Synthetic supramolecular photoystems

BHOSALE, Rajesh

Abstract

In this thesis, three different bioinspired approaches have been introduced to build up vertically oriented SHJ photosystems. Firstly, the halogenated red zipper architecture was assembled from the anionic HH-NDI-OPE initiator and the cationic and anionic NBr-NDI-OPE propagators on a gold electrode. This zipper assembly generates high photocurrent and high efficiency. Secondly, the non-halogenated ON-NDI-OPE zipper assembly was introduced. Compared with the halogenated zipper less photocurrent and same critical thickness was observed. The lower photocurrent was attributed to the higher HOMO energy of the ON-NDI than the NBr-NDI. The third antiparallel redox gradients architecture generates approximately the same photocurrent and double critical thickness than the NBr-NDI-OPE zipper assembly.

Reference


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Synthetic Supramolecular Photosystems

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To my parents
List of Publication


Résumé

Les assemblages Crémaillère (ci-après Zipper) ont été introduits précédemment par le Prof. Stefan Matile comme une méthode élégante de bâtir des photosystèmes orientés verticalement dont les voies de transport des électrons et des trous sont alignées co-axialement résultant à une hétérojonction supramoléculaire (SHJ) bien ordonnée. Dans ce but il est nécessaire d’avoir des bâtons rigides moléculaires (rigid rod molécules) équipés de naphtalènes diimines (NDI) cationiques et anioniques dans le rôle de propagateurs ainsi qu’un initiateur anionique capable de se lier à une surface d’or. En tant que complément au travail précédent qui employé des para-oligophenylènes (POP) en tant que bâton rigide on se sert des Oligo(1,4-phenyléneethynylène) en raison de ses propriétés plus favorables.

Lors de ce travail des différentes approches bio inspirées ont été introduites pour la construction des photosystèmes SHJ verticalement orientés grâce à l’architecture zipper. Tout d’abord, un assemblage zipper halogéné rouge Au-54-(55-56), a été assemblé avec le initiateur anionique HH-NDI-OPE 54 et les propagateurs cationique 55 et anionique 56 NBr-NDI-OPE sur une électrode d’or. L’initiateur HH-NDI-OPE 54 a été synthétisé en 21 étapes partant des substances commerciales. Les propagateurs cationique 55 et anioniques 56 ont été synthétisés en 6 étapes à partir du bâton rigide OPE facilement disponible ainsi que des substances commerciales. La réussite lors de l’assemblage du NBr-NDI-OPE a été confirmée par la inhibition positive de la croissance du zipper lors des expériences de capping.

La comparaison entre le, hautement organisé, assemblage zipper NBr-NDI-OPE, la version moins organisée « couche-par-couche » du NBr-NDI-OPE et l’assemblage zipper NBr-NDI-POP montre des meilleures propriétés pour le assemblage zipper NBr-NDI-OPE soit au niveau du photocourant (101.6 µA/cm² contre 48.2 µA/cm² pour couche-par-couche et 70.0 µA/cm² pour l’assemblage zipper NBr-NDI-POP), soit par rapport à l’épaisseur critique (20 couches contre 8 couche et 10 couches) ainsi que pour l’efficacité (0.033% contre 0.021% et 0.022%). Le spectre d’action de l’assemblage zipper NBr-NDI-OPE indique que les OPE sont planaires et qu’ils contribuent au processus de récolte de la lumière ainsi qu’à la génération de photocourant avec les accepteurs d’électrons NBr-NDIs.
La séparation des charges pour le propagateur cationique NBr-NDI-OPE 55 a été mis en évidence par spectroscopie d'absorption transitoire en collaboration avec le groupe Vauthey. Des mesure dans une microbalance à quartz montrent qu’aussi bien l’assemblage zipper NBr-NDI-OPE comme le assemblage couche-par-couche NBr-NDI-OPE ne s’arrêtent pas mais qu’ils continuent a augmenter en épaisseur au delà de l’épaisseur critique déterminé par les mesure de photocourant. Ceci suggère que la saturation du photocourant est due à la recombinaison des charges.

