBTU, collidine, DMF, RT, Ar (2 steps 11%); f) 1. TMSBr, DCM, RT, 3h, Ar, 2. MeOH, RT, 4h, 3. 121, DMSO, AcOH, RT, 24h.

Direct cyanation of the PDI core using Zn(CN)₂ in the presence a Pd(0) catalyst gave the regiosomerically pure CN₂-PDI 117. Other previous attempts
to first functionalize the carboxylic groups in 116 and then replace the bromine groups with cyano substituents failed. The free carboxylic acid groups in 117 were coupled to t-Bu carbazate using EDCI in DCM at 0°C to give 118 in good yield. The CN$_2$-PDI core showed some sensitivity and likely degraded when this coupling reaction was run at RT. The Cbz-protected ε amine in intermediate 118 was then liberated by hydrogenolysis using Pd/C and H$_2$ at atmospheric pressure and subsequently coupled to the carboxylic acid of t-Bu and Fmoc protected cysteine to give intermediate 119. During hydrogenation of 118, the initially red solution turned progressively to violet. This color persisted after completion of the deprotection, however the red color corresponding to intact CN$_2$-PDI was recovered upon bubbling air in a solution of the violet compound in DCM and methanol. The color change from red to violet in a reducing environment is likely to reflect the formation of a stable radical anion located on the CN$_2$-PDI moiety, then reoxidized upon bubbling oxygen in the solution. The UV-Vis spectrum of radical monoanion has been reported and showed a bathochromic shift compared to the neutral precursor, which correspond to our observation.\[65\]

The possibility that such a redox process could damage the CN$_2$-PDI core due to undesired side reactions was considered. Compounds 118 and 119 were carefully characterized by NMR, UV-Vis absorption spectroscopy and mass spectrometry and the obtained data confirmed the presence of an intact CN$_2$-PDI core in 119. The clean reduction and subsequent reoxidation of CN$_2$-PDI observed here is in accordance with the reported ability of CN$_2$-PDI to undergo reversible one- and two-electron reduction in cyclic voltammetry. In addition, CN$_2$-PDI derivatives were reported to be air-stable n-type semiconductors in OFET, due to their ability to strongly stabilize electrons.\[40\]

The Fmoc protecting groups of intermediate 119 was then taken off to yield free α-amino group on both of the peptide side chains. Initial attempts to use the classical combination of piperidine and DMF failed, as the red starting
material solution immediately decomposed to give a blue compound upon
addition of the base. The exact reason for this decomposition is not known,
although the color change suggested that piperidine likely attacked the
electrophilic core of the molecule. An alternative protocol for Fmoc
deprotection that used TBAF in DMF proved to be successful.\textsuperscript{[197]} The resulting
free α-amino groups on the lateral cysteins were then coupled to the acid 80
using classical peptide chemistry, yielding the fully protected intermediate 120.
The purification of this molecule required several silica gel column and
preparative thin layer chromatography procedures but the compound could be
finally isolated on a 100 mg scale. Boc and benzyl protecting groups in 120
were then removed in one step, using TMSBr followed by methanalysis, to
expose free gem-bisphosphonic acids and hydrazides. The latter functional
groups were immediately reacted with a tenfold excess of aldehyde 121\textsuperscript{[144]} in
DMSO with acetic acid as a catalyst and gave molecule 113. This large and
polar molecule was poorly soluble in common organic solvents, with maximal
concentration in DMSO topping to less than 1 mM. Therefore, it was purified
by repeated solid-liquid extractions, first with diethylether to remove non-polar
impurities and then with methanol, to extract the unreacted excess of aldehyde
121 that showed some solubility in the latter solvent.

The synthesis of propagator 114 started with PDA 14 (Scheme 7). This
molecule was reacted with ε-Cbz-L-Lysine at 100°C in molten imidazole to
afford diimide 122. The latter compound was separated from both the excess of
unreacted L-Lysine and from imidazole by liquid-liquid extraction. 122 was
then engaged in a coupling reaction with t-Bu-carbazate using classical peptide
chemistry to afford the well-soluble, protected intermediate 123. The Cbz
protecting groups were subsequently removed with hydrogen using Pd/C as a
catalyst to expose the ε amines. These were then coupled to the activated ester
96 to give diamide 124. During the latter amide bond formation, pH was
regularly checked and adjusted to the optimal value of 8. These conditions
allowed the reaction to proceed readily but at the same time prevented the uncontrolled polymerization of the strained disulfide rings in 96 and 124 that otherwise occurs readily at higher value of the pH.

**Scheme 7.** a) H-Lys(Z)-OH, imidazole, 100°C, 50 min; b) Boc-NH₂, HBTU, TEA, DMF, RT, Ar, 1h (2 steps 73%); c) 1. H₂, Pd/C, AcOH, MeOH, 2h, RT. 2. 96, TEA, DMF, RT, 1h (2 steps 67%); d) 1. TFA, thioanisole, DCM, RT, 1h. 2. Benzaldehyde, RT, 15 min (2 steps 90%).
From intermediate 124, target molecule 114 was then obtained in high yield upon deprotection of the Boc protecting groups in 124 with TFA and condensation of the exposed hydrazides with a large excess of benzaldehyde in acidic conditions. Freshly prepared 114 had solubility of at least 30 mM in a mixture of CH$_2$Cl$_2$/MeOH or CHCl$_3$/MeOH 3:1, v/v. On the other hand, when solutions of 114 were concentrated to dryness and kept in this state for a few hours, redissolution of the obtained solid was only partially possible, yielding suspensions of red insoluble materials. The same holds true for intermediate 124. Since both of these molecules contained a strained disulfide ring, the observed decomposition phenomenon was best explained as an uncontrolled polymerization of molecule 114 or 124 in the solid state. Accordingly, 124 was stored as a diluted solution (~1 mM) in a mixture of CH$_2$Cl$_2$/MeOH 3:1 before being used for the synthesis of 114. In the same way, freshly purified initiator 124 was kept as a diluted solution in the same mixture of solvents before SOSIP.

3.2.3. Self-Assembled Monolayers

With both the initiator 113 and propagator 114 in hands, the next step to complete was the formation and characterization of SAM made of initiator 113
on ITO. For that purpose, phosphonic acid 113 was dissolved in DMSO to give a 0.5 mM solution. ITO electrodes were prepared and treated with the initiator solution as described in the experimental part. Initiator was expected to self-assemble on the oxide surface and form SAM 125 (Figure 61). In initiator 113, all four bisphosphonic acid “feet” should be able to bind the oxide surface because the peptide backbones linking the rigid CN$_2$-PDI and NDI chromophores to the anchoring groups are flexible and give enough conformational freedom to the molecule. In that way, CN$_2$-PDI and NDI should adopt a parallel alignment with respect to the surface that allows the growth of
propagator stacks perpendicularly to the surface according to the design of SOSIP.

As in the previous case of monolayers 97 and 109, the assembly of 125 was monitored by CV using the coated ITO as a working electrode (Figure 62 A).

Figure 62. A) Cyclic voltammogram of aqueous ferricyanide measured with an ITO electrode (a, chopped line) before the deposition of initiator 113, (b, dotted line) after 24h, and (c, solid line) 48h in the solution of initiator 113 as a working electrode. B) Peak current (absolute values) of the ferricyanide reduction waves as a function of the incubation time.
Upon increasing incubation time, the disappearance of the redox wave of Fe(CN)$_6^{3-}$ reflected the progressive assembly of the SAM. Coverage of the ITO electrode proceeded readily with the diluted solution of 113 in DMSO. After 2 days of immersion, the disappearance of a measurable current confirmed the good coverage of the ITO surface with initiator 113.

Once the assembly of 125 had reached equilibrium, the coated ITO surface was heated in an oven, at 120 °C for 1h to achieve better bonding between phosphonic acids and ITO substrate. Characterization of the monolayer 125 was done by CV (Figure 62 B). The presence of redox active material on the surface of the electrode was probed by using the coated ITO surface as a working electrode in a CV setup. Sweeping the applied voltage between +0.4 and -0.8 V with respect to the Ag/AgCl reference electrode showed the appearance of two reversible waves at -0.07 V and -0.51 V, respectively. The peak current measured at the maximal values of these redox waves showed a linear dependence on the scan rate, confirming that the observed redox processes were taking place on the ITO surface (Figure 62 C). The surface coverage $\Gamma$ was obtained from the charge of the first reduction wave and assuming a single-electron transfer process. The obtained $\Gamma(125) = 0.02$ nmol/cm$^2$ (0.13 molecule/nm$^2$) was consistent with molecular models and nearly complete coverage of the surface by the initiator anchored with all four phosphonates groups to the ITO. This value was lower than $\Gamma(97) = 0.12$ nmol/cm$^2$ and $\Gamma(109) = 0.15$ nmol/cm$^2$, in accordance with the fact that initiator 113 is much larger than initiator 88 and 104, respectively.

With compact monolayers 125 in hands, we next reduced the $t$-Bu disulfide groups sticking out of the surface with DTT to give 126 (Figure 61, details are outlined in the Experimental Section). The latter “activated” SAM was used for SOSIP with propagator 114. To avoid reoxidation of the free thiols, this reduction procedure was carried out just before proceeding to SOSIP, and contact of thiol-rich 126 with air limited to a minimum.
3.2.4. Self-Organizing Surface-Initiated Polymerization

The surface initiated polymerization of propagator 114 was expected to proceed as depicted on Figure 63.

![Figure 63](image_url)

**Figure 63.** Hypothesized mechanism for the polymerization of propagator 114 on monolayer 127 with thiolates. The grey background represents an ITO surface. Dotted lines denote the preorganizing interactions between initiator and propagator, functional groups involved in the disulfide-exchange ring-opening polymerization are in blue.

Monolayer 126 with thiol groups pointing upward would be deprotonated with a base to yield thiolate-rich monolayer 127. Preorganized by the recognition patterns encoded in its structure (Figure 63, dotted lines), propagator 114 and monolayer 127 would then form a supramolecular complex governed by non-covalent interactions. The combination of hydrogen bonds between the lateral peptide chains and π-π interactions between the π-acidic surfaces of the planar H,H-PDI core and the only slightly distorted CN3-PDI would maintain the peptide side-chains of propagator 114 in a parallel
orientation with respect to those of initiator 113. This would ensure the proximity of the thiylates pointing out of the surface and the strained five-membered disulfide rings appended to the propagator. Disulfide-exchange ring-opening polymerization could then proceed readily as a result of the preorganization, breaking the disulfide bond of the ring to generate covalent bonds between the initiator and the propagator. The free thiylates regenerated on the surface of 128 would then continue the polymerization if one other propagator molecule 114 is positioned on top of the covalently-captured stack. The NDI templates placed next to CN$_2$-PDI on the surface of ITO save space on the side of the growing H,H-PDI ladderphanes for subsequent templated stack exchange. Previously published control experiments on NDI SOSIP-TSE photosystem and had shown the need for these NDI spacers.$^{[144]}$ Polymerization from the surface and in solution became indistinguishable when a propagator functionalized with benzaldehyde hydrazones on the side was reacted with a monolayer lacking the corresponding NDI templates. The impossibility to carry out surface-initiated polymerization in that case likely resulted from the mismatches between the steric demands of the propagator with template and the space available around the initiator molecules that are bound to the ITO electrode.

Finding conditions to polymerize propagator 114 by SOSIP from monolayer 127 was undertaken with the knowledge gained during the first part of this thesis work. The experience accumulated so far while developing SOSIP conditions for propagators 92 and 105 had shown that minor structural changes could lead to significantly different outcomes in terms of the solvents needed for SOSIP as well as kinetic of the reaction. In the case of propagator 114, the presence of benzyldihydrazones represented a significant change in the structure as compared to propagator 105 with H,H-PDI core and primary amide instead. Accordingly, it was inferred that the optimized conditions for the SOSIP of propagator 114 would be different than those found for 105.
The general strategy used to find optimized conditions suited for the surface initiated polymerization of 114 was as follow. Systematically, monolayers 126 together with a clean ITO surface were incubated in a vial containing a solution of propagator 114 at a certain concentration in a mixture of solvents and in the presence iPr₂NEt as a base catalyst. The vial was purged with Ar and sealed with parafilm to avoid oxidation of thiols by oxygen that would prevent the polymerization process.

The first trial used the same conditions that had been found to be successful for the SOSIP of H,H-PDI propagator 105: c(114) ~ 13 mM, solvent: CHCl₃/TFE 1:1 with 0.1 mM iPr₂NEt. These conditions failed to yield polymerization of 114 on monolayer 126. No polymerization in solution was found either. Further trials were attempted with chloroform and TFE in various proportions (the chloroform content was decreased stepwise from 10:1 to 1:1) but all failed the same way. Subsequently, the concentration of propagator 114 was also increased stepwise from 13 mM up to 50 mM. It was observed that above c(114) = 30 mM polymerization started in an uncontrolled way: insoluble red solid accumulating both on the electrode covered with monolayer 126 and on the clean ITO surface used as negative control. Therefore, mixtures of chloroform and TFE appeared unsuited for the SOSIP of 114. It is difficult to give a definitive explanation as to why the conditions found successful for the surface initiated polymerization of 105 failed with the close derivative 114. From the experience that we and others in our group gained with the SOSIP of various chromophores, clean surface initiated polymerization requires a finely tuned balance between solubilization and aggregation of the propagator. It is our observation that the introduction of benzylhydrazone substituents markedly increased the solubility of this molecule in mixtures of chloroform and TFE as compared to the case of propagator 105 with primary amide substituents. It was indeed possible then that mixtures of these two solvents solubilized 114 too.
much and outcompeted the preorganizing interactions needed for the recognition between the initiator and propagator, desired for SOSIP.

As a consequence, we directed our further efforts toward the use of chloroform and methanol mixtures for the SOSIP of propagator 114 on monolayer 126. To start with, some preliminary studies were done on the solubility of 114 in these solvents. Our qualitative observations revealed that propagator 114 was very poorly soluble in either pure chloroform or methanol. The maximal concentration remained below 5 mM in CHCl₃/MeOH 1:1, v/v but reached more than 20 mM in CHCl₃/MeOH 3:1, v/v.

Since the understanding of this behavior was central for SOSIP optimization, we shall now say some words concerning the aggregation of PDI. In the literature, numerous studies concerning the self-assembly of PDI are reported. In a particularly comprehensive work, Würthner et al. showed that the aggregation constants of six H,H-PDI derivatives bearing aromatic, aliphatic or hydrophilic (ethylene glycol) substituents at the imide nitrogen varied non-linearly with the polarity of 17 solvents. In non-polar solvents, such as n-hexane or methylcyclohexane, H,H-PDI strongly aggregated because the dipole-dipole interactions between chromophores was not replaced by similar interactions with the solvent molecules. When solvents of higher polarity (such as THF or toluene) were used, the favorable dipolar solvent-PDI interactions decreased the aggregation constants. When chloroform or tetrachloromethane were used, an additional and significant drop in the aggregation constants was observed. According to the authors, strong H,H-PDI-solvent dispersion interactions arouse with these highly polarizable chlorinated molecules that could efficiently disrupt the aggregates. Finally, in highly polar, protic solvents such as ethanol, methanol and water, efficient aggregation was observed again. The authors postulated that the large hydrophobic core of H,H-PDI caused a significant perturbation in the structure of these solvents, giving rise to strong solvophobic effects.
These studies reflected the behavior of \textit{H,H}-PDI with aromatic, aliphatic or ethyleneglycol side chains. On the other hand, propagator 114 contained two primary amide (linking the \(\varepsilon\)-amino group of lysine to the disulfide ring) and two hydrazones with –CO-NH- motifs that strongly influenced the aggregation behavior and solubility. Since these groups could form intermolecular hydrogen bonds, the solubility of 114 was governed not only by the \(\pi\)-\(\pi\) stacking of \textit{H,H}-PDI but also by the possibility to form hydrogen bonds with the solvent.

Taking these elements together, the behavior of propagator 114 could be explained rationally. The observed low solubility in methanol likewise came from the previously mentioned solvophobic effect. On the other hand, chloroform could not dissolve 114 either, because it cannot compete with and disrupt the intermolecular hydrogen bonds that form between adjacent 114 in face-to-face aggregates. Chloroform is generally considered as not capable of significant hydrogen bonding and cannot compete with the formation of \(\beta\)-sheet-like structures.\textsuperscript{199-202} However, mixtures of chloroform and methanol were experimentally found to solubilize the hydrophobic PDI core and simultaneously disrupt the hydrogen bond network, so that solutions of propagator 114 with \(c > 20\) mM were obtained.

After having obtained a better understanding of the solubility of propagator 114, a series of polymerization attempts were carried out with mixtures of chloroform and methanol in various proportions. The screening protocol was as follow: one ITO surface covered with monolayer 126 together with one clean ITO surface (negative control) were incubated for 24 hours in a vial containing a solution of propagator 114 at a certain concentration in a mixture of CHCl\textsubscript{3} and methanol. The ITO plates were then rinsed with a similar mixture of CHCl\textsubscript{3} and methanol and then DMSO. Results were interpreted as following:

- If a film of red solid was obtained on monolayer 127 but the negative control, clean ITO surface remained clean, SOSIP architecture 128 was likely
to be formed (Table 2, column “results”, SOSIP case). The experiment was therefore successful.

-If red solid material was remaining on both monolayer and the negative control, clean ITO, or if no material remained on both surfaces but red solid in suspension was seen in the solvent, we considered that in-Solution Polymerization (ISP) had occurred (Table 2, column “results”, ISP case). The nature of the solid that formed in this case was not experimentally determined but it was insoluble in most organic solvents and in particular DMSO. Since the latter is a good solvent for monomeric propagator 114, thus the insoluble solid was likely to be oligomeric or polymeric material resulting from some decomposition of 114. The experiment was therefore unsuccessful.

-If no solid material was seen on both monolayer and clean ITO, we considered that nothing happened (Table 2, column “results”, “X” case). The experiment was therefore unsuccessful.

Table 2. Summary of solvent and base conditions screened for propagator 114.

<table>
<thead>
<tr>
<th>Entry</th>
<th>C&lt;sub&gt;p&lt;/sub&gt; (mM)</th>
<th>Solv. Syst.</th>
<th>C&lt;sub&gt;b&lt;/sub&gt; (mM)</th>
<th>Result</th>
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</thead>
<tbody>
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<td>X</td>
</tr>
<tr>
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<td>2:1</td>
<td>400</td>
<td>ISP</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>2.5:1</td>
<td>100</td>
<td>SOSIP</td>
</tr>
</tbody>
</table>

*Concentration of propagator 114. ^ Mixture of solvents used, reported as CHCl<sub>3</sub>: MeOH v:v. ^ Concentration of iPr<sub>2</sub>NEt. ^ ISP = in-Solution Polymerization, SOSIP = Self-Organizing Surface-Initiated Polymerization, X = Formation of solid material was not observed.

At first, CHCl<sub>3</sub>/MeOH 2:1, v/v was used with the concentration of base iPr<sub>2</sub>NEt kept at 100 mM and the concentration of propagator 114 varied from 10 to 20 mM (maximal solubility). In all these cases, SOSIP was never
obtained. With concentrations of propagator 114 at 15 and 20 mM, SIP was obtained. We reasoned that thiols on monolayer 126 had been oxidized faster than SOSIP could proceed. For that reason, a next set of experiments was done with the concentration of 114 kept at 15 mM. On the other hand, the concentration of iPr₂NEt was increased stepwise from 100 mM up to 400 mM. It was expected that increasing the concentration of the base would increase the fraction of deprotonated thiols on the monolayer 127 and that in turn the polymerization from the surface would proceed faster. Fast reaction is beneficial for SOSIP because it relies on the availability of thiols sticking out of 126. These oxygen-sensitive groups are prone to get oxidized over time, when air leaks through the simple caps used to close the reaction vessels. However, no satisfying result could be obtained in these cases. At low base concentration, no reaction occurred while ISP was observed at 400 mM of iPr₂NEt. With a high concentration of base, it is possible that the propagator 114 was decomposed and formed some sort of polymer by ISP (Table 2, column “results”). On the other hand, no surface initiated polymerization was observed at lower concentration of the base, presumably because the preorganizing interactions needed for SOSIP were absent in CHCl₃/MeOH 2:1, v/v.

From that point, it was inferred that changing the composition of the solvents mixture while keeping the concentration of both propagator and iPr₂NEt would progressively trigger aggregation and SOSIP. In a series of experiments, the solvent composition was varied systematically between CHCl₃/MeOH 12:4 (= 3:1) and 6:4 (= 1.5:1), v/v. Indeed, it was discovered that polymerization from monolayer 126 proceeded with CHCl₃/MeOH 5:2, v/v (= 2.5:1) to give photosystem 128 while the ITO surface used as negative control remained clean under these conditions. The absorption spectrum of 128 revealed a broad absorption band spanning from 420 up to 600 nm (Figure 64, solid line) together with a band located at 300-330 nm. The latter band originated from the benzaldehyde absorption. The former band featured a fine
structure, with a maximum at 508 nm, a local maximum at 543 nm and a shoulder near 460 nm. On the other hand, the UV-Vis spectrum of a diluted solution of molecule 114 in CHCl₃: MeOH 3:1 (<1.0 · 10⁻⁵ M) showed a main band with maximum at 531 nm corresponding to the S₀-S₁ transition (Figure 64, dotted line) together with the benzaldehyde absorption band at 320 nm and below. In the main band, a distinct vibronic progression was apparent with a local maximum at 494 nm corresponding to the S₀-S₁ transition and a small band at 460 nm.

![Normalized absorption spectra of propagator 114 in solution at a concentration of 5 µM in CHCl₃/MeOH 3:1, v/v (dotted) and of photosystem 128 (solid).](image)

**Figure 64.** Normalized absorption spectra of propagator 114 in solution at a concentration of 5 µM in CHCl₃/MeOH 3:1, v/v (dotted) and of photosystem 128 (solid).

As discussed previously in the case of H,H-PDI photosystem 112, the spectral changes observed when going from the diluted solution of propagator 114 to SOSIP architecture 128 were characteristic of H,H-PDI face-to-face H aggregates with helical pitch. The hypsochromic shift of the absorption maximum from 531 down to 508 nm, came from the allowed transition into the higher energy exciton, while the helical pitch permitted transition in the low energy exciton with non-negligible oscillator strength. From these data, we inferred that the chromophores in 128 adopted an aggregation motif consistent with SOSIP design. It further showed that the presence of benzaldehyde
templates in propagator 114 did not impede a face-to-face contact between 
H,H-PDI chromophores in SOSIP architecture 128.

3.2.5. Structural Characterization

We attempted to determine the relationship between the absorption of 
arquitectura 128, its thickness and the number of face-to-face stacked 
chromophores involved (see Experimental Section for details). For these 
calculation, we used the surface coverage $I = 0.02 \text{ mmol cm}^{-2}$ found for the 
monolayer 125 (vide supra) and the molar absorption coefficient $\varepsilon_{\text{MAX}} \approx 40'000$ 
M$^{-1}$ cm$^{-1}$ reported by Würthner et al for H aggregates of H,H-PDI. With 
these values and for arquitectura 128, an absorption $A_{\text{MAX}} = 0.1$ resulted in a 
thickness $d = 44$ nm. With a constant distance of 3.5 Å between each 
chromophore in the stack, the number of H,H-PDI involved amounts to $n_l = 
125$.

Figure 65. Effect of the area occupied by the initiator on the thickness $d$ of the 
film needed to reach a certain light absorption value. A) With a large initiator, 
the density of polymer brushes on the surface is low and $d_A$ is high. B) With a 
small initiator, the density of brushes is comparatively higher and $d_B < d_A$. 

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The values obtained with 128 were quite different from those obtained with the N,N-PDI system 100 ($d = 7.4$ nm and $n_l = 21$ for $A_{\text{MAX}} = 0.1$) and the H,H-PDI system 112 ($d = 5.8$ nm and $n_l = 17$ for $A_{\text{MAX}} = 0.1$). These differences arise mainly from the higher surface coverages $\Gamma$ of the monolayers on ITO obtained with architectures 100 and 112 as compared to 128. Thus, the packing of the molecular brushes being tighter in the first cases, thinner films are needed to achieve the same value of light absorption (Figure 65). It has to be stressed out that the estimation of $d$ and $n_l$ performed here are very qualitative because light absorption by 128 will be strongly affected by preferential orientation of the chromophores with respect to the ITO surface. Assuming that $\varepsilon_{\text{MAX}}$ is the same for aggregates in solution with random orientation with respect to the incident light as for 128 is correct in a first approximation only.

In AFM height images, the obtained architecture 128 had a smooth surface (Figure 66 A). The obtained surface roughness, $R_a \approx 4.7$ nm was in the same range as $R_a \approx 4.0$ nm found with single N,N-PDI stacks in architecture 100. Moreover, it was coherent with previous results from NDI SOSP as well as bare ITO surfaces. In phase-contrast detection mode, AFM images revealed low-defect organization over very long distances. (Figure 66 B).

**Figure 66.** Imaging of 128. A) AFM height image (Z range: black 0 nm – white 100 nm); B) AFM phase-contrast image (Phase range: 70°).
Further structural details on the arrangement of H,H-PDI chromophores in SOSIP architecture 128 was obtained from electronic circular dichroism (CD) spectroscopy (see Experimental Part for details). The CD spectrum of SOSIP architecture 128 is displayed on figure 67 together with its absorption spectrum, for comparison purpose.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure67.png}
\caption{Absorption (solid, left axis) and CD spectra (bold, right axis) for architecture 128.}
\end{figure}

A fairly strong bisignate signal was observed, with a zero crossing corresponding almost exactly to the electronic transition that appeared at 543 nm on the absorption spectrum. Such a bisignate CD is observed when the transition dipoles of two or more chromophores interact through space in a helical fashion.\[203-204] The sign of this couplet is positive since the Cotton effect at longer wavelengths is positive and the one at shorter wavelengths is negative (Figure 67). According to the exciton chirality theory, a positive couplet corresponds to a right-handed conformation (P-helical arrangement) of the transition dipoles inside the stacks. It is known that the S0-S1 transition dipole is aligned with the long axis of H,H-PDI.\[205] Therefore, we concluded that each H,H-PDI chromophore in the stacks is aligned with small twist angles with respect to its neighbors so that a P-configured helical arrangement is obtained. Similar conclusions were previously drawn from CD spectra measured on PDI aggregates, as reported in the literature.\[96, 205-206] It is worth to note that the
observed chirality of the aggregates demonstrated the structural influence of the chiral peptide side chains on the alignment of the achiral \textit{H,H}-PDI chromophores (transfer of chiral information).

To determine $c_{\text{SOSIP}}$, the critical concentration at which the surface initiated polymerization proceeds with appreciable rate while the uncontrolled solution polymerization is not observed, the concentration of propagator 114 was increased from 5 mM up to 15 mM in CHCl$_3$/MeOH 5:2, v/v with 100 mM \textit{iPr$_2$NEt}. ITO surfaces with 126 were incubated together with bare ITO as negative controls. The accumulation of \textit{H,H}-PDI-containing material on both electrodes was followed by UV-Vis spectroscopy at 543 nm (Figure 68).

![Figure 68](image)

Figure 68. Absorption of SOSIP architecture 128 at 543 nm as a function of the concentration of propagator 114 in CHCl$_3$/MeOH 5:2, v/v, 100 mM \textit{iPr$_2$NEt} during incubation of ITO without (○) and with (●) activated monolayer 126. Film thickness $d$ was estimated from \textit{H,H}-PDI absorption using $A_{543} = 0.1 \sim 44$ nm.

At $c = 5$ mM, no polymerization occurs, neither on monolayer 126, nor on clean ITO. At $c = 15$ mM, red material was accumulating on both surfaces. At $c_{\text{SOSIP}} \sim 13$ mM, polymerization occurred exclusively on the monolayer 126 while no material remained bound to the control electrode after washing with CHCl$_3$/MeOH 5:2, v/v and then DMSO.
3.2.6. Functional Characterization

The ability of photosystem 128 to generate photocurrent was again probed using a photoelectrochemical setup as depicted in the Experimental Section. ITO-bound architecture 128 was used as a working electrode in the presence of an aqueous solution of TEOA (50 mM) as the sacrificial electron donor with 0.1 M Na$_2$SO$_4$ as supporting electrolyte. Upon irradiation of the setup with a solar simulator, an anodic photocurrent was recorded. Repeatable levels of current were obtained with a given electrode upon turning the illumination source on and off several times (Figure 69 A).