Une version non-halogéné jaune ON-NDI-OPE de l’assemblage zipper Au-54-(90-91)ₙ a été introduite par la suite. La synthèse des propagateurs 90 et 91 ON-NDI-OPE a été accomplie en 8 étapes en partant du bâton rigide OPE facilement disponible ainsi que l’acide 1,4,5,8-naphthalènetetracarboxylique dianhydre. Lors de la comparaison avec le assemblage zipper halogéné NBr-NDI-OPE on observe un plus bas photocourant et la même épaisseur critique. Ce photocourant inférieur a été attribué a une énergie de l’HOMO plus haute pour le NO-NDI que pour le NBr-NDI. Cette conclusion a été corroborée par une contribution moins significative du ON-NDI au spectre d’action de photocourant.

Dans le but de prévenir la recombinaison des charges l’idée des gradients redox antiparallèle a été introduit. Pour ceci on a assemblé le zipper rouge NBr-NDI-OPE au-dessus de l’assemblage zipper jaune ON-NDI-OPE. Cette architecture de n/p supramoléculaire hétérojonctions avec des gradients redox orientés, multicolores et antiparallèles (OMARG-SHJs) Au-34-(35-36)ₙ-
35-(56-55)ₙ génère approximativement le même photocourant et un épaisseur critique 2 fois plus important (38 couches) en comparaison au assemblage zipper NBr-NDI-OPE. L’assemblage inverse Au-54-(55-56)ₙ-55-(36-35)ₙ génère une photocourant moins important que l’OMARG-SHJ original. Cette diminution du photocourant prouve la mauvaise disposition des gradients redox aux voies n-conductrice et p-conductrice du OMARG-SHJ inversé. Ce résultat montre que les OMARG-SHJ existent dans cette architecture de zippers et qu’ils ont une importance envers sa fonction.

Pour compléter le concept des OMARGs le raccordement covalent a aussi été envisagé. Pour ceci la synthèse des propagateurs cationique 119 et anionique 124 a été accomplie en 7 étapes. Ces propagateurs sont aussi dotés des unités diacétylène photopolymérisables.
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## Abbreviations

### Analytics

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<tr>
<td>δ</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>ν</td>
<td>Frequency</td>
</tr>
<tr>
<td>[α]_D^20</td>
<td>Specific rotation</td>
</tr>
<tr>
<td>COSY</td>
<td>Correlation spectroscopy</td>
</tr>
<tr>
<td>DEPT</td>
<td>Distortionless enhancement by polarization transfer</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray ionization</td>
</tr>
<tr>
<td>HMBC</td>
<td>Heteronuclear multiple bond connectivity</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>HR</td>
<td>High resolution</td>
</tr>
<tr>
<td>HSQC</td>
<td>Heteronuclear single quantum coherence</td>
</tr>
<tr>
<td>IR or FT-IR</td>
<td>Fourier-transform infrared</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
<tr>
<td>M</td>
<td>Molar mass</td>
</tr>
<tr>
<td>m.p.</td>
<td>Melting point</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectroscopy</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix assisted laser desorption ionization</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PTLC</td>
<td>Preparative thin layer chromatography</td>
</tr>
<tr>
<td>R_f</td>
<td>Retention factor</td>
</tr>
<tr>
<td>RP</td>
<td>Reverse phase</td>
</tr>
<tr>
<td>t_R</td>
<td>Retention time</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>Vis</td>
<td>Visible</td>
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<tr>
<td>z</td>
<td>Charge</td>
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### Abbreviations

#### Protecting Groups
- Alloc: Allyloxycarbonyl
- Cbz: Benzyloxycarbonyl
- Pnz: p-Nitrobenzyloxycarbonyl
- /Bu: tert-Butyl