![Figure 69. A) Photocurrent generated with architecture 128 (\(A = 1\) at \(\lambda_{\text{MAX}} = 508\) nm); B) Photocurrent generated with 128 as a function of the thickness of the film \(d\). Film thickness \(d\) was estimated from H,H-PDI absorption using \(A_{S43} = 0.1\) ~ 44 nm. Conditions were: TEOA concentration = 50 mM, \(P_{in} = 83\) mW cm$^{-2}$.](image)

The photostability of the system was assessed on the timescale of the experiment under the applied conditions (\(P_{in} = 83\) mW cm$^{-2}$). The photocurrent density \(J_{sc}\) recorded under these conditions showed also a strong dependence on the thickness of the photosystem 128 (Figure 69 B). Photosystems with increasing thicknesses were obtained upon polymerization of propagator 114 at \(c_{\text{SOSSP}}\) (~ 13mM, \textit{vide supra}) and increasing polymerization time. Absorption
maxima reached up to $A_{\text{MAX}} > 2$, corresponding approximately to $d \sim 1000 \, \text{nm}$. The photocurrent density $J_{\text{SC}}$ of this panel of systems was recorded under illumination of a solar simulator and plotted as a function of $d$ (Figure 69 B). The profile showed three regimes. In the first one, there was a rapid increase of $J_{\text{SC}}$ in the range $0 < d < 300 \, \text{nm}$ ($A_{\text{MAX}} < 0.5$). In the second one, $J_{\text{SC}}$ saturated and stayed constant around a critical $d_C = 300 \, \text{nm}$. In the last one, $J_{\text{SC}}$ decreased strongly at longer range ($d > 400 \, \text{nm}$).

This behavior was already observed in the case of architecture 100, but in that case the photocurrent density had already saturated and decreased at $d < 100 \, \text{nm}$. In the case of photosystem 112, there weren’t enough datapoint to draw a solid conclusion concerning the critical thickness $d_C$ that gave maximal photocurrent, but no decrease was observed until $d = 80 \, \text{nm}$. With the data in hand, it is possible to state that photosystems 112 and 128 showed about the same behavior in a fist approximation.

An explanation for the observed saturation and decrease of photocurrent density as a function of thickness could be the following. In the first regime, each additional $H,H$-PDI chromophore bound to the the stacks collected an additional fraction of light and photogenerated free holes and electrons. On the other hand, there carriers were then funneled toward ITO (for the electrons) and TEOA (for the holes) that were close enough from the site of charge separation to avoid frequent recombination on the way. Therefore, the $J_{\text{SC}}$ increased linearly with increasing $d$. In the second, saturation regime, the $H,H$-PDI stacks were long enough so that all the light was absorbed in the region $450 < \lambda < 600 \, \text{nm}$. Therefore, adding more $H,H$-PDI chromophores in the stacks did not generate more free charges. It simply lengthened the path that the photogenerated charges had to follow in order to reach the ITO electrode or the TEOA solution. Therefore $J_{\text{SC}}$ does not increase any more when a critical thickness $d_C = 300 \, \text{nm}$ is reached. In thicker films, the additional $H,H$-PDI chromophores did not contribute to the generation of more charge carriers but
the increased length of the stacks and of the path needed to reach to the electrodes increased the probability that holes and electrons recombined on the way. Therefore, the photocurrent density $J_{SC}$ decreased with increasing $d$. Similar conclusions were previously drawn in the case of photosystems made by the zipper assembly of OPE scaffolds functionalized with NDI.\cite{109,111}

The action spectra of single channel photosystem 128 was recorded in the presence of TEOA as a sacrificial hole acceptor (Figure 70).

![Figure 70](image)

**Figure 70.** Action (solid line, □) and UV-Vis (dotted line) spectra of $H,H$-PDI photosystem 128. IPCE was measured with 50 mM TEOA, 0.1 M Na$_2$SO$_4$, 0 V vs. Ag/AgCl. IPCE values were normalized with respect to the value recorded at 380 nm, for which IPCE was set at unity.

The obtained IPCE profile matched with the absorption spectrum of architecture 128. The main contribution to the photocurrent aroused from a region of the spectrum corresponding to the absorption of $H,H$-PDI chromophores (at $450 < \lambda < 600$ nm). The action spectrum displayed a rather broad and flat maximum region (at $500 < \lambda < 550$ nm). At the top of the curve, both the absorption bands located at $\lambda = 505$ nm and $\lambda = 543$ nm contributed equally to the activity of photosystem 128.
3.2.7. Hydrazone-Oxime Exchange

With the architecture 128 in hands, the next step to go to was to exchange the lateral benzaldehyde with more functionally relevant aldehydes by using hydroxylamine-hydrazone exchange and dynamic covalent chemistry. Scheme 8 details the acid-catalyzed exchange between hydrazone 129 and hydroxylamine 130, yielding hydrazide 131 and 132.

\[
\text{R}^\text{O} \begin{array}{c}
\text{N} \\
\text{R}'
\end{array} + \text{NH}_2\text{OH} \xrightarrow{\text{H}^+ (\text{cat})} \text{R}^\text{O} \begin{array}{c}
\text{NH}_2 \\
\text{N} \text{R}'
\end{array} + \text{H}^+ \text{H}_2\text{O}
\]

Scheme 8. Acid-catalyzed exchange between hydrazone 129 and hydroxylamine 130, yielding hydrazide 131 and 132.

We soon discovered that the action of a 1M aqueous solution of NH$_2$OH • HCl at 40 °C could rapidly removed the benzaldehyde templates on architecture 128 to yield 133 with hydrazide-rich pores “drilled” in the film (Figure 71). The capture of benzaldehyde by hydroxylamine was monitored by UV-Vis spectroscopy and characterized by the decrease of an absorption band centered at $\lambda = 300$ nm (Figure 72). In general, the removal of the benzaldehyde was completed in about 24 h. Reaction was considered as completed when two consecutive spectra measured in the range $300 < \lambda < 650$ nm showed no more change of the absorption profile over 1 to 2 hours.
Figure 71. Transformation of architecture 128 into 133 upon removal of the benzaldehyde templates with aqueous hydroxylamine in acidic conditions. The grey background represents an ITO surface. Dotted lines denote possible non-covalent interactions.

Figure 72. Normalized absorption spectra of architectures 128 (○) and 133 after treatment with 1M NH$_2$OH • HCl at 40 °C for 23 h (dotted) and 26 h (bold).
An interesting feature of this hydroxylamine treatment is the slight changes that it triggered in the \(H,H\)-PDI absorption band between 450 and 600 nm. As it can be seen on Figure 72, the ratio of the two bands located at \(\lambda = 505\) and \(\lambda = 543\) nm is \(R_{505/543} = 1.04\) for architecture 128 and \(R_{505/543} = 1.25\) for architecture 133. As it has been outlined earlier, such an increase indicates that the mutual orientation of the \(H,H\)-PDI in the stacks is modified. The exact nature of the modification can’t be told from the UV-Vis spectra but could result from a modification in the rotational displacement between two consecutively stacked chromophores. This tendency was repeatable over several architectures 133. It could be explained by the fact that removing the benzaldehyde templates left voids on the sides of the stacks. This in turn destabilized the initial conformation of the \(H,H\)-PDI stacks and triggered a conformational change to fill the spaces left.

In all cases, architecture 119 was not stored, but rather used immediately for stack exchange experiments. The goal was to limit as much as possible the contamination of the photosystem by traces of volatile carbonyl compounds present at low concentration in the atmosphere of the laboratory, for example acetone. In addition, there was a possibility that the presence of unprotected nucleophilic hydrazide groups in the architecture 133 could have triggered undesired reaction and led to the decomposition of the film. However, no control experiments were done to test this assumption.

3.3. Ion-Gated Photosystems

As shown above, architecture 131 was already able to generate appreciable photocurrent with single \(H,H\)-PDI stacks (maximum \(J_{SC} \sim 8 \mu A \text{ cm}^{-2}\)). This suggested the use of this system as a model to study the effect that fixed charges installed along the single \(H,H\)-PDI stacks could have on the activity of the system. Due to coulombic interaction, the flow of positive (holes) and negative (electrons) charge carriers could possibly be influenced by
electrostatic charges placed along the conductive pathway. Moreover, these charges could also have an effect on the energetics of the frontier molecular orbitals localized on the \(H,H\)-PDI chromophores. The global effect of ionized groups on the photocurrent generation is called here ion gating.

3.3.1. Synthesis of Charged Peptides

To test this hypothesis, we designed aldehydes 134 and 135, each of them carrying an ionizable group. 134 has a carboxylic acid that would be deprotonated at pH < 4.7. 135 has an amine that would become protonated at pH > 10.5. We also prepared the neutral control compound 136 with a neutral amide group. The three molecules have an aromatic aldehyde “handle” for stack-exchange with the hydrazide-rich architecture 133. The synthesis of these stack exchangers is depicted on Scheme 9. For anionic 134, the protected glutamate was used as a convenient starting material. Boc-protected 137 was treated with TFA and the resulting amine 138 coupled to Fmoc-Glu(t-Bu)-OH using classical peptide chemistry, yielding 139 in reasonable yield. Fmoc was then removed with base and the deprotected amine was coupled with the carboxylic acid group from ketal-acid 140, again in reasonable yield, to give 141. Removal of the dimethylketal and t-Bu protecting groups in one step by using acid afforded aldehyde 134 in excellent yield. For cationic 135 and neutral 136, Fmoc-Lys(Boc)-OH was used as the common starting material and was reacted with amine 138 by using classical peptide chemistry to yield the
fully protected common intermediate 142 in good yield. Fmoc was removed with base and the resulting amine reacted with the ketal-acid 140 to give 143 in good yield. Finally, Boc and dimethyl ketal were removed with TFA to give the aldehyde 135 as an ammonium salt in moderate yield. For 136, protected lysine 142 was treated with TFA to remove Boc and subsequently acetylated with acetic anhydride to give 144. Fmoc was then removed with base and the
resulting free amine reacted with the ketal-acid 140 to give ketal 145 in reasonable yield. Aldehyde 136 was finally obtained quantitatively upon treatment with TFA.

3.3.2. Stack Exchange

Aldehydes 134, 135 and 136 were readily soluble in a mixture of dimethylsulfoxide and acetic acid (DMSO/AcOH 9:1, v/v). Architectures 133 containing free hydrazide groups were incubated at 40 °C in 15 mM solutions of these compounds to produce systems 146, 147 and 148, respectively (Figure 73).

The progress of stack exchange and installation of aldehydes was monitored using UV-Vis spectroscopy and appeared as the progressive growth of a band centered on $\lambda = 300$ nm (Figure 74). Due to the identical absorption spectra of aldehydes 134, 135 and 136, the absorption profiles of architectures 146, 147 and 148 were identical in all cases.
Figure 73. TSE with 135 for the synthesis of cationic photosystem 147. TSE with 134 and 136 gave the corresponding neutral and anionic photosystems 146 and 148, respectively.

The yield of stack exchange $\eta_{\text{TSE}}$ was estimated from the absorption spectra measured before and after TSE on architectures 128, 133, 146, 147 and 148, respectively (Figure 74).
Figure 74. UV-Vis absorption spectra of SOSIP architecture 128 (dotted line), of architecture 133 after the removal of benzaldehyde templates by a treatment with NH$_2$OH (dashed line) and of architecture 146 after stack exchange with glutamate 134.

The molar absorption coefficient of benzylhydrazones at $\lambda = 305$ nm (as in single-stack architecture 128) was previously found to be half of the molar absorption coefficient for the benzylhydrazone-amides (such as in 146, 147 and 148). Therefore, quantitative TSE was obtained when the absorption intensity at $\lambda = 305$ nm after TSE doubled as compared to the intensity before the exchange. Additional corrections were applied to account for the partial dissolution of the films when necessary (see Experimental Sections for details). A ratio of two aldehydes per $H,H$-PDI in the central stack was considered to correspond to quantitative stack exchange.

Using 15 mM solutions of glutamate 134 and lysine 135 in DMSO/AcOH 9:1, v/v stack-exchange yields were high ($\eta_{\text{TSE}} \sim 80\%$) with thin photosystems (Table 3, Entries 1, 3, 5 $A_{543} < 1.3$ or $d < 570$ nm) but decreased ($\eta_{\text{TSE}} < 50\%$) with thicker ones (Table 3, Entries 2, 4, 6). By using a more concentrated solution of glutamate 134 at 100 mM in DMSO/AcOH 9:1, v/v it was possible to obtain a still acceptable $\eta_{\text{TSE}} = 66\%$ (Table 3, Entry 7, $A_{543} < 1.3$ or $d < 570$ nm).
Table 3. Summary of TSE Yields with Ion-Gated Photosystems.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cpd</th>
<th>PS</th>
<th>d (nm)</th>
<th>C (mM)</th>
<th>ηTSE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>135</td>
<td>147</td>
<td>22</td>
<td>15</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>135</td>
<td>147</td>
<td>77</td>
<td>15</td>
<td>24</td>
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<tr>
<td>3</td>
<td>136</td>
<td>148</td>
<td>40</td>
<td>15</td>
<td>39</td>
</tr>
<tr>
<td>4</td>
<td>136</td>
<td>148</td>
<td>72</td>
<td>15</td>
<td>4</td>
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<td>5</td>
<td>134</td>
<td>146</td>
<td>19</td>
<td>15</td>
<td>80</td>
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<td>146</td>
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<td>15</td>
<td>47</td>
</tr>
<tr>
<td>7</td>
<td>134</td>
<td>146</td>
<td>561</td>
<td>100</td>
<td>66</td>
</tr>
</tbody>
</table>

*a* Aldehydes used for templated stack exchange, see Figure 73. *b* Photosystem, see Figure 73. *c* Film thickness $d$ was approximated from $H,H$-PDI absorption assuming that $A_{543} = 0.1$ a.u. corresponds to $d \sim 44$ nm. *d* Concentration of aldehydes in DMSO/AcOH 9:1, v/v used for TSE. *e* Yield of templated stack exchange.

3.3.3. Functional Characterization

The importance of ion gating for photocurrent generation with single $H,H$-PDI stacks was first evaluated at pH 7.7. In these conditions, the carboxylate groups in photosystem 146 carried negative charges and the amino groups in 147 had positive charges. To achieve complete equilibration of the charge state, the photosystems were incubated at 40 °C overnight in a phosphate buffer at pH 7.7. During the photocurrent measurement, the mobile hole acceptor TEOA was dissolved in a phosphate buffer to keep the pH of the solution at pH 7.7. Photocurrent $J_{SC}$ produced by photosystems 146, 147 and 148 increased linearly with increasing thickness of the photosystems up to $d \sim 90$ nm. This behavior was independent on the presence or absence of charges (Figure 75 A).

In thicker anionic systems 146, at $A_{543} > 1$, i.e. $d > 400$ nm, $J_{SC}$ was measured in the same range as with single $H,H$-PDI stacks in 128 (Figure 75 B). Previously, 128 was shown to have a bell-shaped dependence of the photocurrent $J_{SC}$ on $d$ (vide supra). It is possible that, with $d$ between 100 and 500 nm, the photocurrent produced by anionic photosystem 146 followed the
same bell-shaped trend, although no data points have been recorded on anionic photosystems that could directly prove this.

**Figure 75.** A) and B) Photocurrent generated by photosystems 147 (○), 148 (●) and 128 (□) irradiated with a solar simulator (P = 83 mW cm$^{-2}$; 50 mM TEOA; 0.2 M Na$_2$HPO$_4$ buffer; pH = 7.7 at 0 V vs. Ag/AgCl). Film thickness $d$ was approximated from $H,H$-PDI absorption assuming that $A_{543} = 0.1$ a.u. corresponds to $d \sim 44$ nm. Dotted lines are added as visual guides.

Here, no experimental evidence was collected that could indicate the presence of long-distance charge transport for the anionic architecture 146. The same was previously found for the original uncharged photosystem 128 (vide supra). This was in contrast with previous results obtained with ion-gated NDI photosystems where anionic side chains were found to support long-distance charge transfer at pH 7.7.$^{[150]}

Photocurrents $J_{sc}$ produced by the cationic, neutral and anionic photosystems were then measured as a function of the pH using appropriately buffered TEOA solutions. Independent from the sign of the charge, the behavior was the same in the three cases. With increasing pH, photosystems 146, 147 and 148 generated gradually more photocurrent (Figure 76). This increase originated from the progressive deprotonation of the TEOA holes acceptor in solution and its concomitant increased ability to donate electrons. It
had nothing to do with the activity of the photosystems themselves, since opposite charges in 146 and 147 showed the same trend.

![Graph showing pH dependence of the activity of photosystems](image)

**Figure 76.** pH dependence of the activity of photosystems 147 (○), 148 (×) and 146 (●) irradiated with a solar simulator (P = 83 mW cm⁻²; 50 mM TEOA; 0.2 M Na₂HPO₄ buffer; pH = 6.5–9.6 at 0 V vs. Ag/AgCl), \( Y = (J - J_{6.5}) / (J_{9.6} - J_{6.5}) \) (c). Grey line is added as visual guide.

Again, this monotonous behavior was contrary to what had been previously observed with ion-gated photosystems based on NDI. In the latter case, a maximal activity was found for anionic photosystems at pH = 7.5. The partial deprotonation of the co-axial strings of carboxylic acids was claimed to help in the isolation, stabilization and transport of holes by a hole/proton antiport mechanism.¹⁵⁰

Finally, photocurrents generated at pH 7.7 were recorded as a function of the temperature to estimate the activation energy \( E_a \) associated with the anionic and cationic photosystems (Table 4).¹³,¹⁵⁰ The obtained values for \( E_a \) did not change much in the presence of co-axial strings of cations and anions (i.e., \( E_a \) (128) = 0.18 eV > \( E_a \) (146) = 0.17 eV > \( E_a \) (147) = 0.13 eV). The found differences presumably originated from differences in thickness rather than from ion gating (i.e., \( A_{543} \) (128) = 0.07 > \( A_{543} \) (146) = 0.05 > \( A_{543} \) (147) = 0.04). Noteworthy, these values remained significantly below the ones obtained with NDI photosystems (0.40 > \( E_a \) > 0.19 eV).¹⁵⁰ Again, these results suggested
that, contrary to the less active single NDI stacks, the more active single H,H-PDI stacks do not respond to ion gating.

Table 4. Dependence of Activation Energies on Charge and Thickness.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cpd (^a)</th>
<th>PS (^b)</th>
<th>(d) (^c) (nm)</th>
<th>(E_a) (^d) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>128</td>
<td>31</td>
<td>180 ± 0.01</td>
</tr>
<tr>
<td>2</td>
<td>134</td>
<td>146</td>
<td>22</td>
<td>170 ± 0.01</td>
</tr>
<tr>
<td>3</td>
<td>135</td>
<td>147</td>
<td>18</td>
<td>130 ± 0.01</td>
</tr>
</tbody>
</table>

\(^a\) Aldehydes used for templated stack exchange, see Figure 73. \(^b\) Photosystem, see Figure 73. \(^c\) Film thickness \(d\) was approximated from \(H,H\)-PDI absorption assuming that \(A_{543} = 0.1\) a.u. corresponds to \(d \sim 44\) nm. \(^d\) Activation energy, estimated from the dependence of photocurrents on temperature.

In summary, photosystems 147, 148 and 146 with cationic, neutral or anionic groups on the side of the central \(H,H\)-PDI stacks did not respond to pH changes, showed the same decreasing activity with increasing thickness \(d\) and comparable, low activation energies \(E_a\). These findings suggest that the central \(H,H\)-PDI stacks do not respond to ion-gating. At the same time, single \(H,H\)-PDI stacks performed well for photocurrent generation, as testified by the high levels of current observed at moderate thickness \(d\) (\textit{vide supra}). Results obtained with NDI stacks were opposite: a strong influence of charges was observed.\(^{180}\) Meanwhile, NDI stacks showed a global, lower intrinsic ability at generating photocurrent as compared to \(H,H\)-PDI stacks. In conclusion, we considered that, since the mechanisms for photoexcitation, charge separation and transport were already efficient in \(H,H\)-PDI stacks, consequently they cannot be still enhanced by ion-gating and charges have no influence on photocurrent generation.

Otherwise, it is worth to note that consistent trends have been obtained in the thickness (Figure 75) and pH (Figure 76) experiments done with photosystems having neutral, cationic or anionic side chains. This illustrates the reproducibility achieved with SOSIP and TSE in our case.
3.4. Double-Channel Photosystems

Our next efforts were directed toward the use of TSE for the installation of co-axial channels of electro- and photoactive materials. This way, p/n-SHJ would be created with potentially increased performances. To efficiently capture light in the visible range, we aimed at using aromatic molecules with high molar absorption coefficient and distinct spectral features as compared to $H.H$-PDI. In such architectures, the central $H.H$-PDI would be an electron conducting channel, as $H.H$-PDI is considered as an electron-transporting (n-type) semiconductor in the literature. On the other hand, the co-axial channels installed by TSE would have to conduct holes and should be semiconductors of the p-type.

3.4.1. Double-Channel Systems with Terthiophene

We first evaluated the terthiophene-aldehyde 149 for TSE with architecture 133 to prepare the double-channel photosystem 150 (Figure 77). The previously reported terthiophene stack exchanger 149 was selected to build hole-transporting channels along the central PDI stack. The aldehyde acceptor at one terminus was needed for TSE, the methoxy donor at the other side to increase the energy of the HOMO and thus maximize hole accepting and transporting abilities. The methyl groups along the scaffold were of interest to further raise the HOMO energy by hyperconjugation and to weakly deplanarize the terthiophene in solution and thus maximize the solubility. As reported elsewhere, the planarization of this chromophore occurred nevertheless easily, as shown by fluorescence measurements in membranes. [207]
The reversible hydrazone formation process was carried out at 40 °C and monitored by UV-Vis spectroscopy. Installation of the co-axial terthiophene stacks next to the central H,H-PDI stacks in structure 150 was reflected by the appearance of an absorption band at 385 nm, the signature of terthiophene chromophores (Figure 78, solid line). Kinetically speaking, TSE
with 149 took between 1 to 4 days to reach an equilibrium, depending on the thickness of the film. After completion of TSE, photosystem 150 was incubated in DMSO for 24 h at 40 °C to dissolve and remove any unbound terthiophene 149.

![Absorption spectra](image)

**Figure 78.** Absorption spectra of photosystem 133 (dotted line), before, and 150 (solid line), after TSE with terthiophene aldehyde 149. The appearance of a characteristic band at $\lambda = 385$ nm evidenced the installation of terthiophene chromophores. $A_{343} = 0.1$ a.u. corresponds to film thickness $d \sim 44$ nm.

Quantification of the TSE yield $\eta_{\text{TSE}}$ could not be done on the sole basis of absorption spectra measured on solid films, in contrast to what had been previously done with charged stack exchangers (vide supra). In the present case, the molar absorption coefficient of $H,H$-PDI chromophores experiences a hypochromic shift upon aggregation in the solid state. The extent of this decrease is not precisely known and might depend on the actual packing of the $H,H$-PDI chromophores in architecture 150. As a result, determination of $\eta_{\text{TSE}}$ would be unreliable if based on spectra measured in the solid state. Therefore, we denatured and dissolved several photosystems 150 by shaking them in a mixture of DMSO, iPr$_2$NEt and β-mercaptoethanol at 40 °C for 1 hour. During this process, the disulfide bonds that maintained the integrity of the architectures were cleaved and solutions that contained $H,H$-PDI and terthiophene chromophores were obtained. In the basic conditions used, it is
likely that the hydrazone bonds were conserved and thus terthiophene-\(H,H\)-PDI-terthiophene triads remained bound together. UV-Vis spectra measured on these solutions showed the characteristic band of terthiophene at \(\lambda = 385\) nm and of \(H,H\)-PDI with \(\lambda = 531\) nm (Figure 79).

![Figure 79](image)

**Figure 79.** Normalized absorption spectra of dissolved photosystem 150 (solid line), terthiophene aldehyde 149 (dotted line) and propagator 114 containing \(H,H\)-PDI (dashed line), in DMSO.

The characteristic vibronic progression of \(H,H\)-PDI between \(\lambda = 450\) and \(\lambda = 650\) nm confirmed that the interactions between the chromophores had been disrupted in the process, allowing a more precise evaluation of the stack-exchange yields. The quantification of \(\eta_{\text{TSE}}\) for 150 was carried out on the basis of these spectra (see Experimental Section for details) and the obtained results are summarized in Table 5. TSE proceeded in quantitative yield in a thickness range 100 \(< d < 940\) nm with the well-soluble and small stack exchanger 149.

**Table 5. Summary of Stack Exchange Yields in 150 with aldehyde 149.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>(d^a) (nm)</th>
<th>(\eta_{\text{TSE}}^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101</td>
<td>quant.</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
<td>quant.</td>
</tr>
<tr>
<td>3</td>
<td>942</td>
<td>quant.</td>
</tr>
</tbody>
</table>

\(a\) Film thickness \(d\) was approximated from \(H,H\)-PDI absorption assuming that \(A_{543} = 0.1\) a.u. corresponds to \(d \sim 44\) nm. \(b\) Yield of templated stack exchange.
3.4.1.2. Structural Characterization

The surface morphology of p/n-SHJ photosystem 150 was studied by AFM. In height images, 150 had a smooth surface. The surface roughness calculated from these data was $R_a \sim 4.9$ nm, similar to $R_a \sim 4.7$ nm previously obtained with single $H,H$-PDI stacks in architecture 128. In phase-contrast detection mode, low-defect organization over very long distances was apparent. The results obtained with SHJ architecture 150 were very similar to those with single channel architecture 128 (vide supra) and supported a preserved organization after TSE with terthiophene aldehyde 149.

Figure 80. Imaging of photosystem 150. A) AFM height image (Z range: black 0 nm– white 100 nm); B) AFM phase-contrast image (Phase range: 70°).

Further insights in the arrangement of the chromophores in the double channel photosystem 150 was gained from CD spectroscopy. A single, positive couplet was apparent with a zero crossing at $\lambda \sim 450$ nm (Figure 81, bold line). The positive Cotton effect aroused between $\lambda \sim 460$ nm and $\lambda \sim 460$ nm, with a maximum at $\lambda_{\text{MAX}} \sim 500$ nm. A fine structure was apparent, with a shoulder at $\lambda \sim 470$ nm and a secondary peak at $\lambda \sim 540$ nm. Both the position and shape of this band corresponded to the absorption band of $H,H$-PDI chromophores in the absorption spectrum of architecture 150 (Figure 81, thin line). The negative Cotton effect was found between $\lambda \sim 440$ nm and $\lambda \sim 340$ nm, with a minimum
at $\lambda_{\text{MIN}} \sim 400$ nm. The position and the shape of this signal corresponded to the absorption band of terthiophene chromophores in the absorption spectrum of architecture 150 (Figure 81, thin line).

![Figure 81](image)

**Figure 81.** Absorption (solid, left axis) and CD spectra (bold, right axis) for architecture 150.

The couplet involving both chromophores suggested preferred, stronger interstack CD coupling between the $H,H$-PDI and terthiophenes rather than weaker, intrastack interactions between superimposed $H,H$-PDI on the one hand and terthiophenes on the other hand. The positive couplet observed with double channel 150 suggested that the stacks had right-handed helicity ($P$-configuration), according to the exciton chirality method.\(^{204, 206}\) The same result had been previously obtained with the single-channel architecture 128, and supported preserved organization in 150 after TSE with 149.

The dominance of interstack hetero-coupling CD signals over those from intrastack homo-coupling was at first surprising but could be explained by a more favorable twist angle between the transition dipoles of the $H,H$-PDI and terthiophene chromophores. Inside the central stacks, comparatively smaller twist angles and weaker CD signals were expected because neighboring $H,H$-PDI chromophores were tethered by covalent bonds that limited their conformational freedom. Although CD spectra of oriented films should be
interpreted with much reservation because of possible contributions from unrelated phenomena, this result suggested the formation of a highly ordered double-channel architecture 150 that maintained a close proximity between terthiophenes and $H,H$-PDI.

3.4.1.3. Functional Characterization

The performances of p/n-SHJ architecture 150 for photocurrent generation were investigated under routine conditions (see Experimental Section for details). When illuminated with a solar simulator, terthiophene (absorption maximum $\lambda_{\text{MAX}} = 385$ nm) and $H,H$-PDI (absorption maximum $\lambda_{\text{MAX}} = 505$ nm) were both photoexcited. The resulting excitons were then to dissociate into free charge carriers flowing toward the ITO electrode and the sacrificial hole acceptor TEOA.

The frontier molecular orbital (FMO) energetic levels of $H,H$-PDI, $CN_2$-PDI and of the relevant hydrazone derivative 151 have been reported elsewhere and are schematically depicted on Figure 82 together with the putative directions of electrons and holes transfer. $H,H$-PDI is the hole donating partner, since its HOMO is placed lower as compared to the one of terthiophene 151. The latter is the electron donating partner, with its high-energy LUMO. Upon photoexcitation, $H,H$-PDI transfers a hole from its HOMO to terthiophene. On the other hand, a photoexcited terthiophene can transfer an excited electron localized in its LUMO, into the LUMO of $H,H$-PDI. In the latter case, one cannot exclude that Förster Resonant Energy Transfer (FRET) from terthiophene donors to $H,H$-PDI acceptors happens as well, because a partial overlap of the terthiophene emission and of $H,H$-PDI absorption exists.150-158

The separated charge carriers are then transported along the $\pi$-stacked n-type $H,H$-PDI and p-type terthiophene toward ITO and TEOA. The monolayer of $CN_2$-PDI chromophores on the ITO surface have low-lying FMO and are likely to accept electrons from either photoexcited $H,H$-PDI or terthiophenes.
Figure 82. Energy levels of the partners involved in the generation of photocurrent upon irradiation of 150. HOMO (bold) and LUMO (dashed) of H,H-PDI 26, CN$_2$-PDI 29, and hydrazone 151 (from ref. [148]) together with HOMO of TEOA and work function of ITO (from ref. [189]), reported relative to -5.1 eV for Fe$^+/Fe$. Full arrow denotes electronic transition resulting from photoexcitation, half arrows illustrate subsequent electrons (e$^-$) and holes (h$^+$) transfers.

Photocurrent was recorded upon switching the light source on and off. Anodic photocurrent rose rapidly upon illumination and could be repeated several times without alteration of the kinetic profile (Figure 83). 150 was therefore stable under the illumination conditions that were used.
Figure 83. Photocurrent generated from 150 ($A_{543} = 1.1$, $d = 485$ nm). Film thickness $d$ was estimated from $H,H$-PDI absorption using $A_{543} = 0.1 \sim 44$ nm. Conditions were: TEOA concentration $= 50$ mM, $P_{in} = 83$ mW cm$^{-2}$.

On the action spectrum of 150, the contribution of terthiophene and $H,H$-PDI were both apparent (Figure 84).

Figure 84. Action (solid line, ■) and UV-Vis (dotted line) spectra of $H,H$-PDI photosystem 150 (■). IPCE was measured with 50 mM TEOA, 0.1 M Na$_2$SO$_4$, 0 V vs. Ag/AgCl. IPCE values were normalized with respect to the value recorded at 360 nm, for which IPCE was set at unity).

A shoulder appearing at $\lambda \sim 400$ nm on the IPCE profile corresponded to the absorption band of terthiophene on the UV-Vis spectrum, and a contribution at $\lambda \sim 520$ nm matched with the absorption band of $H,H$-PDI chromophores
(Figure 84). However, the IPCE values were not proportional to the light absorption intensity. Noteworthy, the contribution of terthiophenes to charge generation was seemingly enhanced as compared to H,H-PDI, despite lower intensity of their band on the UV-Vis spectrum. This observation suggested that electron injection from photoexcited terthiophenes into the LUMO of H,H-PDI was more favorable than hole injection from excited H,H-PDI into the HOMO of terthiophene.

The activity of double channel architecture 150 was measured with increasingly thicker film and compared to the performance of the single channel architecture 128 (Figure 85).

**Figure 85.** Dependence of the short-circuit current density $J_{sc}$ on the thickness $d$ for photosystems 128 (■) and 150 (■) upon irradiation with a solar simulator (83 mW cm$^{-2}$; 50 mM TEOA, 0.1 M Na$_2$SO$_4$, 0 V vs. Ag/AgCl). $d$ was approximated from H,H-PDI absorption assuming that $A_{353} = 0.1$ a. u. corresponds to $d \sim 44$ nm, pertinent values for $\eta_{BR}$ and $E_a$ are indicated. Gray lines were added as visual guides.
In short stacks, that is $0 < d < 260$ nm or $A_{543} < 0.6$, the short-circuit current densities $J_{SC}$ generated by either single- or double-channel architectures were indistinguishable. However, with thicker architecture, a clear discrepancy was evident. In single $H,H$-PDI stacks, the photocurrent saturated at $J_{SC} = 8.0 \mu A \text{ cm}^{-2}$ and soon decreased significantly with longer stacks. On the contrary, photocurrent generated by double-channel photosystem 150 saturated at clearly higher values (with $J_{SC} = 13.8 \mu A \text{ cm}^{-2}$) and clearly longer distances, with critical thickness $d_c \sim 500$ nm. Remarkably, no marked decrease of current was observed with thicker films and photocurrent still as high as $J_{SC} = 12.5 \mu A \text{ cm}^{-2}$ was recorded with long double-channel coaxial stacks ($d = 1 \mu m$). In contrast to single channel architecture 128, long distance charge transport was possible with two co-axial channels in 150.

To better understand the differences observed between the single and double channel architectures concerning the transport of charges over long distance, we measured the bimolecular charge recombination efficiency $\eta_{BR}$ of these systems. This parameter was extracted from the dependence of $J_{SC}$ on the light intensity of the solar simulator (see Experimental Section for details) and expresses the proportion of holes and electrons that recombine together before they can reach to the collecting electrodes.

Pertinent values for $\eta_{BR}$ are displayed on Figure 48. In short stacks ($0 < d < 260$ nm or $A_{543} < 0.6$), the single channel 128 and double channel 150 gave similar results with $\eta_{BR} \sim 30\%$. However, with thick photosystems, results from single and double-channel systems strongly differed. With single-channel architectures, charge recombination rapidly increased with increasing $d$: at $d \sim 625$ nm, the recombination was almost doubled, reaching $\eta_{BR} = 70\%$. In contrast, with the double channel architecture 150 the recombination did not increase with increasing thickness $d$: with $d \sim 940$ nm, it stayed at $\eta_{BR} \sim 29\%$. The constantly low values for $\eta_{BR}$ recorded with double channel architectures showed that the existence of segregated channels for the transport of electrons...
and holes efficiently prevented their recombination. This explained the long distance charge transport observed with terthiophene-\textit{H,H-PDI} double channel architecture 150.

An additional clue concerning the long-distance charge transport in architecture 150 was obtained from the determination of activation energies $E_a$ associated with photocurrent generation. This parameter was extracted from the dependence of $J_{SC}$ on the temperature, as explained in the Experimental Section. Again, interesting differences were observed in the behavior of single- and double-channel architectures 128 and 150, respectively (Figure 85). In single channel 128 and with short stacks (0 < $d$ < 260 nm or $A_{543}$ < 0.6), the activation energy was already reaching $E_a$ = 240 meV. With longer stacks ($d$ ~ 625 nm), it increased by 25% to reach $E_a$ = 298 meV. The situation was much different with double channel architecture 150: $E_a$ was globally lower and at the same time did not increase much with thickness (Figure 85). We measured $E_a$ =169 meV at $d$ ~ 100 nm and $E_a$ =177 meV at $d$ ~ 940 nm, an increase by 5% only. Taken together, the constantly low activation energies and charge recombination found with architecture 150 suggested that the performance of this photosystem resulted from an efficient transport of photogenerated charge carriers toward the collecting electrodes. It underlined that terthiophenes as hole transporter and \textit{H,H-PDI} as electron transporter both performed well.

The success of long-distance charge transport with the electron-rich terthiophene and the electron-deficient \textit{H,H-PDI} was in accordance with most reports in the literature that consider \textit{H,H-PDI} as a n-type semiconductor. However, although scarcely documented, the hole-transporting ability of \textit{H,H-PDI} has been reported as well, making of this material an ambipolar semiconductor.\textsuperscript{[46, 48]} It seems that the overwhelming use of \textit{H,H-PDI} as an electron transporter likely comes from the restrained number of molecules available to perform that task rather than from an impossibility to transport holes with this semiconductor. These reports prompted us to establish up to
which extends the ambipolar character of \( H, H\text{-PDI} \) could be expressed in our systems. Addressing this question required the “umpolung” of the \( H, H\text{-PDI} \) central stacks from electron to hole transporting channel. Being both combinatorial and convergent, our SOSIP-TSE approach was ideal for that because double-channel architectures with hole-transporting \( H, H\text{-PDI} \) stacks were readily accessible by a single modification of the photosystem synthesis: at the last step, \( 133 \) would be treated with electron-poor rather than electron-rich organic materials.

### 3.4.2. Double Channel Systems with Naphatalenediimides

![Energy levels of chromophores](image)

**Figure 86.** Energy levels of chromophores \( H, H\text{-PDI} \), \( H, H\text{-NDI} \) and \( O, O\text{-NDI} \). HOMO (bold) and LUMO (dashed) of \( H, H\text{-PDI} \) (from ref. [37]) and NDIs (from ref. [38]) together with HOMO of TEOA and work function of ITO (from ref. [189]), reported relative to \(-5.1 \text{ eV for Fc}^+/\text{Fc}\). Full arrow denotes electronic transition resulting from photoexcitation, half arrows illustrate subsequent electrons (\( e^- \)) and holes (\( h^+ \)) transfers.

We chose naphtalenediimides (NDI) as electron-deficient partners for \( H, H\text{-PDI} \). These planar, \( \pi \)-acidic aromatic molecules have already been used for
SOSIP and TSE, both in the central and lateral stacks. Synthetically accessible core-substitution patterns allowed for the modification of both their absorption characteristics and FMO energetic levels. The unsubstituted NDI (H,H-NDI) 77 moiety had both HOMO and LUMO clearly below those of H,H-PDI 26 and was envisioned to act as a strong electron accepting, hole donating partner for the latter (Figure 86). Core substitution with two ethoxy- groups gave O,O-NDI 74 with increased electron density and FMO energetic levels, comparable to those of H,H-PDI. As suggested by the energy diagram, O,O-NDI could still act as a mild hole donor, while electron transfer from H,H-PDI LUMO would be strictly isoenergetic (Figure 86).

From the hydrazide-rich architecture 133, synthesis of double-channel systems 152 (with lateral H,H-NDI stacks) and 153 (with lateral O,O-NDI stacks) was done with stack exchangers 154 and 155, respectively (Figure 87). Molecule 154 with H,H-NDI has been proposed previously for stack exchange and was prepared as described. Molecule 155 with O,O-NDI was designed on the same model and prepared for the purpose of this work. Both have an aldehyde “handle” for condensation with hydrazide at one end. At the other one, the allyloxy carbonyl (Alloc) group was used as solubilizing moiety here, but could serve for further elongation of the molecules as well.
Figure 87. Synthesis of double-channel photosystems 152 and 153 from single channels system 133. The grey bar represents an ITO surface.

3.4.2.1. Synthesis

ITO surfaces covered with porous structure 133 were incubated in DMSO/ACOH 9:1, v/v solutions of either 154 (20 mM) or 155 (19 mM) at 40 °C. Covalent capture of H,H-NDI or O,O-NDI chromophores was monitored.
by UV-Vis absorption spectroscopy and evidenced by the appearance of the corresponding absorption bands (for 154, $\lambda_{\text{MAX}}(H,H\text{-NDI}) = 380$ nm; for 155, $\lambda_{\text{MAX}}(O,O\text{-NDI}) = 466$ nm) (Figure 88 A and B). It took about 24 hours to reach an equilibrium, after which the ratio of $H,H\text{-PDI}$ to $H,H\text{-NDI}$ or $O,O\text{-NDI}$ did not change any more. The obtained electrodes were then thoroughly washed with DMSO and incubated in this solvent at 40 °C overnight to remove unbound chromophores.

It is noteworthy that the installation of $H,H\text{-NDI}$ aldehyde 154 triggered a significant change in the shape of the $H,H\text{-PDI}$ absorption band, during TSE from 133 into 152 (Figure 88 A).

![Figure 88. A) Normalized absorption spectra of photosystem 133 (dotted line), before, and 152 (solid line) after TSE with $H,H\text{-NDI}$ aldehyde 154. The appearance of a characteristic band at $\lambda = 380$ nm evidences the installation of $H,H\text{-NDI}$ chromophores. B) Normalized absorption spectra of photosystem 133 (dotted line), before, and 153 (solid line) after TSE with $O,O\text{-NDI}$ aldehyde 155. The appearance of a characteristic band at $\lambda = 466$ nm evidences the installation of $O,O\text{-NDI}$ chromophores.]

Before TSE in 133, the ratio of absorption at $\lambda = 505$ nm to absorption at $\lambda = 543$ nm was $R_{505/543} = 1.28$. After TSE in 152, this ratio decreased down to $R_{505/543} = 0.94$. As it has been explained previously, the shapes of absorption bands at these wavelengths are strongly influenced by the arrangement of $H,H$-
PDI chromophores with respect to their neighbors in the aggregates. In the present case, the observed modification of band shape is likely to reflect a change in the aggregation and mutual orientation of neighboring $H,H$-PDI chromophores in the central stacks.

The same trend was observed during the transformation of the single-channel 133 into the double-channel photosystem 153 by TSE with the $O,O$-NDI aldehyde 155 (Figure 88 B). Although the exact nature of this conformational changes was not determined, it is striking that the decreasing $R_{505/543}$ that was remarked here corresponded well to the increasing $R_{505/543}$ that had been observed previously when benzaldehyde templates in single channel 128 were removed with hydroxylamine to prepare architecture 133 (vide supra). Therefore, the conformational changes involving the central $H,H$-PDI stacks might consist in a kind of contraction and then re-expansion of the whole structure, resulting from an initial decrease (during benzaldehyde removal) and subsequent re-increase of steric hindrance (during TSE).

![Figure 89](image.png)

**Figure 89.** Normalized absorption spectra of propagator 114 containing $H,H$-PDI (dashed line) and of (A) dissolved photosystem 152 (solid line) with $H,H$-NDI aldehyde 154 (dotted line) and of (B) dissolved photosystem 153 (solid line) with $O,O$-NDI aldehyde 155 (dotted line), in DMSO.
The quantification of stack exchange yields $\eta_{\text{TSE}}$ based on the absorption spectra measured with solid state architectures was not accurate since the absorption band of $H,H$-PDI was strongly affected by the exciton coupling arising from the interaction between stacked chromophores. For that reason, photosystems 152 and 153 were dissolved with a denaturing mixture of $\beta$-mercaptoethanol and iPr$_2$NEt in DMSO and the resulting solution used for the ratiometric determination of $\eta_{\text{TSE}}$ (Figure 89, see Experimental Section for details). Results are summarized in Table 6. Globally, the TSE yields were lower with NDI chromophores than previously with terthiophenes. This was in accordance with the lower solubility of NDI 155 and 154. With the less soluble $H,H$-NDI derivative, yields were in the range $52\% < \eta_{\text{TSE}}(154) < 80\%$. With the more soluble $O,O$-NDI derivative, yields were accordingly higher, in the range $60\% < \eta_{\text{TSE}}(155) < 100\%$.

Table 6. Summary of stack exchange yields obtained with double-channel architectures 152 and 153.

<table>
<thead>
<tr>
<th>Entry</th>
<th>PS $^a$</th>
<th>$d$ $^b$ (nm)</th>
<th>$\eta_{\text{TSE}}$ $^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>152</td>
<td>101</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>152</td>
<td>567</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>152</td>
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<td>100</td>
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</tr>
<tr>
<td>6</td>
<td>153</td>
<td>690</td>
<td>60</td>
</tr>
</tbody>
</table>

$^a$ Photosystem, see Figure 87. $^b$ Film thickness $d$ was approximated from $H,H$-PDI absorption assuming that $A_{543} = 0.1$ a.u. corresponds to $d \approx 44$ nm. $^c$ Stack-exchange yield, estimated from absorption spectra of the photosystems.

3.4.2.2. Functional Characterization

Photocurrent generation with double channel photosystems 152 and 153 was measured upon irradiation with a solar simulator, with TEOA as a sacrificial hole acceptor. Photostability of the systems under the applied
conditions was established upon recording the short-circuit photocurrent $J_{SC}$ as a function of the time of irradiation. Constant $J_{SC}$ indicated the compatibility of both photosystems with the applied conditions.

The dependence of $J_{SC}$ on the thickness $d$ of systems 152 and 153 was determined and compared with the trend previously observed with single channel system 128 and double channel architecture 150 (Figure 92).

![Graph showing the dependence of $J_{SC}$ on thickness $d$ for photosystems 128, 150, 152, and 153](image)

**Figure 90.** Dependence of the short-circuit current density $J_{SC}$ on the thickness $d$ for photosystems 128 (■), 150 (■), 152 (●) and 153 (○) upon irradiation with a solar simulator (83 mW cm$^{-2}$; 50 mM TEOA, 0.1 M Na$_2$SO$_4$, 0 V vs. Ag/AgCl). $d$ was approximated from H$_2$PDI absorption assuming that $\lambda_{443} = 0.1$ a. u. corresponds to $d \sim 44$ nm, pertinent values for $\eta_{BR}$ and $E_a$ are indicated. Gray lines were added as visual guides.

In all four cases, the evolution of $J_{SC}$ with $d$ was indistinguishable in short stacks, with $0 < d < 260$ nm ($\lambda_{443} < 0.6$) and a linear increase was observed. As
said above, the single-channel system 128 exhibited a saturation at critical \( d_C \sim 300 \text{ nm} \) and decrease of \( J_{SC} \) at higher \( d \), reaching \( J_{SC} < 1 \mu \text{A cm}^{-2} \) at \( d > 600 \text{ nm} \). With terthiophene architecture 150, the current increased up to \( J_{SC} = 12.5 \mu \text{A cm}^{-2} \). With double channel systems 152 and 153, higher currents were obtained.

In 152, photocurrent increased continuously up to \( J_{SC} = 22 \mu \text{A cm}^{-2} \) with formal stacks of \( d > 1000 \text{ nm} \). No value for critical thickness \( d_C \) could therefore be determined, apart from \( d_C > 1000 \text{ nm} \). This was clearly higher than with single channel photosystem 128 of similar thickness and showed again that long-distance charge transport was promoted by the installation of a second channel along the H,H-PDI stacks. The bimolecular charge recombination \( \eta_{BR} \) in photosystem 152 was determined from the dependance of \( J_{SC} \) on \( P_{in} \) (Figure 90, see Experimental Section for details). \( \eta_{BR}(152) = 37 \% \) measured with \( d(152) = 268 \text{ nm} \) was slightly higher than \( \eta_{BR}(128) = 30 \% \) with \( d(128) = 171 \text{ nm} \). Nevertheless, it did not increase significantly with increasing \( d \) and remained low at \( \eta_{BR}(152) = 39 \% \) with \( d(152) = 1056 \text{ nm} \). This was in contrast with previous results obtained with single channel 128 and showed the ability of segregated hole and electron channels to keep charge recombination to a low level in thick systems.

In 153, photocurrent density increased also with \( d \), up to \( J_{SC} = 17.7 \mu \text{A cm}^{-2} \) with \( d = 690 \text{ nm} \) (Figure 55) and did not exhibit saturation. This was clearly higher than the current generated with 128 or 150 of similar thickness, but lower than with 152. This long distance charge transport was correlated by the evolution of bimolecular recombination efficiencies. Starting from \( \eta_{BR} = 34\% \) in short stacks, it increased only slightly in long stacks, reaching \( \eta_{BR} = 39\% \) at \( d = 690 \text{ nm} \), again in contrast with the results obtained with single-channel architecture 128.

Taken together, the results obtained with double channel systems 150, 152 and 153 revealed that in thin films, these systems were indistinguishable from
single channel system 128. However, the superiority of double channel systems appeared in thick films, where long distance charge transport was observed in all three cases. Data showed that the installation of co-axial, separated channels for electrons and holes transport was essential to keep charge recombination $\eta_{BR}$ under 40% even with $d > 1000$ nm and that this effect was at the origin of the long-distance charge transport. However, differences in maximal $J_{SC}$ were observed, with decreasing activity in this order: 152 > 153 > 150. To explain this trend, we examined the action spectra of the four systems 128, 150, 152 and 153. The IPCE profiles were made comparable after normalization for transmittance $T$ at $\lambda = 543$ nm (Figure 91 C).

In the case of double channel 152, the normalized IPCE values were clearly higher than those from all other systems, indicating a globally better charge-separation capability. Additionally, the profile showed a clearly higher contribution from $H,H$-NDI at $350 < \lambda < 400$ nm as compared with the $H,H$-PDI contribution at $450 < \lambda < 600$ nm, in spite of the obviously lower absorption of $H,H$-NDI on the corresponding absorption spectrum (Figure 91 A). This supported the more efficient hole injection from $H,H$-NDI into $H,H$-PDI as compared to electron injection from $H,H$-PDI to $H,H$-NDI.

The normalized IPCE values recorded with photosystem 153 that contained $O,O$-NDI were intermediate between those of single-channel architecture 128 and of double-channel 152. The intermediate charge generation capability was consistent with the intermediate activity of 153 (Figure 90). The shoulder observed at $\lambda = 470$ nm corresponded to the contribution of $O,O$-NDI to the photocurrent. It is noteworthy that the intensity of this band on the IPCE profile was higher than on the absorption profile of 153, as compared to the band of $H,H$-PDI at $\lambda = 543$ nm (Figure 91 B and C).
Figure 91. Normalized absorption spectra of architectures 152 (A) and 153 (B), and (C) normalized action spectra of photosystems 128 (□), 152 (●), 153 (○) and 150 (■). Activity $Y$ was calculated as follow: $Y = \text{IPCE} / (1 - T_{543})$, IPCE = incident photon-to-current efficiency, $T_{543}$ = transmittance at 543 nm.
This suggested that hole injection from $O,O$-NDI to $H,H$-PDI was more efficient than the electron injection from $H,H$-PDI to $O,O$-NDI and correlated well with the higher driving force for hole, rather than for electron injection inferred from the energy diagrams (Figure 86). However, the imbalance was not as strong as previously observed in the IPCE profile of double channel 152 with $H,H$-NDI, where the hole injection into the HOMO of $H,H$-PDI was found to be exceedingly favoured with respect to electron injection into the LUMO of $H,H$-NDI.

Finally, with tertiothene architecture 150, the normalized IPCE values were globally lower than with the single-channel architecture 128, showing no evidence for enhanced charge separation in that case. As said above, the electron injection from tertiothene into $H,H$-PDI was found to be slightly more favored over the hole injection in the reverse direction. To sum up, IPCE profiles explained that higher $J_{SC}$ observed with NDI as compared to 150 with tertiothene originated from enhanced charge separation capabilities.

Compared to single-channel system 128, double-channel architecture 150 with tertiothene displayed low IPCE values and thus, charge separation was not particularly enhanced in this system. However, long-distance charge transport was clearly observed and current densities in long stacks were higher than with single $H,H$-PDI stacks. These good performances rather came from the much lower $\eta_{BR}$ and $E_a$ measured in photosystem 150 with tertiothene as compared to all the other architectures. For example, in double-channel photosystem 152 with hole-transporting $H,H$-NDI, $E_a$ increased from $E_a = 177$ meV with $d = 268$ nm up to $E_a = 239$ meV with $d = 1056$ nm (Figure 90). On the other hand, $E_a$ remained stable and low over this range of thickness in system 150 that contained tertiothene (Figure 90). The experimental data suggested that 150 was especially capable of avoiding charge recombination, a property that mainly accounted for the performance of this system.
It is noteworthy that higher photocurrent densities and more efficient charge separation were obtained when central $H,H$-PDI stacks transported holes rather than electrons. This evidenced that $H,H$-PDI performed better as p-type rather than n-type semiconductors in the central stack of our double channel photosystems, a conclusion that was not anticipated at the beginning of this work. As said above, a few literature reports have documented the hole-transporting activity of $H,H$-PDI. Recently, a double channel photosystem prepared by SOSIP-TSE was reported, having central $H,H$-NDI stacks and co-axial $H,H$-PDI channels. This is, from a structural point of view, an isomer of $152^{148}$. Remarkably, the p-type behaviour of $H,H$-PDI was also observed in this system very similar to those presented above. Nevertheless, the exceptional benefits gained from double-channel architectures for long-distance charge transport was not evidenced in this precedent study because short stacks were used exclusively ($d < 20 \text{ nm}$).
3.5. Triple-Channel Photosystems

The interesting properties observed with double-channel heterojunctions prompted us to explore the possibility to install one additional, co-axial channel and prepare triple-channel systems. From a functional point of view, this design was thought to increase the stability of the charge-separated states after photoexcitation. By further reducing the charge recombination $\eta_{BR}$, this would enhance the long-distance charge transport in thick photosystems. It is known from studies on soluble donor-sensitizer-acceptor triads that an increase in the distance between donor and acceptor moieties efficiently increased the lifetime of charge-separated-states and decreased the charge recombination.$^{[209-210]}$ Accordingly, studies on dye-sensitized solar cells showed that IPCE and fill-factor were increased when the donor-acceptor distance was increased in similar triads.$^{[211-212]}$

3.5.1. Triple-Channel System with Quarter- and Terthiophenes

We hypothesized that the benefits of the triple-channel design would be maximized if the different components could be arranged in a way that their energy levels aligned in a gradient. Thus, holes and electrons would be driven apart in channels that are separated by the full length of the triad. The electron-poor $H,H$-PDI stacks in architecture 133 would ideally be used as final electron acceptor. $H,H$-PDI have low-lying LUMO (-4.12 eV) and HOMO (-6.31 eV) and two partners with increasing electron density were selected to complete the system (Figure 92). The already used terthiophene aldehyde 149 with terminal methoxy-, electron-donating group was selected as the terminal, electron-rich group. In terthiophene 149, electrons from the $\pi$-donor methoxy ether at the terminal position as well as hyperconjugation from the methyl groups on the thiophene rings rose the HOMO and LUMO to -5.41 eV and -2.81 eV against vacuum, respectively.$^{[148]}$ Finally, the quaterthiophene motif (such as in 156) with intermediate electron density was selected as central chromophore. In
quaterthiophene 156, the electron-withdrawing carbonyl groups at each termini and the absence of methyl groups resulted in intermediate HOMO (-5.78 eV) and LUMO (-3.20 eV) levels, as compared to H,H-PDI and terthiophene.[145]

![Energy levels of chromophores H,H-PDI, quaterthiophene 156 and terthiophene 151 HOMO (bold) and LUMO (dashed) of H,H-PDI (from ref. [37]) and thiophenes (from ref. [145] and [148]) together with HOMO of TEOA and work function of ITO (from ref. [189]), reported relative to -5.1 eV for Fe3+/Fe. Full arrow denotes electronic transition resulting from photoexcitation, half arrows illustrate subsequent electrons (e-) and holes (h+) transfers.](image)

Figure 92. Energy levels of chromophores H,H-PDI, quaterthiophene 156 and terthiophene 151 HOMO (bold) and LUMO (dashed) of H,H-PDI (from ref. [37]) and thiophenes (from ref. [145] and [148]) together with HOMO of TEOA and work function of ITO (from ref. [189]), reported relative to -5.1 eV for Fe3+/Fe. Full arrow denotes electronic transition resulting from photoexcitation, half arrows illustrate subsequent electrons (e-) and holes (h+) transfers.

The dyad-aldehyde 157 was designed for the synthesis of triple-channel system 158 in a one-step procedure from the hydrazide-rich system 133 (Figure 93). In dyad 157 an oxime bond was used to bind together the quater- and terthiophene moieties. The terminal aldehyde served as a handle to bind the hydrazides in 133.
Figure 93. Synthesis of triple-channel photosystem 158 from single channels system 133. The grey bar represents an ITO surface.

3.5.1.1. Synthesis

Aldehyde 157 itself was prepared in a two-steps procedure from previously reported quaterthiophene ketal 156 and terthiophene aldehyde 149 (Scheme 10).[149, 207] The Alloc protecting group in 156 was removed by
Scheme 10. a) Pd(PPh$_3$)$_2$Cl$_2$, n-Bu$_3$SnH, AcOH 2. **149** (2 steps 6%); b) DCM, TFA (25%).

Hydrostannolysis using a palladium catalyst, then the liberated hydroxylamine was condensed with aldehyde **149** to afford a mixture of syn- and anti-**159**. Only the anti-isomer of the oxime could be isolated with sufficient purity. However, when anti-**159** was treated with TFA in DCM, it was converted into the aldehyde of opposite isomery syn-**157**, as revealed by NMR measurements. This was surprising because the anti-oxime is a more stable configuration than the syn-counterpart.$^{[213]}$ This observation suggested that the increasing steric hindrance associated with the interconversion from anti- to syn- was counterbalanced by favorable interactions between the aromatic ter- and quaterthiophene moieties, presumably by π-stacking. Nevertheless, significant
attractive interaction between these two electron-rich moieties was rather surprising. The anti- to syn- interconversion driven by \( \pi \)-stacking interaction had already been observed in a recently reported dyad with \( H,H \)-PDI and terthiophene chromophores linked with an oxime bond.\(^{148}\) However, in that case the interaction between the electron-poor \( H,H \)-PDI and electron rich terthiophene was stronger and of the donor-acceptor type.