#### Reagents and Solvents
- ACN: Acetonitrile
- DCM: Dichloromethane
- DMA: N,N-Dimethylaniline
- DMSO: Dimethylsulfoxide
- DMF: N,N-Dimethylformamide
- DTBP: Di-t-Bu-pyridine
- en: Ethylenediamine
- Fc: Ferrocene
- Glu: L-Glutamic acid
- HATU: 2-(7-Aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
- Lys: L-Lysine
- OPE: Oligophenyleneethynyl
- POP: p-Oligophenyl
- TBAF: Tera-n-butylammonium fluoride
- TEOA: Tetracyanoethylene
- TEA: Triethylamine
- TFE: 2,2,2-Trifluoroethanol
- THF: Tetrahydrofuran
- TFA: Trifluoroacetic acid

#### Symbols and Other Abbreviations
- 1D: One-dimensional
- 2D: Two-dimensional
- Δ: Difference
- μ: Micro (10⁻⁶)
Abbreviations

$Ac$  Acetyl
$c$  Concentration
cat  Catalyzed
d  Diameter
$I_{sc}$  Short-circuit current
$J_{sc}$  Short-circuit current density
$m$  multiplet
$m$  Milli ($10^{-3}$)
$max$  maximum
$\text{Mol. Wt}$  Molecular weight
$P_{in}$  Power of incident light
$P_{\text{max}}$  Maximum power point
$\eta$  Power conversion efficiency
$q$  Quartet
quant  Quantitative
$R$  universal gas constant
$rt$  room temperature
$s$  Singulett
$V_{oc}$  Open-circuit voltage
$T$  Temperature
t  Triplet
t  Time
$\text{vs}$  Versus
wWeak  Weak
$\lambda$  Wavelength

Units

Å  Ångstrom
atm  Atmosphere
$^\circ C$  Degree Celsius
g  Gram
Hz  Hertz
h  Hour
L  Liter
m  Meter
### Abbreviations

<table>
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<tbody>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>M</td>
<td>Moles per Liter</td>
</tr>
<tr>
<td>mol</td>
<td>Moles</td>
</tr>
<tr>
<td>nm</td>
<td>Nano meter</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
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<tr>
<td>%</td>
<td>Percent</td>
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<tr>
<td>s</td>
<td>Seconds</td>
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### Photocurrent Related

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<tr>
<td>BHJ</td>
<td>Bulk $n/p$-heterojunction</td>
</tr>
<tr>
<td>CR</td>
<td>Charge recombination</td>
</tr>
<tr>
<td>CS</td>
<td>Charge separation</td>
</tr>
<tr>
<td>CSS</td>
<td>Charge-separated state</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-current conversion efficiency</td>
</tr>
<tr>
<td>PCS</td>
<td>Photoinduced charge separation</td>
</tr>
<tr>
<td>SHJ</td>
<td>Supramolecular $n/p$-heterojunction</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
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CHAPTER 1

INTRODUCTION

1.1 Introduction

Photosynthesis is of paramount importance for our planet because it converts sunlight energy into the organic molecules of biomass, which are the building blocks of all living organisms. Photosynthetic organisms are ubiquitous on earth and they use many types of light-harvesting and electron transport systems. However, all of these systems use the same basic strategy, in which light is initially absorbed by antenna proteins containing many chromophores. The absorption is followed by excitation energy transfer to the reaction centre proteins that contain a special pair of chlorophylls, in which the captured energy is converted into chemical energy using electron-transfer reactions.

The photosynthetic unit (PSU) of purple bacteria is the most studied and well characterised. By the end of 20th century, X-ray structures of the purple bacteria PSU had been analysed. The PSU unit of purple bacteria contains two types of light harvesting complexes, light-harvesting complex I (LH-I) and light-harvesting complex II (LH-II) (Figure 1). The LH-I light-harvesting antenna surrounds the reaction centre (RC), whereas the LH-II antenna is not in direct contact with the RC. The LH-I and LH-II
light-harvesting antennas are composed of bacteriochlorophylls arranged in a ring form. The light energy absorbed by the LH-II antenna is transferred via an energy cascade to LH-I. The excitation energy reached at LH-I is further transferred effectively to the special pair of chlorophylls in the RC.