3.5.1.2. Structural Characterization

Dyad-aldehyde \textit{syn}-157, as a 10 mM solution in DMSO/AcOH 9:1, v/v was tentatively installed in single-channel 133 to generate 158. Architecture 133 were incubated at 40°C in this solution and the templated stack exchange process was monitored by UV-Vis spectroscopy. For accurate quantification of TSE yield \( \eta_{\text{TSE}} \), the photosystems were ultimately dissolved in a denaturing mixture of DMSO, \( \beta \)-mercaptoethanol and \( \text{iPr}_2\text{NET} \) and ratiometric determination of \( H,H \)-PDI and thiophene contents was performed from absorption in diluted solution (see Experimental Section for details). In thin films \( (A_{543} < 0.8, \ d < 350 \ \text{nm}) \), yield of covalent capture was low at \( \eta_{\text{TSE}} = 49\% \). The yield decreased to \( \eta_{\text{TSE}} = 40\% \) with thicker films \( (A_{543} = 2.5, \ d = 1100 \ \text{nm}) \). Impossibility to obtain higher yields likely came from the steric demand associated with the bulky configuration of \textit{syn}-157. With such low \( \eta_{\text{TSE}} \) values, quantification of photoactivity was irrelevant. Moreover, decreasing \( \eta_{\text{TSE}} \) with increasing \( d \) impeded the preparation of thick architectures 158, which is of most interest to evaluate the benefits of triple-channel over double- and single-channel systems to prevent charge recombination processes. Moreover, the \textit{syn}-conformation would putatively impose a folded structure to 157, that would be incompatible with the formation of segregated triple-channel structure 158. Instead, a donor-acceptor-type superposition of ter- and quaterthiophenes would be promoted (Figure 94).
Figure 94. Putative inactive, folded (A) and active, linear (B) structures resulting from syn- and anti-isomers of the same dyad, respectively.

3.5.2. Triple-Channel System with Thiophene and Triphenylamine

To circumvent these shortcomings, we designed dyad 160, where terthiophene was replaced by triphenylamine in the terminal part (Figure 95). Several reasons directed this choice.
Figure 95. Synthesis of triple-channel photosystems 162 and 165 from single channels system 133. The grey bar represents an ITO surface.
First, the FMOs of pertinent triphenylamine derivative 161 were compatible with the formation of a redox gradient in a triad with \textit{H,H-PDI} and quaterthiophene (Figure 96). The respective HOMO and LUMO position of \textit{H,H-PDI}, quaterthiophene and triphenylamine implied that the photogenerated electrons and holes would be driven apart toward \textit{H,H-PDI} and triphenylamine stacks, respectively. This was in accordance with our initial goal of reducing charge recombination by increasing the distance between hole and electron transporting channels.

![Figure 96](image-url)

**Figure 96.** Energy levels of chromophores \textit{H,H-PDI}, quaterthiophene 156 and triphenylamine 161. HOMO (bold) and LUMO (dashed) of \textit{H,H-PDI} (from ref. [37]), hydrazone 161 (from ref. [110]) and quaterthiophene 156 (from ref.[145]) together with HOMO of TEOA and work function of ITO (from ref. [189]), reported relative to -5.1 eV for \textit{Fc}/\textit{Fc}. Full arrow denotes electronic transition resulting from photoexcitation, half arrows illustrate subsequent electrons (\(e^-\)) and holes (\(h^+\)) transfers.

Second, the propeller-shaped triphenylamine and the linear, planar quaterthiophene have distinct steric demand. This was envisioned to promote
both the formation of anti-160 over the sterically more demanding syn-160 and the segregation of the three channels in architecture 162 (Figure 95).

Third, triphenylamine stacks with exceptional hole transport properties had been previously reported and thus this motif was very appealing to build the hole transporting channel in our photosystem.\cite{88-91}

3.5.2.1. Synthesis

\[ \text{Scheme 11. a) 1. Pd(PPh₃)₂Cl₂, n-Bu₃SnH, AcOH, 2. 163 (2 steps 44%); b) DCM, TFA (6%).} \]

Preparation of dyad-aldehyde 160 was a straightforward, two-steps procedure from ketal 156 (Scheme 11). Alloc protecting group in 156 was removed by hydrostannolysis catalyzed by palladium (0) to afford a free hydroxylamine that was condensed with aldehyde 163.\cite{214} Ketel 164 was obtained as the anti-isomer, as proved by a characteristic peak on the ¹H NMR spectrum (δ = 8.02 ppm). Removal of the ketel protecting group with TFA in dichloromethane afforded aldehyde 160 in the anti-isomer as well. The exclusive formation of anti-oxime correlated well with the higher steric
demand of propeller-shaped triphenylamine as compared to the planarizable terthiophene in 157.

*anti*-160 was dissolved at a concentration of 20 mM in DMSO/AcOH 9:1 v/v for templated stack exchange with the hydrazide-rich architecture 133 (Figure 95). Proceeding of the reaction was monitored by UV-Vis spectroscopy and installation of dyad 160 in triple-channel architecture 162 was evidenced by the growth of a main signal at $\lambda = 420$ nm that corresponded to quaterthiophene absorption band, with a shoulder at $\lambda = 355$ nm due to the contribution of triphenylamine (Figure 97 A).

![Figure 97](image_url)

**Figure 97.** A) Normalized absorption spectra of single channel 133 before TSE (dotted line) and of triple-channel architecture 162 (solid line). In both cases, relative $A = 1$ at $\lambda = 505$ nm. B) Absorption spectra of propagator 114 (thin solid line, left axis) and of quaterthiophene 156 (dotted line, left axis), measured from diluted solutions in DMSO, together with the normalized absorption spectrum of dissolved triple-channel architecture 162 (bold line, right axis).

Stack exchange yields $\eta_{\text{TSE}}$ were determined from absorption spectroscopy. Ratios of *H,H*-PDI and quaterthiophenes chromophores were measured from diluted solutions, after denaturation of 162 with β-mercaptoethanol and dissolution in DMSO (Figure 97 B, see Experimental Section for details). $\eta_{\text{TSE}}$ proved to be almost quantitative over a $d$ range going from 40 to 470 nm (Table...
7). This was in contrast to the situation found previously with dyad syn-157, where TSE was inefficient, and suggested that the anti-160 adopted a conformation more favorable for in-depth diffusion into the hydrazide-rich 133.

**Table 7. Summary of stack exchange yields with architecture 162.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>PS $^a$</th>
<th>$d^b$ (nm)</th>
<th>$\eta_{TSE}^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>162</td>
<td>270</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>470</td>
<td>100</td>
</tr>
</tbody>
</table>

$^a$ Photosystems, see Figure 95. $^b$ Film thickness $d$ was approximated from H,H-PDI absorption assuming that $A_{543} = 0.1$ a.u. corresponds to $d \sim 44$ nm. $^c$ Stack-exchange yield, estimated from absorption spectra of the photosystems.

3.5.2.2. Functional Characterization

Photocurrent generation with triple-channel system 162 was tested under irradiation with a solar simulator and by using TEOA as a sacrificial hole acceptor. Constant short-circuit current densities $J_{SC}$ recorded under prolonged irradiation confirmed the photostability of the system under the applied conditions. However, current densities measured with triple-channel 162 were much lower than those obtained from single-channel 128 of similar thickness. In thin films, current was very weak ($J_{SC} = 2.5 \mu A cm^{-2}$ at $d = 40$ nm or $A_{543} = 0.09$) and decreased significantly with increasing $d$ (Figure 98). Although the number of datapoints was too low to accurately determine the critical thickness, $d_C < 100$ nm seems reasonable, which is three times lower than for single-channel system 128.
Figure 98. Dependence of the short-circuit current density $J_{SC}$ on the thickness $d$ for photosystems 128 (□), 162 (♦) and 165 (▲), upon irradiation with a solar simulator (83 mW cm$^{-2}$, 50 mM TEOA, 0.1 M Na$_2$SO$_4$, 0 V vs. Ag/AgCl). $d$ was approximated from $H.H$-PDI absorption assuming that $A_{345} = 0.1$ a. u. corresponds to $d \sim 44$ nm, pertinent values for bimolecular charge recombination efficiencies $\eta_{BR}$ (from dependence of $J_{SC}$ on $P_m$) and activation energy $E_a$ (from dependence of $J_{SC}$ on temperature) are indicated. Gray lines were added as visual guides.

To understand the poor performances of triple-channel system 162, we prepared double-channel architecture 165 from hydrazide-containing 133 and previously reported aldehyde 166$^{[149]}$ (Figure 95). Using aldehyde solutions at 25 mM in DMSO/AcOH 9:1, v/v stack exchange yields in the range $81\% < \eta_{TSE} < 100\%$ were obtained with thickness $114 < d < 555$ nm. Photocurrent generation with $H.H$-PDI-quaterthiophene system 165 was intermediate between single channel 128 and triple channel 162 over the explored range of $d$ (Figure 98). Critical thickness $d_C = 300$ nm was at best equal to the case of single-channel system 128.

Combination of $H.H$-PDI with quaterthiophenes in 162 and 165 was much less favorable that with terthiophenes in 150 (Table 8). From the the HOMO and LUMO levels of terthiophene, quaterthiophene and $H.H$-PDI, the driving force for both hole and electron injection between $H.H$-PDI and quaterthiophenes is expected to be lower than between $H.H$-PDI and terthiophenes (Figures 82 and 95).
Table 8. Summary of photosystems with thiophenes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>PS&lt;sup&gt;a&lt;/sup&gt;</th>
<th>d&lt;sup&gt;b&lt;/sup&gt; (nm)</th>
<th>η&lt;sub&gt;TSE&lt;/sub&gt; (%)</th>
<th>J&lt;sub&gt;SC&lt;/sub&gt; (µA cm&lt;sup&gt;-2&lt;/sup&gt;)</th>
<th>η&lt;sub&gt;BR&lt;/sub&gt; (%)</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>128</td>
<td>165</td>
<td>---</td>
<td>6.7</td>
<td>30</td>
<td>240</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>625</td>
<td>---</td>
<td>0.9</td>
<td>70</td>
<td>298</td>
</tr>
<tr>
<td>3</td>
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<td>100</td>
<td>quant.</td>
<td>5.2</td>
<td>31</td>
<td>169</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>940</td>
<td>quant.</td>
<td>12.5</td>
<td>29</td>
<td>177</td>
</tr>
<tr>
<td>5</td>
<td>162</td>
<td>270</td>
<td>95</td>
<td>2.5</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>470</td>
<td>quant.</td>
<td>0.9</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>7</td>
<td>165</td>
<td>114</td>
<td>quant.</td>
<td>4.9</td>
<td>44</td>
<td>270</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>555</td>
<td>81</td>
<td>0.9</td>
<td>54</td>
<td>296</td>
</tr>
</tbody>
</table>

<sup>a</sup> Photosystems. <sup>b</sup> Film thickness d was approximated from H,H-PDI absorption assuming that A<sub>543</sub> = 0.1 a.u. corresponds to d ~ 44 nm.

Accordingly, the poorer performances of 165 with quaterthiophenes as compared to 150 with terthiophenes would come from the less favorable charge transfer between the components. However, the HOMO and LUMO levels of triphenylamine lie even above those of terthiophene and thus should restore the charge-separation capability in triple-channel 162. Data suggested that this was not enough to confer high activity to this system. In a previous, independent study, a triple-channel photosystem with triphenylamine stacks displayed high bimolecular charge recombination, presumably resulting from poor π-stacking of these non-planar molecules. It is possible that the same effect resulted in the rapidly decreasing activity with increasing d observed for architecture 162.

In conclusion, the propeller-like shape of triphenylamines was beneficial at the synthesis stage because it promoted the formation of dyad anti-160. However, the non-planar shape was detrimental for function when implemented in architecture 162 as it prevented π–stacking and impeded the efficient transport of holes.
Chapter 4

PERSPECTIVES

Results from the present work showed that electron-transfer to \( H_H \)-PDI required sufficiently electron-rich partners. Terthiophenes performed well but quaterthiophenes were unsuited. Actually, \( H_H \)-PDI performed better as hole transporters, when combined with electron-deficient NDI\(s \). To restore the electron-transporting ability of central PDI stacks, the use of more electron deficient PDI derivative could be explored. In the present work, \( CN_2 \)-PDI with low electron density was used as structural and functional element in the initiator. Independent experiments have showed that the implementation of this electron-poor chromophore in a propagator with disulfides was unfruitful because the \( CN_2 \)-PDI core is incompatible with the basic catalysts used for SOSIP.\(^{[215]} \) However, preliminary studies in our group showed that monocyaano-PDI (\( CN \)-PDI) has lower-lying HOMO and LUMO energy levels as compared to \( H_H \)-PDI but nevertheless resists to organic bases. Photosystem 167 with central \( CN \)-PDI will potentially combine the appealing aggregation and light absorption properties of \( H_H \)-PDI with improved n-semiconductor properties resulting from the electron-attracting cyano group (Figure 99).
Figure 99. A) Schematic structure of proposed architecture 167 with CN$_2$-PDI and CN-PDI chromophores in the central stacks and quaterthiophenes in the lateral stacks, R = solubilizing chain. B) HOMO (bold) and LUMO (dashed) energy levels against vacuum of CN$_2$-PDI (red, from ref. [65]), CN-PDI (brown, from ref. [215]) and quaterthiophene (yellow, from ref. [145]) chromophores, determined from suitable derivatives thereof, reported relative to -5.1 eV for Fc$^+$/Fc.

In the work presented above, homogeneous central stacks were studied that contained either green or unsubstituted PDI. The combination of central H,H-PDI stacks and lateral electron-rich or electron-poor materials has led to formal “horizontal” redox gradients that could drive photogenerated holes and electrons apart. However, in this configuration, performance topped with double-channel systems as compared to less active single- or triple-channel architectures, thus limiting the possibilities to further increase the activity.
Therefore, further development of the project could instead focus on the installation of “vertical” redox gradients along the central PDI stacks.

Figure 100. A) Schematic structure of proposed architecture 168 with CN$_2$-PDI, CN-PDI and H,H-PDI chromophores in the central stacks and ter- and quaterthiophenes in the lateral stacks, R = solubilizing chain. B) HOMO (bold) and LUMO (dashed) energy levels against vacuum of CN$_2$-PDI (red, from ref. [65]), CN-PDI (brown, from ref. [215]), H,H-PDI (pink, from ref. [37]), quaterthiophene (yellow, from ref. [145]) and thriophene (orange, from ref. [148]) chromophores, determined from suitable derivatives thereof, reported relative to -5.1 eV for Fe$^3$/Fe$^2$.

In previous, independent studies, four-component systems with “vertical” redox gradients along both central and lateral stacks have been prepared. Such architectures are called “Oriented Multicolored Antiparallel Redox Gradients” supramolecular heterojunctions (OMARG SHJs) and extend the concept of more simple, two-component SHJs.$^{[6, 111]}$ These multicomponent systems maximize light collection, charge separation and transport. In particular,
installation of vertical redox gradients and formation of OMARGs have been shown to strongly reduce the recombination of photogenerated charge carriers. SOSIP and TSE can be used for the preparation of OMARGs, as it has been recently shown.\textsuperscript{144, 147}

In our single-channel architecture 128, there was already a formal redox gradient: the initiator monolayer binding the H\textsubscript{2}H\textsubscript{2}PDI stacks onto the ITO surface contains the electron deficient CN\textsubscript{2}-PDI chromophore that can inject holes into the H\textsubscript{2}H\textsubscript{2}PDI. In the proposed OMARG SHJ architecture 168, there are true antiparallel redox gradients for efficient hole and electron collection. Again, CN-PDI with intermediate HOMO and LUMO energy levels would be suited because it can inject holes into H\textsubscript{2}H\textsubscript{2}PDI and electrons into CN\textsubscript{2}-PDI (Figure 100). To prepare an OMARG photosystem with central PDI stack and vertical redox gradient, a modified CN-PDI propagator would be polymerized from the CN\textsubscript{2}-PDI monolayer on ITO until a certain thickness would be reached, then an additional layer of H\textsubscript{2}H\textsubscript{2}PDI propagator would be added by SOSIP of propagator 114.

In the lateral stacks, a co-axial vertical gradient of p-type semiconductors would be installed to drive holes toward a sacrificial hole acceptor, such as TEOA. The combination of terthiophene and H\textsubscript{2}H\textsubscript{2}PDI has shown good performance in the present work. Therefore terthiophenes could be used in the upper part of the gradient, where it would be placed next to H\textsubscript{2}H\textsubscript{2}PDI from the central stacks. One other p-type semiconductor that would efficiently inject electrons into CN-PDI would be selected to constitute the lower part of the gradient. Quaterthiophenes could be considered at this stage.
Chapter 5

EXPERIMENTAL SECTION

5.1. General

5.1.1. Reagents, Solvents and Equipment

Reagents for synthesis were purchased from Aldrich, Fluka or Acros, if not otherwise specified. Amino acid derivatives were from Novabiochem and Bachem. The coupling reagents $o$-((Benzotriazole-1-yl)-$N,N'N,N'$-tetramethyluronium hexafluorophosphate (HBTU), $o$-((Benzotriazole-1-yl)-$N,N'N',N'$-tetramethyluronium tetrafluoroborate (TBTU) and $o$-((7-Azabenzotriazol-1-yl)-$N,N'N',N'$-tetramethyluronium hexafluorophosphate (HATU) were from Apollo Scientific. TEOA was from Fluka. TFA, TEA, TFE, acetic acid and DMF were from Fluka or Aldrich. All buffers and salts were from Sigma or Fluka-Aldrich. Reactions were carried out under Ar or N$_2$ when specified, with magnetic stirring.

Solvents used for synthesis were of reagent or HPLC grade purity. Dry DMF used for synthesis was distilled over CaH$_2$. Other solvents such as toluene, tetrahydrofuran, diethyl ether, acetonitrile and dichloromethane were purified using a solvent purification system from Solv-tek. Analytical grade solvents and bidistilled water were used for cleaning and rinsing ITO electrodes as well as to prepare solutions for SAM formation and for SOSIP. Buffer solutions were prepared with bidistilled water.

Solvents were evaporated using a R-200 Rotavapor from Büchi, equipped with a vacuum controller PVK 610 from MLT Labortechnik AG or with a Vacuubrand MZ 2C model and heating bath from Büchi.
All glassware used for synthesis was washed with soap solution, water, and acetone and dried in air.

5.1.2. Chromatographic Methods

Column chromatography was carried out using silica gel 60 (40-63 µm) from Fluka or SiliCycle. Analytical thin-layer chromatography (TLC) was done using aluminium sheets (2 × 5 cm) coated with silica gel 60 F254 from Merck. Preparative thin layer chromatography (PTLC) was performed on glass plates (20 × 20 cm) coated with silica gel 60 F254 (1 mm) from Analtech or SiliCycle. Results are described in the text as follows: (retention factor \( R_f \) with eluent). UV-active compounds were detected with a UV-lamp from CAMAG at a wavelength \( \lambda = 254 \) or 366 nm. Amines were stained with ninhydrin (0.2% ninhydrin in ethanol) and poorly UV-active substances were detected either with a cesium-molybdenum reagent or with iodine staining.

5.1.3. Equipments for Compound Characterization

UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (20 °C), using quartz cells with a pathlength of either 1mm or 1 cm. Optical rotation measurements were carried out at RT on a Perkin-Elmer 241 Polarimeter using a sodium lamp (\( \lambda = 587 \) nm) in water thermostatized quartz cells of 10 cm length and are reported as \([\alpha]_D^{20}\) (c concentration in g/100 mL, solvent). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate) at RT and are reported as wavenumber \( \tilde{\nu} \) in cm\(^{-1}\) with band intensities indicated as w (weak), m (medium) or s (strong).

Melting points were measured on a heating table equipped with a microscope from Reicher (Austria) or on a melting point apparatus M-560 from Büchi and are reported in degrees Celsius as Mp.: temperature range °C. \(^1\)H and \(^{13}\)C\(^{1}\)H NMR spectra were recorded (as indicated) either on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and are reported as chemical shifts
(δ) in ppm relative to TMS (δ = 0) internal reference. Spin multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q) with coupling constants (J) given in Hz, or multiplet (m). Broad peaks are marked as broad (br). 1H and 13C{1H} resonances were assigned with the aid of additional informations from 1D and 2D NMR spectra (1H,1H-COSY, DEPT 135, HSQC and HMBC). Multiplicity of 13C{1H} signals are assigned with the aid of DEPT135, and reported as s (C), d (CH), t (CH2) and q (CH3). Multiplicity due to 13C-31P coupling is reported as p_d, p_t or p_m. ESI-MS (Electron Spray Ionization-Mass Spectroscopy) were performed on an ESI APX 150EX and are reported as m/z (%). Accurate mass determination using ESI (HR ESI-MS) were performed on a Scieq QSTAR Pulsar or Bruker Daltonics maXis mass spectrometer, MALDI-TOF on a Axima CFR’ (Shimadzu).

5.1.4. Equipments used During Experiments

Autoclavable micropipettes from Socorex (Switzerland), Brand (Germany) and Vaudaux-Eppendorf (Switzerland) calibrated for amount 0-10 µL, 10-100 µL, 100-1000 µL were used to prepare aqueous solutions or handle non-volatile solvents. Volatile solvents were dosed with gastight glass syringes from Hamilton (Bonaduz, Switzerland) equipped with steel needles.

pH values were determined using a Consort C832 multi-parameter analyzer equipped with a VWR glass membrane pH electrode. Calibration was done with Titrisol solutions from Merck at pH 4.00 and 7.00.

During activation of self-assembled monolayers with DTT and subsequent SOSIP, vials were shaken at RT on a Rotamax shaker (Heidolph). During hydrazone-oxime experiment and subsequent covalent capture of aldehydes, vials were shaken in an Incubating Mini Shaker (VWR).

Electrochemical measurements were done on an Electrochemical Analyzer with Picoamp booster and Faraday cage (CH Instruments 660C). Photocurrents were measured using a 150 W solar simulator (Newport) and an
Electrochemical Analyzer (CH Instruments 660C). The irradiation power was measured using a radiant power energy meter (Newport model 70260). Action spectra were measured upon excitation by monochromatic light (150 W Xe lamp with Oriel 1/8 m monochromator).

AFM images were acquired with a NanoScope IIIa (Veeco/ Digital Instruments, Santa Barbara, CA) multimode atomic force microscope using Si cantilevers (OMCL-AC160TS, Olympus).

5.2. Synthesis

5.2.1. Synthesis of Initiators

**Compound 89.** This compound was synthesized according to reported procedures.\(^\text{[60]}\)

**Compound 90.** This compound was synthesized according to reported procedures.\(^\text{[60]}\)
Compound (S,S)-91. A solution of 90 (0.150 g, 0.28 mmol) and H-Lys(Cbz)-NH₂ (0.315 g, 1.1 mmol) in pyridine (6 ml) was refluxed (130 °C) for 18 h under Ar. H-Lys(Cbz)-NH₂ (0.08 g, 0.28 mmol) was added and the mixture was further heated at reflux for 1 h. The reaction was then allowed to cool down and carefully poured on 80 ml of 1 M KHSO₄. The aqueous layer was extracted with AcOEt (4 x 50 ml) and the organic layer dried over anhydrous Na₂SO₄, then concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 95:5; R_f 0.1 with DCM/MeOH 95:5) gave pure 91 (0.161 g, 55%) as a green solid. Mp: 154-155 °C; CD (DCM/MeOH 1:1): 709 (+0.56), 432 (-0.91), 339 (+2.60), 283 (-1.59), 26 (-0.42); IR: 3347 (w), 2931 (w), 1685 (s), 1590 (m), 1512 (w), 1415 (m), 1343 (m), 1243 (m), 1126 (w), 735 (w); ¹H NMR (500 MHz, CDCl₃): 8.45-8.40 (m, 2H), 8.22 (s, 2H), 7.49-7.44 (m, 2H), 7.31-7.23 (m, 10H), 6.23-6.15 (m, 1H), 5.73-5.69 (m, 2H), 5.07-5.04 (m, 2H), 5.02-4.97 (m, 4H), 3.85-3.75 (m, 2H), 3.45-3.31 (m, 2H), 3.15-3.00 (m, 4H), 2.38-2.30 (m, 2H), 2.14-2.01 (m, 8H), 1.72-1.64 (m, 2H), 1.60-1.45 (m, 4H), 1.41-1.31 (m, 2H), 1.23-1.15 (m, 2H); ¹³C{¹H} NMR (125 MHz, CDCl₃): 172.4 (s), 164.8 (s), 163.1 (s), 156.4 (s), 146.5 (s), 136.6 (s), 133.3 (s), 129.1 (s), 128.5 (s), 128.0 (s), 126.5 (d), 125.1 (d), 121.7 (s), 121.5 (d), 120.8 (s), 118.5 (s), 117.7 (s), 66.5 (t), 54.48 (d), 53.5 (t), 50.73 (t), 40.8 (t), 29.7 (t), 28.3 (t), 25.8 (t), 23.7 (t); MS (ESI, DCM): 791 (100, [M+H]^+); HRMS (ESI, +ve) calcd for C₆₀H₆₁N₆O₁₀: 1053.4505, found: 1053.4493.

Compound (S,S)-93. A solution of 91 (50 mg, 0.05 mmol), HBr (5.7 M in AcOH, 25 µl, 0.14 mmol), thioanisole (15 mg, 0.10 mmol) and pentamethylbenzene (7 mg, 0.05 mmol) in TFA (680 µl) was stirred for 3 h at RT. The mixture was concentrated in vacuo, and washed with diethylether
(solid-liquid extraction). HCl (1 M in H₂O, 1 ml) was added to the residue and the mixture was concentrated in vacuo. To the residue was added the mixture of Boc-Cys(S-\textit{t}-Bu)-OH (60 mg, 0.19 mmol), TBTU (60 mg, 0.19 mmol), HOBt (25 mg, 0.19 mmol) and 2,4,6-collidine (24 µl, 0.19 mmol) in DMF (600 µl). The pH of the solution was adjusted to about 8 by the addition of more collidine. The resulting mixture was stirred for 1.5 h at RT under Ar, diluted with EtOAc, washed successively with 1 M HCl, brine, saturated NaHCO₃ aqueous solution, and brine, dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 95:5; \( R_f \) 0.5 with DCM/MeOH 9:1) gave pure 93 (39 mg, 60%) as a green solid. Mp: 170-171 °C; CD (DCM): 731 (-0.38), 676 (+0.33), 560 (-0.45), 445 (+0.68), 350 (-0.43), 320 (+0.55); IR: 3345 (w), 2959 (w), 2456 (w), 1688 (s), 1647 (s), 1591 (m), 1456 (m), 1416 (m), 1343 (m), 1244 (m), 1167 (m); \(^1\)H NMR (400 MHz, CDCl₃): 8.37 (d, \(^3\)J (H,H) = 8.0 Hz, 2H), 8.17 (s, 2H), 7.44 (d, \(^3\)J (H,H) = 8.0 Hz, 2H), 6.49 (s, 2H), 5.99 (br s, 2H), 5.69-5.63 (m, 2H), 5.42-5.37 (m, 2H), 4.32-4.26 (m, 2H), 3.79-3.73 (m, 2H), 3.49-3.39 (m, 2H), 3.18-3.06 (m, 4H), 3.02-2.94 (m, 4H), 2.37-2.25 (m, 2H), 2.17-1.95 (m, 8H), 1.67-1.57 (m, 4H), 1.41 (s, 18H), 1.28 (s, 18H), 1.20-1.10 (m, 4H); \(^{13}\)C\{\(^1\)H\} NMR (125 MHz, CDCl₃): 172.3 (s), 170.4 (s), 164.7 (s), 163.3 (s), 155.5 (2), 146.6 (s), 133.5 (s), 129.3 (s), 126.6 (d), 125.0 (d), 121.8 (s), 121.5 (d), 120.9 (s), 118.5 (s), 117.8 (s), 80.5 (s), 54.5 (s), 53.3 (t), 51.1 (t), 48.4 (s), 42.6 (t), 39.4 (t), 29.9 (q), 29.3 (t), 28.5 (t), 28.4 (q), 25.9 (t), 23.8 (t); MS (ESI, DCM/MeOH 9:1): 1368 (50, [M+H]+), 1268 (100, [M+H-Boc]+), 1168 (50, [M+H-2Boc]+), 684 (25, [M+2H]+), 584 (50, [M+2H-
2Boc); HRMS (ESI, +ve) calcd for C_{68}H_{70}N_{16}O_{12}S_{4}: 1367.5695, found: 1367.5685.

**Compound 94.** This compound was synthesized according to reported procedures.[216]

**Compound (S,S)-95.** A solution of 93 (47 mg, 34 µmol) in TFA (1 ml) and DCM (1 ml) was stirred for 2 h at RT under Ar. The mixture was concentrated in vacuo, then redissolved in MeOH (1 ml) and HCl (1 M, 300 µl) and concentrated in vacuo. To the residue was added the mixture of 94 (80 mg, 0.14 mmol), TBTU (44 mg, 0.14 mmol) and 2,4,6-collidine (55 µl, 0.41 mmol) in DMF (0.33 ml) and DCM (0.33 ml). The resulting mixture was stirred for 1.5 h at RT, diluted with DCM, washed successively with 1 M aqueous KHSO_{4}, brine, saturated NaHCO_{3} aqueous solution, and brine, dried over Na_{2}SO_{4}, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 95:5; R_{f} 0.41 with DCM/MeOH 9:1) afforded pure 95 (40 mg, 50%) as a green solid. Mp: 89-90 °C; CD (DCM/MeOH 1:1): 707 (-0.37), 679 (-0.39), 554 (+0.24), 484 (-0.08), 444 (+0.36), 369 (+0.25), 345 (-0.01), 325 (+0.27); IR: 3310 (w), 2923 (m), 2853 (m), 1682 (s), 1655 (s), 1590 (m), 1455 (m), 1415 (m), 1341 (m), 1244 (s), 996 (s), 866 (w), 735 (m), 697
(m); $^1$H NMR (400 MHz, CDCl$_3$): 8.34 (d, $^3$J(H,H) = 8.0 Hz, 2H), 8.25 (br s, 2H), 7.65-7.60 (m, NH), 7.51-7.44 (m, 2H), 7.27-7.2 (m, 40H), 6.55 (br s, NH), 5.70-5.60 (m, 2H), 5.04-4.89 (m, 16H), 4.70-4.60 (m, 2H), 3.68-3.53 (m, 8H), 3.36-3.34 (m, 2H), 3.20-3.10 (m, 4H), 3.10-3.00 (m, 4H), 2.80-2.62 (m, 4H), 2.40-2.25 (m, 2H), 2.22-2.07 (m, 2H), 2.05-1.70 (m, 8H), 1.60-1.45 (m, 4H), 1.42-1.32 (m, 2H), 1.28 (s, 20H); $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): 172.3 (s), 169.8 (s), 164.5 (s), 163.4 (s), 146.6 (s), 146.6 (s), 135.9 (s), 133.7 (s), 129.4 (s), 128.5 (d), 126.7 (d), 124.6 (d), 121.9 (s), 121.4 (d), 121.0 (s), 118.5 (s), 117.8 (s), 68.7-68.2 (t, $^3$J = 13 Hz), 32.4 (t), 29.9 (q), 28.8 (t), 28.4 (t), 25.8 (t), 24.1 (t); MS (ESI, DCM): 2321 (24, [M+H]$^+$), 2302 (16, [M+H-NH$_3$]$^+$), 1183 (45, [M+2Na]$^{2+}$), 1171 (18, [M+H+Na]$^{2+}$), 1160 (100, [M+2H]$^{2+}$); HRMS (ESI, +ve) calcd for C$_{120}$H$_{135}$N$_8$O$_{22}$P$_4$S$_4$: 2319.7580, found: 2319.7570.

**Compound (S,S)-88.** To a solution of 95 (17 mg, 7 µmol) in DCM (440 µl) was added TMSBr (15 µl, 0.11 mmol). The mixture was stirred for 2 h under Ar at RT, and then concentrated in vacuo. To the residue was added MeOH (560 µl), and the resulting mixture was stirred for 0.5 h. The reaction mixture was concentrated in vacuo. The non-polar impurities were removed from the residue by solid-liquid extraction using diethyl ether (5 x 5 ml), petroleum ether (3 x 5 ml) and DCM (3 x 5 ml) to leave pure 88 as a green solid (12 mg, quant). Mp:
>230 °C; CD (DMSO/MeOH 1:1): 679 (+1.36), 478 (+0.31), 421 (-0.83), 342 (+3.68), 290 (-1.51); IR: 3233 (m), 2925 (w), 2857 (w), 1641 (s), 1587 (s), 1552 (s), 1416 (m), 1337 (m), 1233 (m), 1165 (m), 1122 (m), 998 (s), 910 (s), 803 (w), 749 (w); 'H NMR (400 MHz, CD_3OD): 8.32-8.20 (m, 4H), 7.47 (br s, 2H), 5.71-5.65 (m, 2H), 4.54-4.49 (m, 2H), 3.73-3.64 (m, 8H), 3.17-2.81 (m, 14H), 2.34-2.25 (m, 4H), 2.03-1.83 (m, 8H), 1.65-1.58 (m, 4H), 1.43-1.29 (m, 4H), 1.20 (s, 18H); ^13C{^1H} NMR (125 MHz, CD_3OD): 175.3 (s), 173.3 (s), 172.2 (s), 165.6 (s), 165.3 (s), 147.7 (s), 135.3(s), 130.8 (s), 127.9 (d), 125.2 (d), 123.2 (s), 122.4 (s), 122.1 (d), 119.7 (s), 118.8 (s), 55.5 (d), 54.7 (d), 42.6 (t), 40.3 (t), 35.7 (d, ^3J(C,P) = 130 Hz), 32.9 (t), 30.2 (q), 29.9 (t), 29.4 (t), 26.7 (t), 25.0 (t); MS (MALDI) 1598 (60, [M+H]^+), 1582 (100, [M-NH_2]^+).

**Compound (S,S)-106.** A solution of PDA 14 (25 mg, 0.064 mmol) and H-Lys(Cbz)-NH_2 (105 mg, 0.38 mmol) in pyridine (3.4 ml) was refluxed (120 °C) for 24 h. The reaction was then allowed to cool down and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 92:8; R_f 0.55 with DCM/MeOH 9:1) gave pure 106 (43 mg, 74%) as a red solid. Mp: >230 °C; CD (DCM/MeOH 1:1): 542 (-0.75), 522 (-0.62), 496 (+0.07), 482 (-0.24), 350 (+0.27), 294 (-0.46), 265 (+0.44); IR: 2932 (w), 2849 (w), 2476 (w), 1674 (s), 1595 (w), 1437 (m), 1361 (w), 1258 (w), 1163 (w), 1044 (w), 743 (w); ^1H NMR (300 MHz, CDCl_3/CD_3OD 1:1): 8.16 (d, ^3J(H,H) = 9.0 Hz, 4H), 7.85 (d, ^3J(H,H) = 9.0 Hz, 4H), 7.27-7.13 (m, 10H), 5.64-5.55 (m, 2H), 4.89 (s, 4H), 3.14 (t, ^3J(H,H) = 7.0 Hz, 4H), 2.34-2.22 (m, 4H), 1.67-1.57 (m, 4H), 1.50-1.35 (m, 4H); ^13C{^1H} NMR (125 MHz, CDCl_3/CD_3OD 1:1): 173.5 (s), 163.7 (s), 157.9 (s), 137.2 (s), 134.2 (s), 131.7 (d), 129.0 (s), 128.8 (d), 128.3 (d), 128.1 (d), 125.5 (s), 123.6 (d), 122.7 (s), 66.8 (t), 55.2 (d), 41.0 (t), 29.9 (t), 191
28.7 (t), 24.5 (t); MS (ESI, DCM/MeOH 1:1): 938 (100, [M+Na]+), 915 (10, [M+H]+), 898 (20, [M-NH3]+); HRMS (ESI, +ve) calcd for C_{52}H_{46}N_{6}NaO_{10}: 937.3168, found: 937.3161.

**Compound (R,R,S,S)-107.** A solution of 106 (50 mg, 0.05 mmol), HBr (5.7 M in AcOH, 30 µl, 0.05 mmol), thioanisole (7 mg, 0.05 mmol) and pentamethylbenzene (8 mg, 0.05 mmol) in TFA (820 µl) was stirred for 1 h at RT. The mixture was concentrated in vacuo, and washed with diethylether (solid-liquid extraction). HCl (1 M in H_{2}O, 1 ml) was added to the residue and the mixture was concentrated in vacuo. To the residue was added the mixture of Boc-Cys(S-t-Bu)-OH (67 mg, 0.22 mmol), TBTU (70 mg, 0.22 mmol), HOBt (34 mg, 0.22 mmol) and 2,4,6-collidine (28 µl, 0.22 mmol) in DMF (365 µl) and DCM (365 µl). The resulting mixture was stirred for 1 h at RT under Ar, diluted with EtOAc, washed successively with 1 M HCl, brine, saturated NaHCO_{3} aqueous solution, and brine, dried over Na_{2}SO_{4}, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 92:8; R_{f} 0.4 with DCM/MeOH 9:1) gave pure 107 (36 mg, 55%) as a red solid. Mp: 160-161 °C; CD (DCM): 554 (-3.13), 492 (+4.36), 381 (+0.42), 354 (+0.72), 319 (+0.97), 290 (+0.52), 272 (+1.26); IR: 3378 (w), 2962 (w), 2924 (w), 2473 (w), 1696 (s), 1646 (s), 1592 (w), 1434 (m), 1401 (m), 1362 (s), 1258 (s), 1164 (s), 1093 (s), 1019 (s), 861 (m), 746 (m); ^{1}H NMR (400 MHz, CDCl_{3}/CD_{3}OD 1:1): 8.13-8.07 (m, 4H), 7.85-7.75 (m, 4H), 5.59-5.53 (m, 2H), 4.30-4.26 (m, 2H), 3.26-3.20 (m, 4H), 3.05-2.98 (m, 2H), 2.93-2.86 (m, 2H), 2.39-2.29 (m, 2H), 2.25-2.15 (m, 2H), 1.70-1.60 (m, 4H), 1.40 (s, 22H), 1.26 (s,
1H) \(^{13}\)C\(^{1}\)H NMR (125 MHz, CDCl\(_3/\)CD\(_3\)OD 1:1): 172.5 (s), 170.8 (s), 162.6 (s), 155.6 (s), 133.2 (s), 130.7 (d), 128.0 (s), 124.5 (s), 122.6 (d), 121.8 (s), 79.7 (s), 54.2 (d), 47.5 (s), 42.2 (t), 38.9 (q), 29.0 (q), 28.5 (t), 27.9 (t), 27.6 (q), 23.69 (t); MS (ESI, DCM/MeOH 1:1): 1251 (100, [M+Na]+), 1229 (10, [M+H]+), 1211 (20, [M-NH\(_2\)]+); HRMS (ESI, +ve) calcd for C\(_{60}\)H\(_{78}\)N\(_8\)Na\(_2\)O\(_{12}\)S\(_4\): 637.2125, found: 637.2123.

**Compound (R,R,S,S)-108.**

A solution of \(107\) (32 mg, 26 \(\mu\)mol) in TFA (0.55 ml) and DCM (0.55 ml) was stirred for 2 h at RT under Ar. The mixture was concentrated *in vacuo*, then redissolved in MeOH (1 ml) and HCl (1 M, 0.5 ml) and concentrated *in vacuo*. To the residue was added the mixture of \(103\) (62 mg, 0.10 mmol), TBTU (33 mg, 0.10 mmol) and 2,4,6-collidine (30 \(\mu\)l, 0.23 mmol) in DMF (0.65 ml). The resulting mixture was stirred for 1 h at RT, then 2,3,6-collidine (30 \(\mu\)l, 0.23 mmol) was added and the resulting mixture stirred for 1 h more. It was then diluted with EtOAc, washed successively with 1 M aqueous HCl, brine, saturated NaHCO\(_3\) aqueous solution, and brine, dried over Na\(_2\)SO\(_4\) and concentrated *in vacuo*. Silica gel column chromatography of the residue (DCM/MeOH 93:7; \(R_f\) 0.37 with DCM/MeOH 93:7) afforded pure \(108\) (40 mg, 71%) as a red solid. Mp: 114-115 ºC; CD (CHCl\(_3\)): 554 (-11.14), 493 (+12.87), 382 (-2.03), 360 (+0.53), 322 (-2.22), 300 (+0.29), 271 (-7.2), 257 (-4.10); IR: 3391 (s), 1656 (m), 1591 (m), 1403 (w), 1343 (w), 1250 (w), 998...
(w), 741 (w), 697 (w); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}/CD\textsubscript{3}OD 1:1): 8.45 (d, \textsuperscript{3}J(H,H) = 8.0 Hz, 4H), 8.31 (d, \textsuperscript{3}J(H,H) = 8.0 Hz, 4H), 7.22-7.17 (m, 40H), 5.62-5.57 (m, 2H), 4.95-4.85 (m, 16H), 4.56-4.51 (m, 2H), 3.39-3.31 (m, 2H), 3.12-3.04 (m, 6H), 2.92-2.85 (m, 2H), 2.75-2.71 (m, 4H), 2.26-2.18 (m, 4H), 1.55-1.50 (m, 4H), 1.41-1.32 (m, 2H), 1.23 (s, 20H); \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (125 MHz, CDCl\textsubscript{3}/CD\textsubscript{3}OD 1:1): 171.9 (s), 169.3 (s), 169.2 (s), 169.1 (s), 162.5 (s), 134.7 (s), 133.6 (s), 130.7 (d), 128.2 (s), 127.7 (d), 127.2 (d), 127.0 (d), 125.0 (s), 122.5 (d), 121.8 (s), 67.7-67.5 (t, \textsuperscript{3}P), 53.7 (d), 52.4 (d), 40.9 (t), 38.3 (t), 31.9 (d, \textsuperscript{3}J(C,P) = 136 Hz), 30.5 (t), 28.8 (q), 27.7 (t), 27.2 (t), 22.9 (t); MS (ESI): 2199 (31, [M+NH\textsubscript{4}\textsuperscript{+}], 2182 (9, [M+H]\textsuperscript{+}), 1473 (69, [2M+3NH\textsubscript{4}\textsuperscript{+}]), 1466 (28, [2M+H+2NH\textsubscript{4}\textsuperscript{+}]), 1109 (84, [M+2NH\textsubscript{4}\textsuperscript{+}]), 1101 (31, [M+H+Na]\textsuperscript{2+}), 1092 (100, [M+2H]\textsuperscript{2+}); HRMS (ESI, +ve) calcd for C\textsubscript{112}H\textsubscript{120}N\textsubscript{8}Na\textsubscript{2}O\textsubscript{22}P\textsubscript{4}S\textsubscript{4}: 1113.3067, found: 1113.3061.

**Compound (R,R,S,S)-104.** To a solution of \textbf{108} (60 mg, 27 \textmu mol) in DCM (1630 \textmu l) was added TMSBr (54 \textmu l, 0.41 mmol). The mixture was stirred for 2 h under Ar at RT, and then concentrated in \textit{vacuo}. To the residue was added MeOH (1080 \textmu l), and the resulting mixture was stirred for 0.5 h. The reaction mixture was concentrated in \textit{vacuo}. The non-polar impurities were removed from the residue by solid-liquid extraction using diethyl ether (3 x 5 ml) and DCM (3 x 5 ml) to leave pure \textbf{104} as a red solid (40 mg, quant). Mp: >230 ºC;
CD (DMSO): 549 (-9.49), 492 (+10.04), 381 (-1.08), 352 (+2.66), 276 (-3.66), 259 (-0.06); IR: 3295 (w), 2925 (w), 2865 (w), 1694 (m), 1648 (w), 1592 (w), 1436 (w), 1402 (w), 1342 (m), 1270 (m), 1129 (m), 998 (m), 911 (m), 808 (w), 746 (w); 1H NMR (300 MHz, DMSO-d$_6$): 8.92 (d, $^3$J(H,H) = 8.0 Hz, 4H), 8.56 (d, $^3$J(H,H) = 8.0 Hz, 4H), 8.34-8.29 (m, 2H), 8.18 (s, 2H), 7.45 (s, 2H), 6.98 (s, 2H), 5.43-5.35 (m, 2H), 4.33-4.26 (m, 2H), 3.17-3.15 (m, 2H), 3.05-2.85 (m, 6H), 2.60-2.50 (m, 2H), 2.30-2.19 (m, 2H), 2.12-1.98 (m, 2H), 1.47-1.33 (m, 4H), 1.18 (s, 22 H); 13C{1H} NMR (125 MHz, DMSO-d$_6$): 170.7 (s), 169.4 (s), 162.8 (s), 134.0 (s), 131.0 (d), 128.8 (s), 125.6 (s), 124.0 (d), 123.0 (s), 54.0 (d), 52.5 (d), 47.4 (s), 41.5 (t), 38.6 (t), 34.8 (d, $^3$J(C,P) = 127 Hz), 31.7 (t), 29.5 (q), 28.8 (t), 27.5 (t), 23.6 (t).

Compound 115. This compound was synthesized according to reported procedures.$^{[64]}$

Compound (S,S)-116. A solution of 115 (200 mg, 0.37 mmol) and H-Lys(Cbz)-OH (218 mg, 0.78 mmol) in NMP (50 mL) and AcOH (2 mL) was stirred at 75 °C for 24 h. The mixture was then allowed to cool down to RT and pH adjusted to 1 upon addition of concentrated HCl. The resulting solution was poured into water (50 mL) and a red precipitate formed that was collected by filtration. Silica gel column chromatography of the residue (DCM/MeOH/AcOH 50:1:1, $R_f$ 0.1 with DCM/MeOH/AcOH 50:1:1) gave 116 (210 mg, 87%) as a red solid. Mp: > 200 °C; CD (DCM): 565 (-2.74), 538 (+0.35), 531 (-0.56), 503 (+0.87), 459 (-0.70), 355 (+0.77); IR: 2932 (w), 1698...
(s), 1658 (s), 1590 (s), 1332 (m), 1238 (s), 1144 (m), 741 (m), 692 (m); \(^1\)H NMR (400 MHz, acetone-\(d_6\)): 9.30 (d, \(^3\)J(H,H) = 8.2 Hz, 2H), 8.71 (s, 2H), 8.60 (d, \(^3\)J(H,H) = 8.2 Hz, 2H), 7.17 (s, 10H), 6.26 (s, br, 2H), 5.85 – 5.65 (m, 2H), 4.87 (s, 4H), 3.17 (s, br, 4H), 2.39 (s, br, 4H), 1.75 – 1.48 (m, 8H); \(^{13}\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)/CD\(_3\)OD 1:1): 171.8 (s), 162.8 (s), 162.3 (s), 157.0 (s), 138.3 (d), 136.5 (s), 133.1 (s), 133.0 (s), 130.4 (d), 129.1 (s), 128.6 (d), 128.2 (d), 127.8 (d), 127.6 (d), 127.1 (s), 122.7 (s), 122.3 (s), 120.8 (s), 66.3 (t), 53.6 (d), 40.4 (t), 29.3 (t), 28.3 (t), 23.6 (t); MS (ESI, +ve): 1098 (100, [M+Na]\(^+\)).

**Compound (S,S)-117.** A solution of 116 (108 mg, 101 \(\mu\)mol), Zn(CN)\(_2\) (77 mg, 664 \(\mu\)mol), 1,1’-bis(diphenylphosphino)ferrocene (1 mg, 2 \(\mu\)mol) and tris(dibenzylideneacetone) dipalladium (2 mg, 2 \(\mu\)mol) were refluxed in \(p\)-dioxane (2 mL) for 19 h under \(N_2\) atmosphere. The crude mixture was diluted with chloroform, filtered through a celite pad and volatile removed in vacuo. Silica gel column chromatography of the residue (DCM/MeOH/AcOH 50:1:1, \(R_f\) 0.4 with DCM/MeOH/AcOH 50:1:1) gave pure 117 (90 mg, 90%) as a red solid. Mp: 110.5-111.5 \(^\circ\)C; CD (DCM/MeOH 1:1): 542 (+0.25), 509 (+0.06), 483 (-0.06), 389 (+0.05), 309 (-0.05); IR: 3371 (m), 2939 (m), 2604 (w), 1703 (s), 1663 (s), 1599 (s), 1531 (m), 1409 (s), 1335 (s), 1251 (s), 1071 (m), 812 (w), 700 (w); \(^1\)H NMR (400 MHz, CDCl\(_3\)/CD\(_3\)OD 1:1): 9.61-9.44 (m, 2H), 8.94-8.61 (m, 4H), 7.24-6.95 (m, 2H), 5.66-5.77 (m, 2H), 4.76 (s, 4H), 3.10-2.97 (m, 4H), 2.37-2.14 (m, 4H), 1.62-1.16 (m, 8H); \(^{13}\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)/CD\(_3\)OD 1:1): 163.0 (s), 162.6 (s), 137.6 (s), 136.9 (d), 134.2 (d), 130.5 (s), 129.7 (d), 129.0 (d), 124.4 (d), 128.0 (d), 125.4 (s), 119.8 (s), 66.8 (t), 54.7 (d), 41.0 (t), 30.1 (t), 29.0 (t), 24.3 (t); MS (ESI, +ve): 967 (10, [M+H]\(^+\)).
Compound (S,S)-118. To a mixture of 117 (800 mg, 0.828 mmol) and dry DCM (49 ml) stirred at 0 °C under Ar was added EDCI (640 mg, 3.31 mmol) and BocNHNH₂ (440 mg, 3.31 mmol). After 25 minutes of stirring, the mixture was allowed to reach RT. After 25 additional minutes of stirring, the mixture was concentrated in vacuo. Silica gel column chromatography of the residue (DCM/acetone 3/1; Rf 0.33 with DCM/MeOH 93:7) gave pure 118 (644 mg, 65%) as a red solid. Mp: >200 °C; CD (DCM): 522 (+0.79), 503 (-0.05), 488 (+0.64), 334 (-0.85); IR: 2931 (w), 1698 (s), 1658 (s), 1588 (m), 1530 (w), 1390 (s), 1332 (m), 1239 (m), 1295 (s), 1239 (m), 1207 (m), 1103 (s), 831 (s), 68.1 (t), 55.8 (d), 42.2 (t), 31.5 (s), 31.1 (t), 29.4 (q), 29.1 (t), 25.2 (t); MS (ESI, +ve): 1195 (100, [M+H]+).

Compound (R,R,S,S)-119. A suspension of 118 (640 mg, 0.536 mmol), acetic acid (500 µl) and Pd-C (1.1 g) in methanol (18 ml) was stirred under hydrogen atmosphere for 100 min at RT. The mixture was filtered through a celite pad,
the blue-violet filtrate was bubbled with air for 1h at RT until color turned to dark red and then concentrated in vacuo. To the residue was added a solution of Fmoc-Cys(S-t-Bu)-OH (1.15 g, 2.67 mmol), HBTU (2.15 g, 5.67 mmol), HOBT (330 mg, 2.14 mmol), TEA (40 µl) and 2, 4, 6-collidine (350 µl, 2.67 mmol) in DMF (12 ml). The mixture was stirred under Ar for 1h at RT, then diluted with AcOEt, washed successively with 1M HCl, brine, sat. NaHCO₃ aq., and brine, dried over Na₂SO₄ and concentrated in vacuo. Column chromatography of the residue (DCM/acetone 3/1; Rf 0.73 with DCM/MeOH 95/5) gave pure 121 (200 mg, 21%) as a red solid. Mp: >200 ºC; CD (DCM): 542 (+0.37), 491 (-0.79), 356 (+0.96), 324 (-1.28); IR: 2932 (w), 1698 (s), 1658 (s), 1588 (m), 1529 (w), 1390 (s), 1332 (m), 1239 (s), 1044 (m), 740 (s); ¹H NMR (300 MHz, CDCl₃/CD₃OD 3:1): 9.33 (d, 3J(H,H) = 7.8 Hz, 2H), 8.69 (s, 2H), 7.55-7.44 (m, 4H), 7.37-7.28 (m, 4H), 7.20-7.09 (m 4H), 4.31-4.20 (m, 2H), 4.10-4.00 (m, 2H), 3.93-3.81 (m, 2H), 3.71-3.61 (m, 2H), 3.28-3.15 (m, 4H), 3.06-2.96 (m, 2H), 2.95-2.90 (m, 2H), 2.43-2.33 (m, 4H), 1.67-1.56 (m, 4H), 1.49-1.40 (m, 4H), 1.30 (s, 18H), 1.23 (s, 18H); ¹³C{¹H} NMR (100 MHz, CDCl₃/CD₃OD 1:1): 170.7 (s), 162.4 (s), 162.0 (s), 156.1 (s), 143.5 (s), 140.8 (s), 136.2 (d), 133.6 (d), 132.1 (s), 131.8 (s), 129.5 (s), 128.5 (d), 127.6 (d), 127.0 (d), 126.5 (s), 124.7 (d), 124.0 (s), 123.5 (s), 123.0 (s), 119.8 (d), 118.9 (s), 108.2 (s), 81.3 (s), 66.8 (t), 54.7 (d), 52.4 (d), 48.1 (s), 46.8 (d), 42.1 (t), 39.1 (t), 29.4 (q), 28.3 (t), 27.6 (q), 27.2 (t), 23.2 (t); MS (ESI, +ve): 1776 (20, [M+Na⁺]), 1554 (100, [M–2Boc+H]⁺), 1521 (50, [M+H–2Boc–N₂H₄]⁺).
To a solution of \textbf{119} (200 mg, 0.114 mmol) in DMF (4.9 ml) was added TBAF (1M in THF, 800 µl, 0.799 mmol) and the resulting blue solution was stirred under Ar for 2h at RT. The crude mixture was then diluted with THF and washed twice with brine, dried over Na$_2$SO$_4$ and concentrated \textit{in vacuo}. To the residue was added a solution of \textbf{94} (340 mg, 0.57 mmol), HBTU (520 mg, 1.37 mmol), HOBt (100 mg, 0.57 mmol) and TEA (190 µl, 1.37 mmol) in DMF (12 ml). The mixture was stirred under Ar for 30 min at RT, then diluted with AcOEt, washed successively with 1M HCl, brine, sat. NaHCO$_3$ aq. and brine, dried over Na$_2$SO$_4$ and concentrated \textit{in vacuo}. Column chromatography of the residue (DCM/MeOH 95/5, $R_f$ 0.8 with DCM/MeOH 9/1) and then PTLC (DCM/acetone/AcOH 4/1/0.1, at least three elution rounds) afforded pure \textbf{120} (90mg, 32%) as a red solid. Mp: 129-130 ºC; CD (CHCl$_3$/MeOH 1:1): 622 (-0.14), 550 (+0.21), 522 (+0.35), 478 (+0.16), 332 (-0.43); IR: 3310 (m), 2941 (m), 2831 (w), 1714 (m), 1708 (m), 1666 (s), 1599 (w), 1546 (m), 1455 (w), 1366 (s), 1244 (s), 1093 (s), 813 (w), 734 (m); $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 3:1): 9.60 (d, $^3$J(H,H) = 7.8 Hz, 2H), 8.88 (s, 2H), 8.80 (d, $^3$J = 7.8 Hz, 2H), 7.29-7.15 (m, 40H), 5.73-5.67 (m, 2H), 5.04-4.82 (m, 16H), 4.53 (dd, $^3$J(H,H) = 8.0 Hz, $^3$J(H,H) = 13Hz, 2H), 3.39 (dt, $^3$J(H,P) = 8.5 Hz, $^3$J(H,P) = 24 Hz, 2H), 3.16-3.04 (m, 4H), 2.90 (dd, $^3$J(H,H) = 13 Hz, $^3$J(H,H) = 8.0 Hz, 4H), 2.80-2.65 (m, 4H), 2.40-2.30 (m, 2H), 2.25-2.15 (m, 2H), 1.56 (q, $^3$J(H,H) = 8.0 Hz, 4H), 1.45-1.35 (m, 22H), 1.22 (s, 9H), 1.18 (s, 9H), 1.14 (s, 9H), 1.13 (s, 9H), 1.12 (s, 9H).
1.30-1.20 (m, 22H); $^{13}$C$[^{1}H]$ NMR (125 MHz, CDCl$_3$/CD$_3$OD 2:1): 170.8 (s), 170.5 (s), 170.4 (s), 170.0 (s), 163.7 (s), 162.6 (s), 162.1 (s), 156.6 (s), 136.7 (s), 136.4 (d), 136.1 (s), 136.0 (s), 135.9 (s), 133.8 (d), 132.7 (s), 130.1 (s), 128.9 (d), 128.8 (d), 128.5 (d), 128.4 (d), 128.3 (d), 127.6 (s), 127.2 (s), 125.0 (s), 124.1 (s), 119.4 (s), 108.7 (s), 81.8 (s), 69.0 (t), 68.9 (t), 68.8 (t), 54.5 (d), 53.7 (d), 48.4 (s), 41.9 (t), 39.5 (t), 31.7 (t), 29.9 (q), 28.6 (t), 28.3 (q), 27.8 (t), 24.0 (t); MS (ESI): 2486 (50, [M+Na]$^+$), 2364 (100, [M+H-Boc]$^+$), 2264 (50, [M+H-Boc]$^+$); HRMS (ESI +ve) calcd for C$_{124}$H$_{136}$N$_{12}$O$_{26}$P$_{5}$S$_{4}$: 1231.3834, found: 1231.3862.

**Compound 121.** This compound was synthesized according to reported procedures.$^{[144]}$

**Compound (R,R,S)-113.** To a solution of 120 (10 mg, 4.07 μmol) in DCM (800 μl) were added TMSBr (11 μl, 81.5 μmol). The mixture was stirred under Ar for 3h at RT and was then concentrated in vacuo. To the residue was added MeOH (1700 μl) and the resulting red solution was stirred for 4h at RT and was
then concentrated in vacuo. The residue was washed with diethyl ether (solid-liquid extraction) to give a red solid. To this material was added 121 (23 mg, 40.7 µmol), AcOH (20 µl) and DMSO (580 µl) and the resulting red solution was stirred overnight at RT. To the mixture was then added diethyl ether and the obtained red precipitate was successively washed with diethyl ether and then methanol (10x) to give compound 113 (7mg, 65%) as a red solid.