**Figure 1:** The arrangement of light-harvesting complexes in the photosynthetic unit of purple bacteria. LH-I and LH-II are light-harvesting antennas with protein backbones marked in purple and blue. The green and yellow molecules in LH-I and LH-II are chlorophylls and carotenoids respectively. The subunits of reaction centre RC are in yellow, red and grey.⁹

The key molecular components of the RC are the bacteriochlorophyll “special pair” (a₁/a₂), a bacteriochlorophyll monomer (a₃), bacterioiophenophytin (a₄) and ubiquinone (a₅/a₆). In the RC, excitation of the “special pair” of chlorophylls (a₁/a₂) is followed by very fast (~3 ps) cascade electron transfer to the primary acceptor (a₄). The next step involves fast (~200 ns) electron transfer from the primary acceptor (a₄) to the remote ubiquinone
acceptor (a/aₐ) (Figure 2). The hole left behind is transferred in the opposite direction along an orthogonal redox gradient, where it is ultimately oxidised by water. To achieve the high efficiency of photosynthesis these cascade electron/hole transfer pathways are essential.

**Figure 2**: a) A simplified structure of the reaction centre of the biological photosystems (a₁/a₂, special pair of bacteriochlorophylls; a₃, bacteriochlorophyll monomer; a₄, bacteriopheophytin; a₅/a₆, ubiquinone), b) Orbital energy diagram showing (solid, HOMO; dashed, LUMO) electron (e⁻; a, electron acceptors) and hole (h⁺; d, electron donor = hole acceptors) transfers to the final destinations.

The understanding of electron/hole transfer reactions in photosynthesis enables the development of key designs for fuel production through artificial photosynthesis and the development of organic photovoltaics. Natural photosynthetic systems have been mimicked in various clever ways by synthetic chemists, who have produced photosynthetic ring-like structures using covalent or supramolecular approach. In the construction of organic photovoltaics, the most straightforward approach is to place a macroscopic layer of electron- or n-semiconducting material next to that of a hole- or p-semiconducting material. In such a bilayer structure, photogenerated excitons dissociate at the donor-acceptor interface and generate electrons and
holes (Figure 3 (a)). The generated charges are transported to their respective electrodes to generate photocurrent. The drawback of this approach is that the active interfacial areas and the exciton dissociation efficiency are limited in the bilayer structure.

Increased active interfacial areas and thus improved exciton dissociation efficiencies can be achieved by blending the $n$-semiconducting and $p$-semiconducting materials. The interlaced donor/acceptor-layers in such organic solar cells are referred to as bulk $n/p$-heterojunctions (BHJs) (Figure 3 (b)). These BHJ photosystems are normally prepared by co-sublimation or the spin-coating of a mixture of donor/acceptor material. This kind of BHJ architecture provides continuous pathways in each material from the interface to the respective electrodes. A maximized exciton dissociation is achieved at an increased donor-acceptor interface, hence, the photon-to-electron conversion efficiency is dramatically increased. However, the charge (electron and hole) mobility is reduced in BHJs due to the poor organization and increasingly discontinuous donor and acceptor domain.

![Exciton dissociation diagram](image)

**Figure 3:** Exciton dissociation at the donor-acceptor interface in a) bilayer and b) bulk $n/p$-heterojunction architecture.
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The top-down approaches to improve the organization and thus the conductivity in photosystems have been done in various clever ways including the use of different solubilizers, dendritic polymers, covalent dyad systems and mixed crystals.\textsuperscript{19,22-26} Increasing organization of BHJs ultimately lead to a situation where \textit{n}- and \textit{p}-conducting channels are separated and aligned on the molecular level. These highly organized systems are referred to as supramolecular \textit{n/p}-heterojunctions (SHJs) (Figure 4).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{The energy diagram (left) and the architectur design (right) of supramolecular \textit{n/p}-heterojunctions.}
\end{figure}