5.2.2. Synthesis of Propagators

Compound 96. This compound was prepared according to reported procedures.[135, 217-219] The product was recrystallized from EtOAc before use.

Compound (S,S)-92. To a solution of 91 (0.2 g, 0.19 mmol) in TFA (2.7 ml) were added pentamethylbenzene (28 mg, 0.19 mmol), thioanisole (24 mg, 0.19 mmol) and HBr (5.7 M in AcOH, 100 µl, 0.55 mmol). The mixture was stirred for 3 h at RT, then HBr (5.7 M in AcOH, 100 µl, 0.55 mmol) was added again and the mixture stirred for 1.5 h more. After concentration, the residue was washed with diethyl ether (solid-liquid extraction), diluted with MeOH (1 ml) and 1 M HCl (0.5 ml), concentrated in vacuo, treated with TEA (0.2 ml) and concentrated in vacuo. The resulting product was dissolved in DCM (6.5 ml) and DMF (9.3 ml), and the pH of the solution was adjusted to ~8 by the addition of TEA. To this solution was added 96 (190 mg, 0.76 mmol), and the mixture was stirred for 40 min. TEA was added to the solution to maintain the
pH at ~8. Saturated NH$_4$Cl aqueous solution was added to the solution, and the product was extracted with DCM, washed with brine, dried over Na$_2$SO$_4$ and concentrated in vacuo with small amount of silica gel (solid deposit). Column chromatography of the residue (DCM/MeOH 9:1; $R_f$ 0.71 with DCM/MeOH 4:1) afforded pure 92 (130 mg, 65%) as a green solid. Disulfide 92 polymerized readily when dry and was therefore kept as a solution in CHCl$_3$/MeOH 1:1.

Mp: >230 ºC; CD (CHCl$_3$/MeOH 1:1): 713 (+0.48), 446 (+0.54), 347 (-0.50), 322 (+0.80); IR: 3322 (w), 2931 (w), 1678 (s), 1643 (s), 1588 (s), 1574 (s), 1556 (s), 1414 (s), 1341 (s), 1234 (m), 1200 (w), 1120 (m), 954 (w), 865 (w), 804 (w), 754 (w), 730 (w); $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 2:1): 8.40 (s, 2H), 8.38 (d, $^3$J (H,H) = 8.0 Hz, 2H), 7.63 (d, $^3$J (H,H) = 8.0 Hz, 2H), 5.68 (t, $^3$J (H,H) = 7.5 Hz, 2H), 3.74-3.68 (m, 4H), 2.69-2.55 (m, 4H), 2.30-2.20 (m, 4H), 2.15-1.85 (m, 8H), 1.65-1.45 (m, 4H), 1.40-1.25 (m, 2H), 1.25-1.14 (m, 2H); $^{13}$C{[$^1$H]} NMR (100 MHz, CDCl$_3$/CD$_3$OD 2:1): 174.9 (s), 173.6 (s), 166.0 (s), 165.5 (s), 148.2 (s), 136.0 (s), 131.3 (s), 128.4 (d), 125.9 (d), 123.6 (q), 122.8 (d), 122.6 (q), 119.9 (q), 119.6 (q), 55.7 (d), 53.7 (d), 43.7 (t), 40.5 (t), 30.1 (t), 29.3 (t), 27.3 (t), 24.9 (t); MS (ESI, DCM): 1071 (7, [M+Na]$^+$), 1049 (43, [M+H]$^+$), 1032 (100, [M-NH$_2$]$^+$); HRMS (ESI, +ve) caleld for C$_52$H$_{57}$N$_8$O$_8$S$_4$: 1049.3176, found: 1049.3178.
Compound (S,S)-105. To a solution of 106 (185 mg, 0.2 mmol) in TFA (3.0 ml) were added pentamethylbenzene (30 mg, 0.2 mmol), thioanisole (25 mg, 0.2 mmol) and HBr (5.7 M in AcOH, 110 µl, 0.2 mmol). The mixture was stirred for 80 min. After concentration, the residue was washed with diethylether and petroleum ether (solid-liquid extraction), diluted with MeOH (1 ml) and 1 M HCl (0.5 ml), concentrated in vacuo, treated with TEA (2 ml) and concentrated in vacuo. The resulting product was dissolved in DCM (13 ml) and the pH of the solution was adjusted to ~8 by the addition of TEA. To this solution was added 96 (200 mg, 0.8 mmol), and the mixture was stirred for 30 min. Compound 96 (100 mg, 0.4 mmol) was added again and the mixture stirred for 1.5 h more. TEA was added to the solution to maintain the pH at ~8. The crude mixture was concentrated in vacuo with small amount of silica gel (solid deposit). Column chromatography of the residue (DCM/MeOH 91:9; Rf 0.47 with DCM/MeOH 17:3) afforded pure 105 (114 mg, 62%) as a red solid. Disulfide 105 polymerized readily when dry and was therefore kept as a solution in CHCl₃/TFE 1:1. Mp: 214-215 °C; CD (CHCl₃/TFE 1:1): 556 (-2.44), 492 (+2.78), 380 (-0.76), 313 (-1.59), 286 (+0.05); IR: 3289 (w), 3210 (w), 3082 (w), 2931 (w), 2867 (w), 2738 (w), 2677 (w), 1680 (s), 1632 (s), 1593 (w), 1536 (m), 1434 (w), 1332 (w), 1252 (w), 1207 (w), 1171 (w), 1035 (w), 980 (w), 807 (w); 1H NMR (300 MHz, DMSO-d₆): 9.03-8.93 (m, 4H), 8.61-8.55 (m, 4H), 8.00-7.96 (m, 2H), 7.50-7.45 (m, 2H), 7.03-6.97 (m, 2H), 5.44-5.39 (m, 2H), 3.14-2.82 (m, 14H), 2.29-2.20 (m, 2H), 2.15-2.03 (m, 2H), 1.50-1.32 (m, 4H), 1.30-1.10 (m, 4H); 13C{¹H} NMR (100 MHz, DMSO-d₆/CDCl₃ 9:1): 170.7 (s), 170.0 (s), 134.1 (s), 131.0 (d), 125.7 (s), 124.0 (d), 123.1 (s), 53.9 (d), 51.5 (d), 41.7 (t), 38.4 (t), 29.0 (t), 27.4 (t); MS (ESI, MeOH): 933 (51, [M+Na]+), 911 (34, [M+H]+), 894 (100, [M-NH₂]+).
Compound (S,S)-103. This compound was prepared following literature procedures.\textsuperscript{[103]}

Compound (S,S)-102. To a solution of 103 (190 mg, 0.24 mmol) in TFA (4.4 ml) were added pentamethylbenzene (16 mg, 0.11 mmol), thioanisole (61 mg, 0.49 mmol) and HBr (5.7 M in AcOH, 102 µl, 0.2 mmol). The mixture was stirred overnight at RT. After concentration, the residue was washed with diethylether (solid-liquid extraction), diluted with 1 M HCl (1 ml), concentrated in \textit{vacuo}, dissolved in MeOH (1 ml) and TEA (1 ml) and concentrated in \textit{vacuo}. The resulting product was dissolved in DCM (1.6 ml) and DMF (3.2 ml), and the pH of the solution was adjusted to ~8 by the addition of TEA. To this solution was added 96 (237 mg, 0.96 mmol), and the mixture was stirred for 15 min. TEA was added to the solution to maintain the pH at ~8. The crude mixture was diluted with DCM and washed with saturated NH\textsubscript{4}Cl aqueous solution. The product was extracted with DCM, washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in \textit{vacuo} with small amount of silica gel (solid deposit). Column chromatography of the residue (DCM/MeOH 9:1; \textit{R}_f 0.62 with DCM/MeOH 4:1) afforded pure 102 (113 mg, 60%) as a brown solid. 102 polymerized readily when dry and was therefore kept as a solution in CHCl\textsubscript{3}/MeOH 1:1. Mp: 159-160 °C; CD (CHCl\textsubscript{3}/MeOH 1:1): 377 (-0.38), 344 (+0.28), 307 (-0.37), 259 (+1.13); IR:
$^{1}H$ NMR (400 MHz, CDCl$_3$/CD$_3$OD 1:1): 8.75 (s, 4H), 5.64 (t, $^{3}J$(H,H) = 7.5 Hz, 2H), 3.18-3.07 (m, 8H), 3.02-2.94 (m, 6H), 2.28 (q, $^{3}J$(H,H) = 7.8 Hz, 4H), 1.65-1.43 (m, 4H), 1.40-1.27 (m, 2H), 1.27-1.15 (m, 2H);
$^{13}$C($^{1}H$) NMR (100 MHz, CDCl$_3$/CD$_3$OD 2:1): 174.5 (s), 173.8 (s), 166.45 (s), 132.5 (d), 128.4 (s), 128.2 (s), 56.0 (d), 53.4 (d), 43.7 (t), 40.3 (t), 30.3 (t), 29.1 (t), 25.0 (t); MS (ESI, MeOH): 808 (100, [M+Na]$^+$); HRMS (ESI, +ve) calcd for C$_{34}$H$_{39}$N$_6$O$_8$S$_4$: 787.1706, found: 787.1684.

**Compound (S,S)-122.** PDA 14 (1.5 g, 3.83 mmol), H-Lys(Cbz)-OH (2.25 g, 8.04 mmol) and imidazole (8.0 g, 118 mmol) were placed in a round-bottom flask and heated at 100°C. The resulting red molten mixture was stirred under Ar for 50 min at 100°C. The reaction was then allowed to cool down and the obtained red solid dissolved in a mixture of DCM and MeOH. The organic layer was then washed with 1M HCl, filtered, dried over Na$_2$SO$_4$, and concentrated in vacuo. Compound 122 (3.21 g, 91%) was obtained as a red solid and used without further purification. Mp: 137.5-138 °C; CD (DCM/MeOH 1:1): 554 (-1.12), 492 (+0.97), 408 (-0.23), 360 (+0.34); IR: 3349 (w), 2934 (w), 1695 (s), 1658 (s), 1592 (s), 1530 (s), 1502 (m), 1402 (m), 1359 (m), 1343 (s), 1250 (s), 1220 (s), 1172 (m), 1129 (m), 1021 (w), 808 (m), 745 (m); $^{1}H$ NMR (400 MHz, CDCl$_3$/CD$_3$OD 3:1): 8.47 (d, $^{3}J$(H,H) = 8.0 Hz, 4H), 7.40-7.25 (m, 4H), 7.30-7.05 (m, 10H), 5.66 (dd, $^{3}J$(H,H) = 4.0 Hz, $^{3}J$(H,H) = 8.0 Hz, 2H), 4.89 (s, 4H), 3.11 (t, $^{3}J$(H,H) = 7.8 Hz, 4H), 2.42-2.31 (m, 4H), 2.29-2.17 (m, 4H), 1.70-1.50 (m, 4H), 1.47-1.30 (m, 4H); $^{13}$C($^{1}H$) NMR (100 MHz, CDCl$_3$/CD$_3$OD 3:1): 163.8 (s), 156.9 (s), 156.8 (s), 136.9 (s), 135.1 (s), 132.2 (d), 128.8 (d), 128.3 (d), 128.2 (d), 123.7 (d),
Compound (S,S)-123. Boc-NNH$_2$ (1.7 g, 13.1 mmol) was added to a solution of compound 122 (3.0 g, 3.27 mmol), HBTU (5.0 g, 13.1 mmol) and TEA (1.84 ml, 13.1 mmol) in DMF (19 ml). The resulting mixture was stirred for 1 h at RT under Ar, diluted with EtOAc, washed successively with 1M HCl, brine, saturated NaHCO$_3$ aqueous solution, and brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 95:5; $R_f$ 0.6 with DCM/MeOH 92:8) gave pure 123 (2.56 g, 68%) as a red solid. Mp: 150-151 °C; CD (CHCl$_3$/MeOH 1:1): 638 (+0.59), 495 (+4.46), 323 (-1.30), 288 (+0.58), 271 (-1.14); IR: 3320 (w), 2993 (w), 1690 (s), 1592 (m), 1518 (w), 1341 (m), 1246 (s), 1159 (s), 1016 (s), 743 (m); $^1$H NMR (400 MHz, DMSO-d$_6$): 9.72 (s, NH), 8.86 (d, $^3$J (H,H) = 8.0 Hz, 4H), 8.76 (s, NH), 8.53 (d, $^3$J (H,H) = 8.0 Hz, 4H), 7.32-7.14 (m, 12H), 5.51 (m, 2H), 4.84 (s, 4H), 2.95 (q, $^3$J (H,H) = 8.0 Hz, 4H), 2.40-2.25 (m, 2H), 2.20-2.10 (m, 2H), 1.52-1.38 (m, 4H), 1.37 (s, 18H), 1.35-1.20 (m, 4H); $^{13}$C($^1$H) NMR (100 MHz, DMSO-d$_6$): 168.9 (s), 163.2 (s), 156.5 (s), 155.7 (s), 137.5 (s), 134.4 (s), 131.5 (d), 129.4 (s), 128.6 (d), 128.0 (d), 127.9 (d), 126.1 (s), 124.4 (d), 123.5 (s), 79.4 (s), 65.4 (t), 53.5 (d), 40.4 (t), 29.6 (t), 28.5 (q), 27.9 (t), 23.6 (t); MS (ESI): 1168 (70, [M+Na$^+$]), 1045 ([M+H-Boc$^+$]) 1013 (40, [M+H$_2$N-NHBoc$^+$]), 946 (80, [M+H-2Boc$^+$]), 913 ([M+H-Boc-H$_2$N-NHBoc$^+$]); HRMS (ESI, +ve) calcd for C$_{42}$H$_{38}$N$_4$O$_{12}$Na: 1167.4434, found: 1167.4453.
Compound (S,S)-124. A suspension of 123 (600 mg, 0.524 mmol) and Pd-C 10% in acetic acid (600 µl) (1.11 g) and methanol (17 ml) was stirred under hydrogen atmosphere for 3h at RT. The mixture was filtered through a celite pad, and the filtrate was concentrated in vacuo. To a solution of the residue in DMF (13 ml) were added TEA (to adjust pH to ~8) and 96 (390 mg, 1.572 mmol). After 5 min of stirring, more TEA was added (to adjust pH to ~8). After 5 more minutes of stirring, the mixture was diluted with DCM/MeOH (300 / 100 ml) and concentrated in vacuo with small amount of silica gel (solid deposit). Column chromatography of the residue (DCM/MeOH 94:6; \( R_f \) 0.47 with DCM/MeOH 9/1) resulted in the compound 124 (360 mg, 2 steps 60%) as a red solid. Disulfide 124 polymerized readily when dry and was therefore kept as a solution in \( \text{CH}_2\text{Cl}_2/\text{MeOH} \) 1:1. Mp: >200 °C (decomposition); CD (DCM/MeOH 1:1): 671 (+0.89), 558 (-1.48), 497 (+3.52), 361 (+0.47), 286 (+1.77); IR: 3317 (w), 2923 (w), 2849 (w), 1700 (m), 1655 (m), 1593 (w), 1575 (w), 1546 (w), 1532 (w), 1545 (w), 1435 (w), 1365 (m), 1291 (m), 1251 (m), 1163 (m), 1016 (w); \(^1^H\) NMR (400 MHz, DMSO-d\(_6\)): 9.72 (s, NH), 8.99 (d, \(^3^J\)(H,H) = 7.5 Hz, 2H), 8.75 (s, NH), 8.59 (d, \(^3^J\)(H,H) = 7.5 Hz, 2H), 7.96 (t, \(^3^J\)(H,H) = 7.5 Hz, NH), 5.56-5.46 (m, 2H), 3.16-3.06 (m, 2H), 3.05-2.98 (m, 4H), 2.94-2.85 (m, 8H), 2.35-2.25 (m, 2H), 2.21-2.08 (m, 2H), 1.54-1.40 (m, 4H), 1.37 (s, 18H), 1.30-1.10 (m, 4H); \(^1^C\)\(^{1^H}\) NMR (100 MHz, DMSO-d\(_6\)): 170.4 (s), 169.0 (s), 168.0 (s), 134.7 (s), 131.6 (d), 129.4 (s), 126.2 (s), 124.6 (d), 123.5 (s), 79.4 (s), 53.5 (d), 52.0 (d), 42.2 (t), 38.8 (t), 29.4 (t), 29.1 (t), 28.5 (q), 27.7 (t); MS (ESI): 1163 (100, [M+Na]^+), 1063 (20, [M+Na-Boc]^+), 963 (50, [M+Na-2Boc]^+), 909 (60, [M+H-Boc-H\_2N-NHBoc]^+); HRMS (ESI, +ve) calcd for C\(_{54}\)H\(_{60}\)O\(_{12}\)N\(_2\)S\(_4\)Na: 1163.3106, found: 1163.3136.
Compound (S,S)-114. A solution of 124 (360 mg, 0.316 mmol) and thioanisole (600 µl, 50.52 mmol) in TFA (15 ml) and DCM (15 ml) was stirred for 1h at RT. To the mixture was added benzaldehyde (12.9 ml, 126 mmol). After 15 more minutes of stirring, the mixture was diluted with DCM/MeOH (300 / 100 ml) and concentrated in vacuo with small amount of silica gel (solid deposit). Column chromatography of the residue (DCM/MeOH 94:6; Rf 0.36 with DCM/MeOH 9:1) resulted in the pure title compound (275 mg, 2 steps 78%) as a red solid. Disulfide 114 polymerized readily when dry and was therefore kept as a solution in CH₂Cl₂/MeOH 1:1. Mp: >230 ºC (decomposition); CD (CHCl₃/MeOH 2:1): 582 (-0.75), 522 (+3.15), 498 (+0.93), 491 (+1.67), 314 (-6.84), 274 (-17.3); IR: 3269 (w), 2924 (w), 1736 (s), 1700 (s), 1657 (s), 1593 (m), 1433 (w), 1366 (s), 1254 (w), 1226 (m), 1216 (m); ¹H NMR (500 MHz, DMSO-d₆): 8.95-8.85 (m, 4H), 8.75-8.62 (br s, NH), 8.62-8.52 (m, 4H), 8.47 (br s, NH), 8.19-7.05 (m, 12H), 5.95-5.55 (m, 2H), 3.35-2.82 (m, 14H), 2.44-2.25 (m, 2H), 2.16-1.97 (m, 2H), 1.60-1.37 (m, 8H); MS (ESI) 1140 (50, [M+Na]+), 1029 (50, [M+H-PhCHO]+), 997 (100, [M+H₂N-N=CH-Ph]).

5.2.3. Synthesis of Stack Exchangers

5.2.3.1. Charged Peptides

BoocHN~O-NHAlloc Compound 137. This compound was synthesized according to reported procedures.¹⁴⁸
**Compound 138.** A solution of 137 (0.62 g, 2.38 mmol) in TFA (1 ml) and DCM (9 ml) was stirred for 1 h at RT. More TFA (1 ml) was added and the resulting mixture stirred for 45 minutes more. Volatiles were subsequently removed in vacuo to yield 138 as an oil that was used without further purification.

![Diagram of Compound 138]

**Compound (S)-142.** A solution of Fmoc-Lys(Boc)-OH (3.51 g, 7.5 mmol), HBTU (2.84 g, 7.5 mmol) and TEA (1.06 g, 10.5 mmol, 1.5 ml) in DMF (10.5 ml) was stirred for 10 min at RT under N₂ atmosphere and this solution was then added over neat 138 (770 mg, 3.0 mmol). The resulting mixture was stirred at RT under N₂ for 1 h, diluted with EtOAc, washed successively with 1 M HCl, brine, saturated NaHCO₃ aqueous solution, and brine, dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/Acetone 5:1; Rf 0.42 with DCM/MeOH 97:3) gave pure 142 (1.1 g, 82%) as a colorless oil. [α]D²⁰ = 1.3 (c 0.23, EtOAc); IR (neat): 3322 (w), 2976 (w), 2936 (w), 2865 (w), 1697 (s), 1662 (s), 1524 (m), 1449 (m), 1366 (w), 1251 (s), 1169 (m), 1112 (m), 1043 (w), 760 (w), 737 (w); ¹H NMR (300 MHz, CD₃OD): 7.78 (d, J(H,H) = 7.5 Hz, 2H), 7.68 (d, J(H,H) = 7.5 Hz, 1H), 7.65 (d, J(H,H) = 7.5 Hz, 1H), 7.38 (t, J(H,H) = 7.5 Hz, 2H), 7.30 (t, J(H,H) = 7.5 Hz, 2H), 5.91-5.83 (m, 1H), 5.26 (d, J(H,H) = 18.0 Hz, 1H), 5.16 (d, J(H,H) = 9.0 Hz, 1H), 4.53 (d, J(H,H) = 4.5 Hz, 2H), 4.37 (d, J(H,H) = 4.3 Hz, 2H), 4.23 (t, J(H,H) = 4.3 Hz, 1H), 4.06 (t, J(H,H) = 5.0 Hz, 1H), 3.84 (t, J(H,H) = 4.5 Hz, 2H), 3.43 (t, J(H,H) = 4.5 Hz, 2H), 3.03 (t, J(H,H) = 5.0 Hz, 2H), 1.88-1.72 (m, 1H), 1.70-1.56 (m, 1H), 1.55-1.30 (m, 1H); ¹³C{¹H} NMR (75 MHz, CD₃OD); 173.7 (C), 158.3 (C), 157.1 (C), 144.0 (C), 143.7 (C), 141.2 (C), 132.3 (CH), 127.4 (CH), 126.7 (CH), 124.8 (CH), 119.5 (CH), 116.8 (CH₂), 78.4 (C), 74.4 (CH₂), 66.5 (CH₂), 65.6 (CH₂), 55.2 (CH), 39.6 (CH₂), 37.3 (CH₂), 31.4 (CH₂), 209
27.4 (CH₃), 22.8 (CH₂); MS (ESI, MeOH): 611 (90, [M+H]+), 511 (100, [M+H-Boc]+); HRMS (ESI, +ve) calcd for C₁₂H₁₃N₄O₈: 611.3075, found: 611.3077.

**Compound 140.** This compound was synthesized according to reported procedures.[²²⁰]

**Compound (S)-143.** A solution of 142 (200 mg, 0.32 mmol) in piperidine (360 µl) and DMF (3.2 ml) was stirred for 20 min at RT. The mixture was then concentrated in vacuo and the remaining solid purified by silica gel column chromatography (DCM/MeOH 85:15; Rₗ 0.1 with DCM/MeOH 85:15) to give the corresponding free amine as a colorless oil. To this material was added a mixture of 140 (77 mg, 0.33 mmol), HATU (150 mg, 0.39 mol), iPr₂NEt (85 mg, 0.66 mmol, 115 µl) and dry DCM (8 ml). The resulting mixture was stirred for 25 minutes at RT under N₂ atmosphere, then diluted with EtOAc and washed successively with saturated NaHCO₃ aqueous solution (twice), water and finally brine (twice), dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 95:5, then DCM/Acetone 3:1; Rₗ 0.81 with DCM/MeOH 9:1) afforded pure 143 (150 mg, 80%) as a colorless oil. [α]D₂⁰ = +1.9 (c 1.1, DCM); IR (neat): 3297 (w), 2939 (w), 1686 (s), 1642 (s), 1527 (s), 1446 (w), 1392 (m), 1364 (m), 1249 (s), 1168 (m), 1101 (s), 1052 (s), 987 (w), 836 (w), 763 (w); ¹H NMR (300 MHz, CD₃OD): 7.90 (d, ³J (H,H) = 8.0 Hz, 2H), 5.95-5.85 (m, 1H), 5.44 (s, 1H), 5.28 (d, ³J (H,H) = 20.0 Hz, 1H), 5.19 (d, ³J (H,H) = 12.0 Hz, 1H), 4.55-4.53 (m, 3H), 3.87 (t, ³J (H,H) = 4.0 Hz, 2H), 3.46 (t, ³J (H,H) = 8.0 Hz, 2H), 3.32 (s, 6H), 3.05 (t, ³J (H,H) = 8.0 Hz, 2H).
Compound (S)-135. A solution of 143 (50 mg, 0.08 mmol) in DCM (1 ml) was cooled down to 0 °C and TFA (1 ml) was added. The resulting mixture was allowed to reach to RT and stirred for 20 min and then concentrated in vacuo. The remaining solid was washed with Et₂O (solid-liquid extraction) and then purified by PTLC (DCM/MeOH 9:1 +1% NH₄OH; Rf 0.14 with DCM/MeOH 9:1). 135 was obtained as a colorless oil (19 mg, 53%). 

N.H₄H₃TFA

\[ [\alpha]_D^{20} = -0.08 \text{ (c 0.5, DCM); IR (neat): 3281 (w), 3087 (w), 2944 (w), 2320 (m, 1668 (s), 1540 (m), 1274 (w), 1202 (m), 1137 (m); \] 

\[ ^1H NMR (500 MHz, D}_2O + 5% TFA-d): 9.87 (s, 1H), 7.90 (d, \_3J(H,H) = 8.0 Hz, 2H), 7.81 (d, \_3J(H,H) = 8.0 Hz, 2H), 5.78-5.70 (m, 1H), 5.13 (d, \_3J(H,H) = 20.0 Hz, 1H), 5.09 (d, \_3J(H,H) = 10.0 Hz, 1H), 4.40 (d, \_3J(H,H) = 5.0 Hz, 2H), 4.35 (t, \_3J(H,H) = 4.0 Hz, 1H), 3.81 (t, \_3J(H,H) = 8.0 Hz, 2H), 3.36 (t, \_3J(H,H) = 8.0 Hz, 2H), 2.86 (t, \_3J(H,H) = 8.0 Hz, 2H), 1.85-1.70 (m, 2H), 1.61-1.55 (m, 2H), 1.45-1.30 (m, 2H); \] 

\[ ^1C\{^1H\} NMR (125 MHz, D}_2O + 5% TFA-d): 195.6 (CH), 173.9 (C), 170.0 (C), 158.8 (C), 138.6 (C), 138.0 (C), 131.8 (CH), 130.1 (CH), 128.0 (CH), 118.0 (CH₂), 73.5 (CH₂), 66.5 (CH₂), 54.6 (CH), 39.1 (CH₂), 37.7 (CH₂), 30.3 (CH₂), 26.2 (CH₂), 22.2 (CH₂); MS (ESI, MeOH): 475 (100, [M+MeOH+Na]^+), 453 (70, [M+MeOH+H]^+), 443 (100, [M+Na]^+), 421 (75, [M+H]^+); HRMS (ESI, +ve) calcd for C₂₀H₂₈N₄O₆: 421.2082, found: 421.2088.

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Compound (S)-144. To a solution of 142 (500 mg, 0.82 mmol) in DCM (9 ml) was added TFA (1 ml), the resulting mixture was stirred for 1 h 45 at RT and then concentrated in vacuo. To the residue was added acetic anhydride (92 mg, 0.90 mmol, 85 µl), TEA (250 mg, 2.50 mmol, 350 µl) and dry DCM (5 ml). The resulting mixture was stirred for 1.5 h at RT under N₂ atmosphere, then diluted with EtOAc and washed successively with 1 M HCl, brine, saturated NaHCO₃ aqueous solution, and brine, dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 95:5; Rf 0.47 with DCM/MeOH 9:1) afforded pure 144 (370 mg, 82%) as a colorless oil. [α]D²⁰ = -1.2 (c 1.0, DCM); IR (neat): 3295 (w), 2941 (w), 1718 (m), 1654 (s), 1535 (m), 1449 (w), 1251 (s), 1111 (m), 1040 (w), 741 (w); ¹H NMR (400 MHz, CD₃OD): 7.80 (d, ³J (H,H) = 8.0 Hz, 2H), 7.69 (t, ³J (H,H) = 8.0 Hz, 1H), 7.39 (t, ³J (H,H) = 8.0 Hz, 2H), 7.31 (t, ³J (H,H) = 8.0 Hz, 2H), 5.93-5.83 (m, 1H), 5.27 (d, ³J (H,H) = 16.0 Hz, 1H), 5.17 (d, ³J (H,H) = 12.0 Hz, 1H), 4.53 (d, ³J (H,H) = 4.0 Hz, 2H), 4.38 (d, ³J (H,H) = 8.0 Hz, 2H), 4.23 (t, ³J (H,H) = 8.0 Hz, 1H), 4.06-4.04 (m, 1H), 3.84 (t, ³J (H,H) = 4.0 Hz, 2H), 3.43 (t, ³J (H,H) = 4.0 Hz, 2H), 3.16 (t, ³J (H,H) = 8.0 Hz, 2H), 1.91 (s, 3H), 1.85-1.75 (m, 1H), 1.69-1.60 (m, 1H), 1.55-1.48 (m, 2H), 1.44-1.33 (m, 2H); ¹³C{¹H} NMR (100 MHz, CD₃OD): 173.6 (C), 171.8 (C), 158.3 (C), 157.1 (C), 144.0 (C), 141.2 (C), 132.3 (CH), 127.4 (CH), 126.7 (CH), 124.8 (CH), 119.5 (CH), 116.8 (CH₂), 74.4 (CH₂), 66.5 (CH₂), 65.5 (CH₂), 55.2 (CH), 40.0 (CH), 38.8 (CH₂), 37.2 (CH₂), 31.3 (CH₂), 28.5 (CH₂), 22.9 (CH₂), 21.1 (CH₃); MS (ESI, MeOH): 575 (15, [M +Na⁺]), 553 (100, [M +H⁺]); HRMS (ESI, +ve) calcd for C₂₉H₃₆N₄O₇: 553.2657, found: 553.2665.

Compound (S)-145. A solution of 144 (300 mg, 0.54 mmol) in piperidine (540 µl) and DMF (4.8 ml) was stirred for 30 min at RT. The mixture was then concentrated in vacuo and the remaining solid purified by solid liquid
extraction using Et<sub>2</sub>O to give the corresponding free amine as a colorless oil. To this material was added a mixture of 140 (130 mg, 0.65 mmol), HATU (250 mg, 0.65 mol), iPr<sub>2</sub>NEt (140 mg, 1.09 mmol, 190 µl) and dry DCM (13 ml). The resulting mixture was stirred for 45 min at RT under N<sub>2</sub> atmosphere, then diluted with EtOAc and washed successively with saturated NaHCO<sub>3</sub> aqueous solution (twice), water and finally brine (twice), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 93:7; R<sub>f</sub> 0.63 with DCM/MeOH 9:1) afforded pure 145 (180 mg, 65%) as a colorless oil. [α]<sub>D</sub><sup>20</sup> = 0.8 (c 1.0, DCM); IR (neat): 3296 (w), 2940 (w), 2663 (w), 2492 (w), 1732 (m), 1644 (s), 1538 (s), 1450 (w), 1253 (m), 1101 (s), 1052 (m), 988 (w), 841 (m), 766 (w); ¹H NMR (400 MHz, CD<sub>3</sub>OD): 7.91 (d, J<sub>H,H</sub> = 8.0 Hz, 2H), 7.53 (d, J<sub>H,H</sub> = 8.0 Hz, 2H), 5.95-5.85 (m, 1H), 5.44 (s, 1H), 5.29 (d, J<sub>H,H</sub> = 16.0 Hz, 1H), 5.19 (d, J<sub>H,H</sub> = 12.0 Hz, 1H), 4.55-4.52 (m, 3H), 3.87 (t, J<sub>H,H</sub> = 8.0 Hz, 2H), 3.46 (t, J<sub>H,H</sub> = 8.0 Hz, 2H), 3.32 (s, 6H), 3.17 (t, J<sub>H,H</sub> = 8.0 Hz, 2H), 1.99-1.87 (m, 1H), 1.90 (s, 3H), 1.86-1.78 (m, 1H), 1.59-1.49 (m, 2H), 1.49-1.41 (m, 2H); ¹³C<sup>¹</sup>H NMR (100 MHz, CD<sub>3</sub>OD): 173.3 (C), 171.8 (C), 168.7 (C), 158.4 (C), 141.9 (C), 134.0 (C), 132.4 (CH), 127.2 (CH), 126.5 (CH), 116.9 (CH<sub>2</sub>), 102.6 (CH), 74.5 (CH<sub>2</sub>), 65.6 (CH), 54.2 (CH<sub>2</sub>), 51.9 (CH<sub>3</sub>), 38.8 (CH<sub>2</sub>), 37.4 (CH<sub>2</sub>), 31.2 (CH<sub>2</sub>), 28.6 (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 21.2 (CH<sub>3</sub>); MS (ESI, MeOH): 531 (20, [M+Na]<sup>+</sup>), 509 (40, [M+H]<sup>+</sup>), 477 (100, [M+H-MeOH]<sup>+</sup>); HRMS (ESI, +ve) caled for C<sub>24</sub>H<sub>36</sub>N<sub>4</sub>O<sub>8</sub>: 531.2425, found: 531.2450.

**Compound (S)-136.** A solution of 145 (50 mg, 0.10 mmol) in DCM (1 ml) and TFA (1 ml) was stirred at 0°C for 25 minutes under air and then concentrated in vacuo. The remaining solid was purified by PTLC (DCM/Acetone 1:1; R<sub>f</sub> 0.17 with DCM/MeOH 9:1) to give 136 as a colorless oil (45 mg, quantitative).
[α]D<sup>20</sup> = -0.25 (c 1.0, DCM); IR (neat): 3223 (w), 2935 (w), 2861 (w), 2452 (w), 1730 (m), 1703 (m), 1635 (s), 1571 (w), 1430 (m), 1258 (w), 1208 (w), 1114 (w), 821 (w), 759 (w);

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/D<sub>2</sub>O): 10.08 (s, 1H), 8.04 (d, <sup>3</sup>J (H,H) = 8.0 Hz, 2H), 7.94 (d, <sup>3</sup>J (H,H) = 8.0 Hz, 2H), 5.94-5.84 (m, 1H), 5.31 (d, <sup>3</sup>J (H,H) = 20.0 Hz, 1H), 5.25 (t, <sup>3</sup>J (H,H) = 12.0 Hz, 1H), 4.73-4.68 (m, 1H), 4.60 (d, <sup>3</sup>J (H,H) = 8.0 Hz, 2H), 3.96-3.89 (m, 2H), 3.61-3.48 (m, 2H), 3.30-3.22 (m, 2H), 2.02-1.84 (m, 2H), 1.94 (s, 3H), 1.61-1.54 (m, 2H), 1.49-1.39 (m, 2H);

<sup>1</sup>C<sup>{1}H</sup> NMR (100 MHz, CDCl<sub>3</sub>/D<sub>2</sub>O): 191.6 (CH), 171.8 (C), 170.8 (C), 166.3 (C), 158.0 (C), 138.9 (C), 138.3 (C), 131.7 (CH), 129.7 (CH), 128.0 (CH), 118.8 (CH<sub>2</sub>), 75.1 (CH<sub>2</sub>), 66.5 (CH<sub>3</sub>), 53.5 (CH), 38.5 (CH<sub>2</sub>), 37.4 (CH<sub>2</sub>), 32.1 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 23.1 (CH<sub>3</sub>), 22.3 (CH<sub>3</sub>);

MS (ESI, MeOH): 517 (100, [M+MeOH+Na]<sup>+</sup>), 495 (30, [M+MeOH+H]<sup>+</sup>), 485 (60, [M+Na]<sup>+</sup>), 477 (50, [M+MeOH+H-H<sub>2</sub>O]<sup>+</sup>) 463 (40, [M+H]<sup>+</sup>); HRMS (ESI, +ve) calcd for C<sub>22</sub>H<sub>30</sub>N<sub>4</sub>O<sub>7</sub>: 463.2187, found: 463.2188.

**Compound (S)-139.** A solution of Fmoc-Glu(t-Bu)-OH (3.83 g, 8.6 mmol), HBTU (4.6 g, 12.1 mmol) and TEA (1.57 g, 15.5 mmol, 2.1 ml) in DMF (14.0 ml) was stirred for 10 min at RT under N<sub>2</sub> atmosphere and this solution was then added over neat 138 (889 mg, 3.4 mmol). The resulting mixture was stirred at RT under N<sub>2</sub> atmosphere for 1 h, diluted with EtOAc, washed successively with 1 M HCl, brine, saturated NaHCO<sub>3</sub> aqueous solution, and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/Acetone 5:1, then DCM/MeOH 95:5; R<sub>f</sub> 0.67 with DCM/MeOH 97:3) gave pure 139 (1.5 g, 76%) as a colorless oil. [α]<sub>D</sub><sup>20</sup> = +0.2 (c 1.0, DCM); IR (neat): 3294 (w), 2976 (w), 1716 (s), 1658 (s), 1527 (m), 1449 (m), 1367 (w), 1326 (w), 1242 (s), 1150 (s), 1106 (m), 1045 (m), 936 (w), 845 (w), 758 (m), 735 (s); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>/D<sub>2</sub>O): 10.08 (s, 1H), 8.04 (d, <sup>3</sup>J (H,H) = 8.0 Hz, 2H), 7.94 (d, <sup>3</sup>J (H,H) = 8.0 Hz, 2H), 5.94-5.84 (m, 1H), 5.31 (d, <sup>3</sup>J (H,H) = 20.0 Hz, 1H), 5.25 (t, <sup>3</sup>J (H,H) = 12.0 Hz, 1H), 4.73-4.68 (m, 1H), 4.60 (d, <sup>3</sup>J (H,H) = 8.0 Hz, 2H), 3.96-3.89 (m, 2H), 3.61-3.48 (m, 2H), 3.30-3.22 (m, 2H), 2.02-1.84 (m, 2H), 1.94 (s, 3H), 1.61-1.54 (m, 2H), 1.49-1.39 (m, 2H).
MHz, CD$_3$OD): 7.77 (d, $^3J$(H,H) = 6.0 Hz, 2H), 7.67 (d, $^3J$(H,H) = 6.0 Hz, 1H), 7.65 (d, $^3J$(H,H) = 6.0 Hz, 1H), 7.37 (t, $^3J$(H,H) = 6.0 Hz, 2H), 7.29 (t, $^3J$(H,H) = 6.0 Hz, 2H), 5.93-5.80 (m, 1H), 5.25 (d, $^3J$(H,H) = 18.0 Hz, 1H), 5.15 (d, $^3J$(H,H) = 9.0 Hz, 1H), 4.52 (d, $^3J$(H,H) = 6.0 Hz, 2H), 4.36 (d, $^3J$(H,H) = 6.0 Hz, 2H), 4.20 (t, $^3J$(H,H) = 6.0 Hz, 1H), 4.15-4.11 (m, 1H), 3.84 (t, $^3J$(H,H) = 6.0 Hz, 2H), 2.31 (t, $^3J$(H,H) = 6.0 Hz, 2H), 2.18-1.98 (m, 1H), 1.92-1.80 (m, 1H), 1.44 (s, 9H); $^{13}$C{$_1^1$H} NMR (75 MHz, CD$_3$OD): 173.0 (C), 172.5 (C), 158.3 (C), 157.0 (C), 143.8 (C), 141.1 (C), 132.3 (CH), 127.4 (CH), 126.7 (CH), 124.8 (CH), 119.5 (CH), 116.8 (CH$_2$), 80.4 (s), 74.4 (CH$_2$), 66.6 (CH$_2$), 65.6 (CH$_2$), 54.5 (CH), 47.0 (CH), 37.3 (CH$_2$), 31.3 (CH$_2$), 27.1 (CH$_3$), 27.0 (CH$_2$); MS (ESI, MeOH): 590 (10, [M+Na]$^+$), 568 (95, [M+H]$^+$), 512 (100, [M+H-t-Bu]$^+$); HRMS (ESI, +ve) calcd for NaC$_{30}$H$_{37}$N$_3$O$_8$: 590.2473, found: 590.2470.

**Compound (S)-141.** A solution of 139 (380 mg, 0.67 mmol) and piperidine (400 µl) in DMF (3.6 ml) was stirred for 30 min at RT under N$_2$ atmosphere. The mixture was then concentrated in vacuo and the remaining solid purified by silica gel column chromatography (DCM/MeOH 88:12; $R_f$ 0.4 with DCM/MeOH 95: 5) to give the corresponding free amine as a colorless oil. To this material was added a mixture of 140 (200 mg, 1.01 mmol), HATU (380 mg, 1.01 mol), iPr$_2$NEt (215 mg, 1.68 mmol, 292 µl) and dry DCM (16 ml). The resulting mixture was stirred for 35 min at RT under N$_2$ atmosphere, then diluted with EtOAc and washed successively with saturated NaHCO$_3$ aqueous solution (twice), water and finally brine (twice), dried over Na$_2$SO$_4$, and concentrated in vacuo. Silica gel column chromatography of the residue (DCM/MeOH 95:5; $R_f$ 0.57 with DCM/MeOH 9:1) afforded pure 141 (273 mg, 78%) as a colorless oil. [α]$_D$$^{20}$ = +1.3 (c 1.3, DCM); IR (neat): 3291 (w), 2976 (w), 2938 (w), 2833 (w), 2724 (m), 1641 (s), 1595 (s), 1482 (m), 1380 (m), 1292 (m), 1257 (s), 1146 (s), 1060 (s), 839 (w), 752 (w), 692 (w), 660 (w).
1529 (m), 1497 (w), 1466 (m), 1249 (s), 1151 (s), 1101 (s), 1052 (s), 987 (m), 842 (m), 762 (m); \(^1\)H NMR (400 MHz, CD\(_3\)OD): 7.91 (d, \(^3\)J (H,H) = 8.0 Hz, 2H), 7.53 (d, \(^3\)J (H,H) = 8.0 Hz, 2H), 5.94-5.85 (m, 1H), 5.44 (s, 1H), 5.28 (d, \(^3\)J (H,H) = 16.0 Hz, 1H), 5.19 (d, \(^3\)J (H,H) = 12.0 Hz, 1H), 4.61-4.57 (m, 1H), 4.53 (d, \(^3\)J (H,H) = 8.0 Hz, 2H), 3.87 (t, \(^3\)J (H,H) = 8.0 Hz, 2H), 3.46 (t, \(^3\)J (H,H) = 8.0 Hz, 2H), 3.32 (s, 6H), 2.41 (t, \(^3\)J (H,H) = 8.0 Hz, 2H), 2.27-2.19 (m, 1H), 2.10-2.01 (m, 1H), 1.43 (s, 9H); \(^{13}\)C{\(^1\)H} NMR (100 MHz, CD\(_3\)OD): 172.8 (C), 172.6 (C), 168.5 (C), 158.4 (C), 141.9 (C), 133.8 (C), 132.4 (CH), 127.2 (CH), 126.5 (CH), 116.9 (CH\(_3\)), 102.6 (CH), 80.5 (C), 74.5 (CH\(_2\)), 65.6 (CH\(_2\)), 53.6 (CH), 51.9 (CH\(_3\)), 37.4 (CH\(_2\)), 31.5 (CH\(_2\)), 27.0 (CH\(_3\)), 26.7 (CH\(_2\)); MS (ESI, MeOH): 546 (30, [M+Na]+), 524 (60, [M+H]+), 492 (10, [M+H-MeOH]+), 468 (60, [M+H-t-Bu]+), 436 (100, [M+H-t-Bu-MeOH]+); HRMS (ESI, +ve) calcd for C\(_{25}\)H\(_{37}\)N\(_3\)O\(_9\): 524.2603, found: 524.2577.

**Compound (S)-134.** A solution of 141 (50 mg, 0.10 mmol) in DCM (1 ml) was cooled down to 0 °C and TFA (1 ml) was added. The resulting mixture was allowed to reach RT and stirred for 70 min and then concentrated in vacuo. The remaining solid was purified by PTLC (DCM/MeOH 8:2; \(R_f\) 0.51 with DCM/MeOH 9:1) to give 134 as a colorless oil (37 mg, 93%).[\(\alpha\]_D\(^{20}\) = -0.08 (c 0.5, DCM); IR (neat): 3290 (w), 3103 (w), 2948 (w), 1662 (s), 1544 (w), 1447 (w), 1268 (w), 1198 (s), 1198 (s), 1139 (s), 841 (w), 800 (w), 722 (w); \(^1\)H NMR (500 MHz, D\(_2\)O + 5% TFA-d); 9.87 (s, 1H), 7.91 (d, \(^3\)J (H,H) = 8.0 Hz, 2H), 7.82 (d, \(^3\)J (H,H) = 8.0 Hz, 2H), 5.79-5.69 (m, 1H), 5.13 (d, \(^3\)J (H,H) = 16.0 Hz, 1H), 5.09 (d, \(^3\)J (H,H) = 12.0 Hz, 1H), 4.44-4.41 (m, 3H), 3.82 (t, \(^3\)J (H,H) = 8.0 Hz, 2H), 3.36 (t, \(^3\)J (H,H) = 8.0 Hz, 2H), 3.07-2.97 (m, 1H); \(^{13}\)C\(^{13}H\) NMR (100 MHz, D\(_2\)O + 5% TFA-d): 195.5 (CH), 176.9 (C), 173.2 (C), 169.8 (C), 158.7 (C), 158.0 (C), 138.0 (C), 131.7 (CH), 130.0 (CH), 128.0 (CH), 117.9 (CH\(_3\)), 74.4 (CH\(_2\)), 66.5 (CH\(_2\)), 54.0 (CH), 37.6 (CH\(_2\)),
30.1 (CH$_2$), 26.0 (CH$_2$); MS (ESI, MeOH): 476 (90, [M+MeOH+Na]$^+$), 454 (30, [M+MeOH+H]$^+$), 444 (100, [M+Na]$^+$), 422 (40, [M+H]$^+$); HRMS (ESI, +ve) calcd for C$_{19}$H$_{23}$N$_2$O$_4$: 422.1558, found: 422.1553.

5.2.3.2. Oligothiophenes

**Compound 149.** This compound was synthesized according to reported procedures.$^{[207]}$

**Compound (S)-156.** This compound was synthesized according to reported procedures.$^{[149]}$

**Compound (S)-anti-159.** To a solution of 156 (50 mg, 65.8 μmol) in DCM (6.6 ml) and AcOH (530 μl) were added Pd(PPh$_3$)$_2$Cl$_2$ (23 mg, 33.0 μmol) and n-Bu$_3$SnH (445 μl, 1.64 mmol). The resulting mixture was stirred for 15 min at RT and then more n-Bu$_3$SnH (445 μl, 1.64 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (23 mg, 33.0 μmol) were added. After 30 min more at RT TLC showed complete deprotection of the starting material and 149 (130 mg, 0.40 mmol) was added as a solution in DCM (3 ml). The resulting mixture was stirred for 10 min at RT and then diluted with DCM, washed successively with saturated NaHCO$_3$ aqueous solution and water and then concentrated *in vacuo*. Column chromatography of the residue (DCM/MeOH 94/6, $R_f$ 0.66 with DCM/MeOH 95/5) and PTLC (DCM/acetone 4/1) afforded pure 159 (4 mg,
6%) as a yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 8.09 (s, 1H), 7.40 (d, \(^3\)J(H,H) = 4.7 Hz, 2H), 7.12 (d, \(^3\)J(H,H) = 3.8 Hz, 2H), 7.08 (d, \(^3\)J(H,H) = 3.8 Hz, 2H), 7.05-7.01 (m, 2H), 6.91 (d, \(^3\)J(H,H) = 11.0 Hz, 2H), 6.76 (d, \(^3\)J(H,H) = 4.0 Hz, 1H), 6.75-6.67 (m, 2H, NH), 6.65-6.62 (m, 2H, NH), 6.17 (d, \(^3\)J(H,H) = 4.0 Hz, 1H), 4.73-4.63 (m, 1H), 3.51 (t, \(^3\)J(H,H) = 5.2 Hz, 1H), 3.27-4.17 (m, 2H), 3.91 (s, 3H), 3.72-3.62 (m, 2H), 6.25 (t, \(^3\)J(H,H) = 5.7 Hz, 1H, NH), 6.17 (d, \(^3\)J(H,H) = 4.0 Hz, 1H), 3.25-3.15 (m, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 1.82-1.68 (m, 3H), 0.98 (s, 6H); \(^13\)C\{\(^1\)H\} NMR (125 MHz, CDCl\(_3\)): 172.7 (s), 166.6 (s), 161.8 (s), 161.6 (s), 146.7 (s), 144.1 (d), 142.4 (s), 142.0 (s), 141.6 (s), 137.0 (s), 136.9 (s), 136.7 (s), 136.6 (s), 135.7 (s), 135.6 (s), 134.5 (d), 133.6 (s), 133.5 (s), 133.4 (s), 132.6 (s), 132.3 (s), 131.7 (s), 130.0 (d), 129.3 (d), 129.1 (d), 125.8 (d), 125.7 (d), 124.8 (d), 124.0 (d), 123.9 (d), 123.5 (s), 122.3 (s), 104.4 (d), 102.8 (d), 72.6 (t), 60.4 (q), 54.8 (q), 52.4 (d), 41.6 (t), 41.3 (t), 39.5 (t), 25.0 (d), 23.1 (d), 15.7 (q), 15.4 (q); MS (ESI): 993 (100, [M+H]\(^+\)), 961 (70, [M+H-MeOH]\(^+\)); HRMS (ESI, +ve) calcd for C\(_{46}\)H\(_{65}\)O\(_7\)N\(_4\)S\(_7\): 993.1641, found: 993.1540.

**Compound (S)-syn-157.** To a solution of *anti-*159 (4 mg, 40.3 \(\mu\)mol) in DCM (1 ml) was added TFA (0.5 ml). Then immediately the mixture was concentrated *in vacuo*. PTLC of the residue (DCM/Acetone 7/3, \(R_f\) 0.42 with DCM/Acetone 2/1) afforded pure *syn-*157 (1.0 mg, 25%) as a yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 9.79 (s, 1H), 7.52 (s, 1H), 7.49 (d, \(^3\)J(H,H) = 4.0 Hz, 2H), 7.32 (d, \(^3\)J(H,H) = 4.0 Hz, 2H), 7.18 (m, 6H), 6.78 (d, \(^3\)J(H,H) = 4.0 Hz, 1H), 6.71 (t, \(^3\)J(H,H) = 4.0 Hz, 1H, NH), 6.57 (t, \(^3\)J(H,H) = 4.0 Hz, 1H, NH), 6.42 (d, \(^3\)J(H,H) = 4.0 Hz, 1H, NH), 6.18 (d, \(^3\)J(H,H) = 4.0 Hz, 1H), 4.68-4.58 (m, 1H), 4.44 (d, \(^3\)J(H,H) = 5.0 Hz, 2H), 4.41-4.34 (m, 2H), 3.92 (s, 3H), 3.75-3.66 (m, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 1.85-1.60 (m, 3H), 0.93 (s, 6H); MS (ESI): 947 (100, [M+H]\(^+\)).
Compound 163. This compound was synthesized according to reported procedures.\[214\]

Compound (S)-anti-164. To a solution of 156 (50 mg, 65.8 \( \mu \)mol) in DCM (3.4 ml) and AcOH (530 \( \mu \)l) were added Pd(PPh\(_3\))\(_2\)Cl\(_2\) (46 mg, 65.8 \( \mu \)mol) and \( n \)-Bu\(_3\)SnH (445 \( \mu \)l, 1.64 mmol). The resulting mixture was stirred for 20 min at RT and 163 (40 mg, 0.14 \( \mu \)mol) was added. The resulting solution was stirred for 30 min at RT and then diluted with DCM, washed successively with saturated NaHCO\(_3\) aqueous solution and brine and then concentrated \textit{in vacuo}. Column chromatography of the residue (DCM/MeOH 94/6, \( R_f \) 0.67 with DCM/MeOH 9/1) and PTLC (DCM/acetone 3/1) afforded pure anti-164 (27 mg, 44\%) as a yellow solid. \(^1\)H NMR (500 MHz, CDCl\(_3\)): 8.02 (s, 1H), 7.44 (d, \(^3\)J(H,H) = 3.7 Hz, 2H), 7.43-7.37 (m, 2H), 7.27 (t, \(^3\)J(H,H) = 7.8 Hz, 6H), 7.15-7.0 (m, 12H), 7.00-6.95 (m, NH), 6.87-6.77 (m, NH), 6.55-6.48 (m, NH), 4.70-4.64 (m, 1H), 4.54 (t, \(^3\)J(H,H) = 5.1 Hz, 1H), 4.28-4.21 (m, 2H), 3.74-3.66 (m, 1H), 3.65-3.55 (m, 1H), 3.60 (t, \(^3\)J(H,H) = 5.5 Hz, 2H), 3.47 (s, 6H), 1.85-1.66 (m, 3H), 1.00-0.90 (m, 6H); \(^13\)C\{\(^1\)H\} NMR (125 MHz, CDCl\(_3\)): 172.7 (s), 161.8 (s), 161.6 (s), 149.5 (s), 149.1 (d), 147.0 (s), 141.8 (s), 141.4 (s), 136.9 (s), 136.8 (s), 136.7 (s), 135.6 (s), 135.4 (s), 129.3 (d), 129.1 (d), 128.9 (d), 128.0 (d), 125.6 (d), 125.4 (d), 125.0 (d), 124.9 (s), 124.7 (d), 124.6 (d), 123.8 (d), 123.7 (d), 123.6 (d), 122.1 (d), 102.7 (d), 72.0 (t), 54.6 (q), 52.3 (d), 41.5 (t), 41.2 (t), 39.6 (t), 24.8 (d), 22.9 (q), 22.1 (q); MS (ESI): 932 (100, [M+H]\(^+\)).
**Compound (S)-anti-160.** To a solution of 164 (20 mg, 20.5 \( \mu \text{mol} \)) in DCM (1 ml) was added TFA (0.5 ml). Then immediately the mixture was concentrated *in vacuo*. PTLC of the residue (DCM/MeOH 94/6, \( R_f \) 0.34 with DCM/MeOH 94/6) afforded pure 160 (1.2 mg, 6%) as a yellow solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)/MeOD 3/1): 9.58 (s, 1H), 7.92 (s, 1H), 7.75-6.75 (m, 22H), 4.51 (m, 1H), 4.20-4.15 (m, 2H), 4.15-4.10 (m, 2H), 3.60-3.40 (m, 2H), 1.65-1.55 (m, 3H), 0.95-0.75 (m, 6H); MS (ESI): 886 (100, [M+H]+).
5.3. Methods

5.3.1. Self-Assembled Monolayers

5.3.1.1. Initiation with Green Perylenediimide

ITO electrodes were cut to give the area \( \sim 1 \cdot 2 \, \text{cm}^2 \), cleaned in a boiling mixture of \( \text{H}_2\text{O} / 24 \, \% \text{NH}_4\text{OH} / 30 \, \% \text{H}_2\text{O}_2 \), 5 : 1 : 1, v/v/v for 5 min, rinsed with bidistilled water and MeOH, dried and placed by pairs in vials containing the solution of initiator 88 (1 mM, DMSO/MeOH 4 : 3, v/v/v). Pairs of electrodes were assembled back-to-back with the ITO coated side exposed to the initiator solution to ensure a good coverage. The vials were wrapped in aluminium foil to protect from light, sealed with plastic caps and gently shaken at RT. Coating of the electrode was monitored by testing for pinholes in the monolayer. For that purpose, electrodes were taken out of the solution of initiator, rinsed with DMSO/MeOH 4:3, v/v, then with MeOH and dried in flow of \( \text{N}_2 \). Then, CV of potassium ferricyanide (0.5 mM \( \text{K}_4\text{Fe(CN)}_6 \), 0.2 M \( \text{Na}_2\text{SO}_4 \)) was recorded using the covered ITO as a working electrode (Pt wire as a counter electrode and Ag/AgCl as a reference). Nearly complete disappearance of the redox waves after 1 day of immersion confirmed the good coverage of the electrode by the initiator. The obtained ITO electrodes were then stirred in a mixture of DMSO/MeOH 4:3, v/v at RT for 0.5 hour to wash out the unbound initiator molecules, rinsed with EtOH, dried in air and then heated in an oven for 1 h at 120 °C to achieve better bonding between phosphonic acid groups and the ITO substrate (annealation procedure).

5.3.1.2. Initiation with Unsubstituted Perylenediimide

The procedure was the same as described in “5.3.1.1. Initiation with Green Perylenediimide” except that the solution of initiator 104 used for monolayer formation was 0.5 mM in DMSO. Correspondingly, the freshly covered
electrodes were stirred in DMSO at RT to wash out the unbound initiator molecules.

5.3.1.3. Initiation with Dicyano Perylenediimide.

The procedure was the same as described in "5.3.1.2. Initiation with Unsubstituted Perylenediimide", except that solutions of initiator 113 at 1 mM in DMSO were used for monolayer formation.

5.3.2. Activation of Monolayers

The annealed electrodes with monolayers 97, 109 and 125 were activated using a common procedure, namely by a treatment with DTT (20 mM in a 10 mM NH$_4$HCO$_3$ aqueous solution) for 1h at RT. Activated monolayers 98, 110 and 126 were obtained. To protect the free thiols released during the process from reoxygenation by ambient oxygen, Ar was continuously bubbled in the DTT solution. The activated monolayers were then successively dipped in bidistilled water and ethanol and then dried in a flow of N$_2$.

5.3.3. Self-Organizing Surface-Initiated Polymerization

5.3.3.1 Screening of Solvents

Electrodes with activated monolayers of initiator 98, 110 and 126 and clean ITO surfaces (used as control) were placed back-to-back to expose their conducting face in a saturated solution of the appropriate propagator 92, 105, 102 or 114. Solutions were previously deaerated by bubbling Ar. A volume of $i$Pr$_2$NEt was then added to obtain a final concentration of the base equal to 100 mM. The vial was subsequently filled with Ar using a balloon and needle, capped and the vial cap sealed with parafilm. The whole setup was then wrapped in aluminum foil and shaken at RT. Total volume was usually 300 µl and the vials were tilted to ensure the wetting of a sufficiently large area of the electrode during the polymerization process. After 24h the electrodes were taken out of the propagator solution, washed with the same solvent mixture as
used for the polymerization process and then with DMSO. In the case of architecture 128, the electrode was subsequently stirred in DMSO at 50°C overnight. Finally, the obtained architectures were rinsed with CHCl₃ and dried under flow of N₂. The UV-Vis spectrum of each electrode was recorded, from which a baseline spectrum measured on a clean ITO surface was subtracted.

5.3.3.2. Dependence on Concentration of Monomer

Procedure was the same as described under “5.3.3.1. Solvents Screening”. The propagator concentrations and solvent mixtures were as follows: propagator 92 (10-30 mM in CHCl₃/MeOH 1:1, v/v), 105 (2-30 mM, CHCl₃/TFE 1:1, v/v), 102 (5-17 mM in CHCl₃/MeOH 1:1, v/v) or 114 (5-15 mM in CHCl₃/MeOH 5:2, v/v).

5.3.3.3. Co-Polymerization

ITO electrodes were coated with 88 as described in “5.3.1.1. Initiation with Green Perylenediimide” and activated with DTT as described in “5.3.2. Activation of Monolayers”. Then the electrodes were shaken at RT in a solution of 92 (11 mM) and 102 (11 mM) in CHCl₃/MeOH 1:1, v/v with 100 mM iPr₂NEt for 24 h under Ar atmosphere. The electrodes were briefly sonicated in MeOH, then in DMSO and finally dried under flow of N₂. The UV-Vis spectrum of each electrode was recorded, from which a baseline spectrum obtained with a clean ITO surface was subtracted.

5.3.4. Templated Stack Exchange

5.3.4.1. Hydrazone-Oxime Exchange

An ITO electrode with benzaldehyde-hydrazone SOSIP 128 was placed in an aqueous solution of NH₂OH•HCl (1.0 ml, 1 M, pH 3) and stirred at 40 °C. At increasing reaction times, electrode was taken out of the vial, rinsed successively with bidistilled water and ethanol, dried in a flow of N₂ and UV-Vis absorption spectrum recorded. The electrode was then dipped in the
NH$_2$OH•HCl solution again. Cleavage of benzaldehyde-hydrazone was monitored by the disappearance of an absorption band at 300 nm. When no more changes were seen on two successive spectra, electrodes were taken out of the NH$_2$OH•HCl solution, rinsed successively with bidistilled water and ethanol, dried in a flow of N$_2$ and immediately used for covalent capture of aldehyde (vide infra).

5.3.4.2. Covalent Capture of Aldehydes

Coated ITO electrodes after NH$_2$OH treatment were placed in solutions of aldehydes (134, 135 and 136: 15 mM; 149: 15 mM; 154: 20 mM; 155: 19 mM; 157: 10 mM; 160: 20 mM; 166: 25 mM) in DMSO/AcOH 95:5, v/v. Vials were sealed with a plastic cap and parafilm and stirred in a shaking incubator. Temperature was set at 40, 45 or 50 °C, depending on the kinetic of the process. Rotation speed was set at 100 rpm. Hydrazone formation was monitored by UV-Vis measurements. For that purpose, electrodes were taken out of the aldehyde solutions, rinsed with DMSO and then ethanol, dried in a flow of N$_2$ and UV-Vis absorption spectrum recorded. The capture process took between 2 to 24h to reach an equilibrium after which no more changes were seen on the successive spectra. At this point, the resulting films on ITO electrodes (146, 147, 148, 150, 152, 153, 158, 162 and 1165) were rinsed with DMSO and stirred in the same solvent at 40° C overnight to dissolve and remove any unbound aldehydes. In addition, ion gated systems 146 to 148 were subsequently dipped in a buffer (10 mM Tris, 100 mM NaCl, pH 7.4) at 40 °C for overnight to reach protonation equilibrium.

5.3.4.3. Quantification of the Stack Exchange Yields in Ion-gated Systems

For ion-gated systems 146, 147 and 148, the yield of stack exchange $\eta_{TSE}$ was estimated from the change in absorbance at 305 nm before hydrazone-oxime exchange (128), after the removal of benzaldehyde (133) and after installation of aldehydes 135, 136 and 134, as follow. The decrease in
absorption at 305 nm $\Delta A_{305}(1)$ resulting from the removal of benzaldehyde templates was first measured on UV-Vis spectra as:

$$\Delta A_{305}(1) = A_{305}(128) - A_{305}(133) \quad \text{(Equation 13)}$$

Where $A_{305}(128)$ and $A_{305}(133)$ are the absorbance of 128 and 133 at 305 nm before and after removal of the benzaldehyde templates, respectively. Then the expected increases of absorbance at 305 nm $\Delta A_{305}(2)$ resulting from the covalent capture of aldehydes 135, 136 and 134 was calculated

$$\Delta A_{305}(2, X) = \Delta A_{305}(1) \cdot 2.09 \cdot \left[ \frac{A_{543}(128)}{A_{543}(X)} \right] \quad \text{(Equation 14)}$$

Where X stands for 147, 148 or 146 and $A_{543}$ is the absorbance of the corresponding architecture at 543 nm. Finally $\eta_{TSE}$ (in %) was determined as follow:

$$\eta_{TSE}(X) = \left[ \frac{\Delta A_{305}(3)}{\Delta A_{305}(2, X)} \right] \cdot 100 \quad \text{(Equation 15)}$$

Where $\Delta A_{305}(3)$ is the increase in absorbance experimentally measured by UV-Vis spectroscopy at 305 nm after covalent capture of aldehydes by 133 and X stands for 147, 148 or 146.

5.3.3.4. *Quantification of the Stack Exchange Yields in Double-channel Architectures*

For double channel architectures 150, 152, 153, and 165, a different procedure was applied.

First, one architecture of each type with unknown yield of stack exchange $\eta_{TSE}$ (ref) was dissolved in a mixture of DMSO/iPr$_2$NEt/$\beta$-mercaptoethanol 5000:85:7, v/v/v. The coated electrode was dipped in the denaturing mixture and stirred for 15 min at 40 °C. When the film was totally dissolved, a UV-Vis spectrum of the resulting mixture was recorded against a blank mixture of DMSO/iPr$_2$NEt/$\beta$-mercaptoethanol. In all cases, PDI was the only species that absorbed light at 530 nm. Therefore the concentration of PDI $c_{PDI}$ (in mM) in
the solution was related to the absorption of the solution at 530 nm $A_{530,\text{solution}}$ according to the Beer’s law:

$$A_{530,\text{solution}} = \varepsilon_{PDI,530} \cdot I \cdot c_{PDI} \quad \text{(Equation 16)}$$

Where $I$ is the optical path (in cm) and $\varepsilon_{PDI,530}$ is the molar absorption coefficient of PDI at 530 nm.

The other chromophore (terthiophene, $H,H$-NDI, $O,O$-NDI or quaterthiophene) present in the solution generated a blue-shifted band. Absorption maximum was at 400 nm (for terthiophene, 150), or 380 nm (for $H,H$-NDI, 152), or 476 nm (for $O,O$-NDI, 153) or 440 nm (for quaterthiophene, 165), respectively. Nevertheless, in all cases there was a partial overlap between the absorption band of the given chromophore and of PDI. Therefore, absorbance of the solution $A_{\lambda,\text{solution}}$ at the absorption maximum wavelength $\lambda$ of the chromophore, is the sum of the contributions of the two colored species.

$$A_{\lambda,\text{solution}} = \varepsilon_{PDI,\lambda} \cdot I \cdot c_{PDI} + \varepsilon_{X,\lambda} \cdot I \cdot c_{X} \quad \text{(Equation 17)}$$

Where $\varepsilon_{PDI,\lambda}$ (in mM$^{-1}$cm$^{-1}$) is the molar absorption coefficient of PDI at $\lambda$, $\varepsilon_{X,\lambda}$ (in mM$^{-1}$cm$^{-1}$) is the molar absorption coefficient of chromophore X at $\lambda$, $c_X$ (in mM) is the concentration of chromophore X and $l$ is optical path (in cm).

From these equations, $c_X$ and $c_{PDI}$ were extracted and calculated from the values of Table 9 and the ratio $R$ calculated as follow:

$$R = c_X / c_{PDI} \quad \text{(Equation 18)}$$

Quantitative yield $\eta_{TSE} = 100 \%$ was assumed for $R = 2.0$ (2:1 ratio).
Table 9. Wavelengths and molar absorption coefficients used for the calculation of stack exchange yields.

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>X</th>
<th>λ (nm)</th>
<th>εX,λ (mM⁻¹ cm⁻¹)</th>
<th>εPDI,λ (mM⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H,H-PDI</td>
<td>---</td>
<td>530</td>
<td>---</td>
<td>67.8</td>
</tr>
<tr>
<td>terthiophene</td>
<td>400</td>
<td>16.0[148]</td>
<td>16.0[148]</td>
<td>0.16</td>
</tr>
<tr>
<td>H,H-NDI</td>
<td>380</td>
<td>18.9[221]</td>
<td>18.9[221]</td>
<td>3.2</td>
</tr>
<tr>
<td>O,O-NDI</td>
<td>466</td>
<td>18.2[38]</td>
<td>18.2[38]</td>
<td>14.5</td>
</tr>
<tr>
<td>quaterthiophene</td>
<td>440</td>
<td>34.8[145]</td>
<td>34.8[145]</td>
<td>4.8</td>
</tr>
</tbody>
</table>

From these results the parameter ρ, describing how the ratio of absorbance at 530 nm to absorbance at λ (in nm) changed with increasing ηTSE, could be calculated.

\[
ρ = \frac{[R_{\text{TSE(ref)}} - R_{\text{SOSP(ref)}}]}{η_{\text{TSE(ref)}}} \quad \text{(Equation 19)}
\]

\[
R_{\text{SOSP(ref)}} = \frac{A_{\text{SOSP,λ(ref)}}}{A_{\text{SOSP,530(ref)}}} \quad \text{(Equation 20)}
\]

Where \( A_{\text{SOSP,λ(ref)}} \) and \( A_{\text{SOSP,530(ref)}} \) were the absorption of 128 at 530 nm and at λ, respectively.

\[
R_{\text{TSE(ref)}} = \frac{A_{\text{TSE,λ(ref)}}}{A_{\text{TSE,530(ref)}}} \quad \text{(Equation 21)}
\]

Where \( A_{\text{TSE,λ(ref)}} \) and \( A_{\text{TSE,530(ref)}} \) were the absorption of the respective reference architecture at 530 nm and at λ, respectively.

The stack exchange yield \( η_{\text{TSE}} \) for any given architecture was related to \( ρ \) and \( R_{\text{SOSP(ref)}} \) as follow.

\[
R_{\text{TSE}} = η_{\text{TSE}} \cdot ρ + R_{\text{SOSP(ref)}} \quad \text{(Equation 22)}
\]

Where \( R_{\text{TSE}} \) was calculated as:

\[
R_{\text{TSE}} = \frac{A_{\text{TSE,λ}}}{A_{\text{TSE,530}}} \quad \text{(Equation 23)}
\]
With $A_{TSE,\lambda}$ and $A_{TSE, 530}$ being the absorption values of the architecture at wavelength $\lambda$ and 530 nm, respectively.

5.3.5. Electrochemistry

5.3.5.1. Cyclic Voltammetry in Solution

Cyclic voltammogramms of 106 (1 mM in DMF) and 89 (0.25 mM in DCM) in solution were determined using a glassy carbon working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode. The supporting electrolyte was 100 mM Bu$_4$NPF$_6$ and the scan rate was set at 100 mV s$^{-1}$.

5.3.5.2. Cyclic Voltammetry on ITO Surfaces

Cyclic voltammograms of the bound initiators in SAMs 97, 109 and 125 were obtained using the ITO electrode as a working electrode, with a Pt wire counter electrode and an Ag/AgCl reference electrode, with 100 mM Bu$_4$NPF$_6$ in DMF as the supporting electrolyte.

The surface coverage $\Gamma$ (in mol m$^{-2}$) of the initiator was calculated from the charge corresponding to one reduction or oxidation wave $Q$ (in C), the number of electrons $N_e$ transferred during the process and the surface of the electrode $A_e$ (in m$^2$) as follow:

$$\Gamma = \frac{Q}{(N_e \cdot F \cdot A_e)}$$

(Equation 24)

Where $F$ is the Faraday constant (in C mol$^{-1}$).

5.3.6. Structural Characterization

5.3.6.1. UV-Vis Spectroscopy on ITO Surfaces

ITO electrodes coated with the different architectures were fixed on a specially designed plastic holder that maintained the samples perpendicular to the light beam of the UV-Vis spectrometer. The holder acted as a mask that
covered the entire electrode except for a small surface of 4 x 7 mm² at the bottom. The absorption spectrum of a clean ITO electrode was used as baseline.

The surface coverage \( \Gamma \) (in mol m\(^{-2}\)) of the initiator was also calculated from the absorbance of the initiator at maximum \( A_{\text{MAX}} \) (in a. u.) as follow:

\[
\Gamma = \frac{10 \cdot A_{\text{MAX}}}{\varepsilon_{\text{MAX}}}
\]  

(Equation 25)

Where \( \varepsilon_{\text{MAX}} \) (in M\(^{-1}\) cm\(^{-1}\)) is the molar absorption coefficient at the maximal absorption wavelength.

5.3.6.2. Determination of the Film Thickness

An estimate of the film thickness \( d \) (in nm) was obtained by using:

\[
d = n_{\text{layer}} \cdot d_{\text{layer}}
\]  

(Equation 26)

Where \( n_{\text{layer}} \) is the number of molecular layers in the film and \( d_{\text{layer}} \) is the intralayer distance which was assumed to be 0.35 nm. \( n_{\text{layer}} \) was calculated using:

\[
n_{\text{layer}} = \frac{x_{\text{mol}}}{(\Gamma \cdot A_{e})}
\]  

(Equation 27)

Where \( \Gamma \) (in mol m\(^{-2}\)) is the surface coverage of the electrode and \( x_{\text{mol}} \) (in mol) is the amount of molecules covering a certain area \( A_{e} \) (in m\(^2\)) of the electrode. \( x_{\text{mol}} \) was calculated using:

\[
x_{\text{mol}} = \frac{10 \cdot A_{\text{MAX}} \cdot A_{e}}{\varepsilon_{\text{MAX}}}
\]  

(Equation 28)

Where \( A_{\text{MAX}} \) (in a. u.) is the maximal absorbance of the polymer film and \( \varepsilon_{\text{MAX}} \) (in M\(^{-1}\) cm\(^{-1}\)) is the corresponding molar absorption coefficient.

5.3.6.3. Circular Dichroism Spectroscopy on ITO Surfaces

ITO electrodes coated with 128 or 150 were fixed with tape on a metallic holder that maintained the electrode perpendicular to the light beam of the CD spectrometer. The holder acted as a mask that covered the entire electrode except for a hole of 1 cm in diameter. The spectrum of a clean ITO electrode
was used as baseline and subtracted from the spectra obtained with the architectures. 10 scans were accumulated for each sample.

5.3.6.4. Atomic Force Microscopy

AFM images were acquired in tapping mode at scan rates of 1 Hz (0.25 Hz for scan area of 100 x 100 µm²). Optical images were taken using a microscope equipped on AFM.

5.3.7. Functional Characterization

5.3.7.1. Photocurrent Measurements

Coated ITO electrodes were used as a working electrode with a Pt wire counter electrode and an Ag/AgCl reference electrode. The electrodes were immersed in 4 ml of a deaerated (by bubbling Ar gas) aqueous solution of TEOA (50 mM) in Na₂SO₄ (0.1 M). The setup was irradiated with a solar simulator (area of electrode simultaneously immersed and irradiated: \( A_e \sim 0.6 \text{ cm}^2 \)). \( P_{in} \) could be varied using optics fixed on the lamp. Changes in current upon on-off switching of irradiation were measured at 0 V vs. Ag/AgCl unless stated. Current densities \( J \) (in A cm⁻²) were calculated using Equation 27.

\[
J = \frac{I}{A_e} \quad \text{(Equation 29)}
\]

Where \( I \) is the measured photocurrent (in A) generated by the area \( A_e \) (in cm²) of the electrode simultaneously irradiated and immersed in the electrolyte solution. To facilitate comparison, current densities \( J \) were normalized to give \( J_{\text{norm}} \) using transmittance \( (T) \) of the film at 737 nm (for SOSIP architectures 100 and 101), at 505 nm (for SOSIP architecture 112) or at 543 nm (for SOSIP architecture 128, double channel architectures 152, 153, 150, 165 and triple channel architectures 158 and 162) as in Equation 28.

\[
J_{\text{norm}} = \frac{J}{1-T} \quad \text{(Equation 30)}
\]
5.3.7.2. Bimolecular Recombination Efficiency

The setup was as in “5.3.7.1. Photocurrent Measurements”. Neutral density filters were used to vary the light intensity and bimolecular recombination efficiencies $\eta_{BR}$ (in %) were calculated from the dependence of $J$ (in $\mu A \text{cm}^{-2}$) on $P_{in}$ (in W cm$^{-2}$) using Equations 29 and 30.$^{[15]}$

\[
J \propto P_{in}^\alpha \quad \text{(Equation 31)}
\]

\[
\eta_{BR} = (\alpha^{-1} - 1) \cdot 100 \quad \text{(Equation 32)}
\]

5.3.7.3. I-V Curves

The setup was as in “5.3.7.1. Photocurrent Measurements”. Short circuit current $I_{SC}$ (in A) and open circuit voltage $V_{OC}$ (in V) were determined by systematically varying the applied voltage $V$ vs. Ag/AgCl on the working electrode and recording the resulting current $I$. Fill Factors FF were calculated from the maximum power $P_m$ (in W cm$^{-2}$), $I_{SC}$ and $V_{OC}$ using Equation 31.

\[
FF = \frac{P_m}{I_{SC} \cdot V_{OC}} \quad \text{(Equation 33)}
\]

5.3.7.4. Action Spectra

Coated ITO electrodes were used as working electrodes with a Pt wire counter electrode and an Ag/AgCl reference electrode. The electrodes were immersed in 4 ml of a deaerated (by bubbling Ar gas) aqueous solution of TEOA (50 mM) and Na$_2$SO$_4$ (0.1 M). The setup was irradiated with a monochromatic light (150 W Xe lamp with Oriel 1/8 m monochromator, area of electrode simultaneously immersed and irradiated: $A_e \sim 0.6 \text{ cm}^2$). Photocurrent densities $J_{SC}$ (A cm$^{-2}$) were measured at 0 V vs. Ag/AgCl and were converted into IPCE (in %) by using the Equation 32.$^{[104]}

\[
\text{IPCE} = 100 \cdot 1240 \cdot \frac{J_{SC}}{(\lambda \cdot P_{in,\lambda})} \quad \text{(Equation 34)}
\]

in which $\lambda$ (in nm) is the irradiation wavelength and $P_{in,\lambda}$ (in W cm$^{-2}$) is the irradiation intensity at $\lambda$.  

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To facilitate the comparison between systems having different thicknesses, the obtained IPCE values were further normalized using the transmittance ($T_{543}$) of the film at 543 nm to give activity $Y_{IPCE}$.

$$Y_{IPCE} = \frac{IPCE}{1-T_{543}} \quad \text{(Equation 35)}$$

5.3.7.5. Photocurrent pH Dependence

Photocurrent measurements were done as described in the above “5.3.7.1. Photocurrent Measurements” using solution of TEOA (50 mM) mobile carrier in Na$_2$HPO$_4$ (0.2 M) buffer as supporting electrolyte. Initial pH of 9.6 was decreased stepwise by addition of concentrated HCl until 6.5. Photocurrent was measured for each pH value at a $P_{in} = 83$ mW cm$^{-2}$. The current density $J_{pH}$ (in $\mu$A cm$^{-2}$) obtained at a given pH was further normalized using the current densities $J_{9.6}$ (in $\mu$A cm$^{-2}$) recorded at pH = 9.6 and $J_{6.5}$ (in $\mu$A cm$^{-2}$) at pH = 6.5 to give the activity $Y_{pH}$ according to Equation 34.

$$Y_{pH} = \frac{(J_{pH} - J_{6.5})}{(J_{9.6} - J_{6.5})} \quad \text{(Equation 36)}$$

5.3.7.6. Photocurrent Temperature Dependence

Photocurrent was recorded as described in the above “5.3.7.1. Photocurrent Measurements”. The electrochemical cell was placed in a water bath that was either cooled down below RT using ice or heated up with an electrical heating plate. Temperature T in the bath was measured with a mercury thermometer and rised stepwise by 5 °C increments, from 10 to 40 °C. Between each increment, enough time was given to the system to reach thermal equilibrium. This equilibrium was monitored upon recording photocurrent and was assumed to be reached when a constant value that did not change over a period of 100 sec was obtained. The obtained current densities $J_{SC}(T, P_{\text{light}})$ (in $\mu$A cm$^{-2}$) were fitted to the Arrhenius’ equation to give the activation energy $E_a$ (in eV) associated with each photosystem as in Equation 35.$^{[13]}$

$$J_{SC}(T, P_{\text{light}}) = J_{SC,00} \cdot \exp \left(-\frac{E_a}{k_B T}\right) \quad \text{(Equation 37)}$$
Where $J_{SC,00}$ is a factor that depends only on the light intensity, $k_B$ is the Boltzmann’s constant ($8.6173 \cdot 10^{-5}$ eV K$^{-1}$) and $T$ is the temperature (in K) at which $J_{SC}$ ($T, P_{light}$) was measured.

In the case of architectures 150, 152, 153, 158, 162 and 165, the electrochemical cell was filled with 4 ml of an aqueous solution of TEOA (50 mM) in Na$_2$SO$_4$ (0.1 M). $P_{in} = 83$ mW cm$^{-2}$.

For ion gated systems 146 and 147, the cell was filled with 4 ml of an aqueous solution of TEOA (50 mM) in Na$_2$H$_2$PO$_4$ (0.2 M) buffer at pH 7.7. $P_{in} = 63$ mW cm$^{-2}$. For comparison purpose, 128 was measured in those conditions as well.
5.4. Abbreviations

A = Ampere
a. u. = Absorption Unit
AFM = Atomic Force Microscope
Alloc = Allyloxycarbonyl-
AM1 = Austin Model 1
Γ = Surface Coverage
Boc = tert-Butyloxycarbonyl-
\( c \) = Concentration
\( \varepsilon_{\text{SOSIP}} \) = Critical SOSIP Concentration
C = Coulomb
Cbz = Carboxybenzyl-
CD = Circular Dichroism
CN\(_2\)-PDI = 1,7-Dicyano PDI
CN-PDI = Monocyano PDI
co-SOSIP = co-Polymerization by SOSIP
c-PDI = Core-Substituted PDI
CV = Cyclic Voltammetry
d = Thickness
d\( c \) = Critical Thickness
dba = Tris(dibenzylideneacetone)dipalladium(0)
DCM = Dichloromethane
DFT = Density Function Theory
DMF = N,N-Dimethylformamide
DMSO = Dimethylsulfoxide
DOSY = Diffusion-Ordered Spectroscopy
dppf = 1,1’-Bis(diphenylphosphino)ferrocene
DTT = DL-Dithiothreitol
\( \Delta E_g \) = Optical Bandgap
\( \Delta \varepsilon \) = Davydov Splitting
\( \varepsilon \) = Molar Absorption Coefficient
E = Electric Field
\( E \) = Energy
\( e^- \) = Electron
\( E_{1/2} \) = Half-wave Potential
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Term</th>
</tr>
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<tbody>
<tr>
<td>$E_a$</td>
<td>Activation Energy</td>
</tr>
<tr>
<td>EDCI</td>
<td>$N'-(3$-Dimethylaminopropyl$)-N'$-ethylcarbodiimide hydrochloride</td>
</tr>
<tr>
<td>$E_{\text{HOMO}}$</td>
<td>HOMO Energy</td>
</tr>
<tr>
<td>$E_{\text{LUMO}}$</td>
<td>LUMO Energy</td>
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<tr>
<td>$E_{\text{ox}}$</td>
<td>Oxidation Potential</td>
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<tr>
<td>$E_{\text{red}}$</td>
<td>Reduction Potential</td>
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<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
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<td>eV</td>
<td>Electron-Volt</td>
</tr>
<tr>
<td>F</td>
<td>Faraday Constant</td>
</tr>
<tr>
<td>Fc</td>
<td>Ferrocene</td>
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<tr>
<td>FF</td>
<td>Fill Factor</td>
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<tr>
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<td>Frontier Molecular Orbitals</td>
</tr>
<tr>
<td>Fmoc</td>
<td>Fluorenylmethyloxycarbonyl-</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster Resonant Energy Transfer</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
</tr>
<tr>
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</tr>
<tr>
<td>H,H-PDI</td>
<td>Unsubstituted PDI</td>
</tr>
<tr>
<td>$h^+$</td>
<td>Hole</td>
</tr>
<tr>
<td>HATU</td>
<td>$o-(7$-Azabenzo[a]triazole-1-yl$)-N,N,N',N'$-tetramethyluronium hexafluorophosphate</td>
</tr>
<tr>
<td>HBTU</td>
<td>$o-(Benzotriazole-1-yl$)-$N,N,N',N'$-tetramethyluronium hexafluorophosphate</td>
</tr>
<tr>
<td>HMBC</td>
<td>Heteronuclear Multiple-Bond Connectivity</td>
</tr>
<tr>
<td>HOBt</td>
<td>Hydroxybenzotriazole</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>HSQC</td>
<td>Heteronuclear Single-Quantum Coherence</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
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<tr>
<td>$i\text{Pr}_2\text{NEt}$</td>
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</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>$J$</td>
<td>Current Density</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann Constant</td>
</tr>
<tr>
<td>$l$</td>
<td>Optical Path</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>Electron Mobility</td>
</tr>
</tbody>
</table>
μ_h: Hole Mobility
MeOH: Methanol
Mp.: Melting Point
MV: Methylviologen
η: Power Conversion Efficiency
η_{BR}: Bimolecular Charge Recombination Efficiency
N,N-PDI: 1,7-Dipyrrrolidinyldi PDI
NDI: Naphtalediimide
N_e: Number of Electrons
n_{layer}: Number of Layers
NMP: N-Methylpyrrolidinone
NMR: Nuclear Magnetic Resonance
NOESY: Nuclear Overhauser Effect Spectroscopy
N_v: Number of Photons
\( o-\): ortho-
\( O,O-NDI\): Diethoxy-NDI
OC: Open Circuit
OFET: Organic Field-Effect Transistor
OMARG: Oriented Multicomponent Antiparallel Redox Gradients
OPE: \( para\)-Oligophenylethynyl
OPV: Organic Photovoltaics
OpV: Oligo(\( para\)-phenylene vinylenes)
PCBM: Phenyl C_{61} Butyric Acid Methyl Ester
PCE: Power Conversion Efficiency
PDA: Perylenedianhydride
PDI: Perylenediimide
\( p-\): para-
P_{in}: Irradiation Intensity
POP: \( para\)-Octiphenyl
P_{out}: Output Power Density
QD: Quantum Dot
R_a: Average Roughness
ROP: Ring-Opening Polymerization
rpm: Revolution Per Minute
RT: Room Temperature
\( \sigma_c\): Electrical conductivity

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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAM</td>
<td>Self-Assembled Monolayer</td>
<td></td>
</tr>
<tr>
<td>SAXS</td>
<td>Small Angle X-Ray Scattering</td>
<td></td>
</tr>
<tr>
<td>SC</td>
<td>Short Circuit</td>
<td></td>
</tr>
<tr>
<td>SHJ</td>
<td>Supramolecular Heterojunction</td>
<td></td>
</tr>
<tr>
<td>SIP</td>
<td>Surface-Initiated Polymerization</td>
<td></td>
</tr>
<tr>
<td>SOSIP</td>
<td>Self-Organizing Surface-Initiated Polymerization</td>
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</tr>
<tr>
<td>T</td>
<td>Temperature</td>
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<tr>
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<td>( o-\text{(Benzotriazole-1-yl)}-N,N',N'\text{-tetramethyluronium Tetrafluoroborate} )</td>
<td></td>
</tr>
<tr>
<td>( t)-Bu</td>
<td>tert-Butyl-</td>
<td></td>
</tr>
<tr>
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<td>Triethanolamine</td>
<td></td>
</tr>
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<td>Trifluoroacetic Acid</td>
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Chapter 6

REFERENCES


[215] Y. Zhao, unpublished results.