A supramolecular approach for the formation of \textit{n/p}-heterojunctions allows for the development of ordered nanostructures with high conductivity and the ability to implement complexity in the system. In ordered nanostructures, the different colored chromophores (donor and acceptor) absorb light over the entire visible range efficiently and generate holes and electrons at the \textit{n/p}-heterojunction. The generated holes and electrons should funnel quickly, direct them in opposite directions to the respective electrodes via oriented co-axial molecular \textit{n}- and \textit{p}-conducting channels, and produce photocurrent. This ideal ordered and oriented SHJ architecture having
multicoloured antiparallel redox gradients has been termed OMARG-SHJs (Figure 5).

![Energy diagram and architecture of oriented multicoloured antiparallel redox gradient supraomolecular heterojunctions (OMARG-SHJs) photosystems.](image)

**Figure 5**: Energy diagram and architecture of oriented multicoloured antiparallel redox gradient supraomolecular heterojunctions (OMARG-SHJs) photosystems.

### 1.2 Characterisation Methods of Synthetic Supramolecular Photosystems

To understand the electron transfer process and the generation of photocurrent, the characterisation of synthetic supramolecular photosystems begins with the determination of frontier energy orbital levels (HOMO-LUMO levels) of the $n$- and $p$-conducting materials by cyclic voltammetry and absorption spectroscopy. The charge separation (CS) and the charge recombination (CR) kinetics are measured using various spectroscopic measurements including time-resolved fluorescence and transient absorption measurements.$^{27}$

The performance of supramolecular photosystems is mainly characterised by a photocurrent-voltage curve ($J$-$V$ curve or profile) and a
photocurrent-layer profile (J-L profile). A typical J-V curve is depicted in Figure 6 and describes the dependence of the photocurrent density (J) on the applied voltage (V). The performance of a supramolecular photosystem is determined by extracting key parameters from the J-V curve such as: 1) short-circuit current density \(J_{sc}\), 2) open-circuit voltage \(V_{oc}\), 3) fill factor \(FF\) and 4) power conversion efficiency \(\eta_{eff}\).

\[ J \quad \text{(\(\mu\text{A/cm}^2\))} \]

\[ V \quad \text{(mV)} \]

\[ J_{mp}, V_{mp}, V_{oc} \]

\[ J_{sc}, \eta_{eff} \]

\[ FF \]

\[ P_{max} \]

**Figure 6:** Ohmic (dashed) and non-ohmic (solid) J-V curves with indication of key parameters.

The short-circuit current \(I_{sc}\) is the electric current that flows through the cell under illumination at zero applied voltage. Considering the dependence of \(I_{sc}\) on the active area of the cell, one can introduce the short circuit current density \(J_{sc}\) by dividing \(I_{sc}\) through the area of the architecture. The \(J_{sc}\) is determined by dividing the measured \(I_{sc}\) by the active area of the cell. The \(V_{oc}\) is the maximum photovoltage that can be generated in the cell and corresponds to the voltage where current under illumination is zero. In organic photovoltaics the \(V_{oc}\) is the difference between the HOMO energy level of the \(p\)-conductor material and the LUMO energy level of the \(n\)-conducting material.
material. The $V_o$ is strongly influenced by other parameters such as dark current, device connections in series, thickness of the layers, temperature and Fermi levels of the working electrodes.

The maximum power point ($P_{\text{max}}$) is the point where the product of current density ($J$) and voltage ($V$) reaches its maximum value ($J_{\text{mp}} \times V_{\text{mp}}$) and is given as $P_{\text{max}} = J_{\text{mp}} \times V_{\text{mp}}$. This product also corresponds to the area of the smaller grey rectangle indicated in Figure 6. The $FF$ is a ratio of the $P_{\text{max}}$ (grey rectangle) and the product of the $J_{\text{sc}}$ and the $V_{oc}$ (larger rectangle in Figure 6) and describes the squareness of the $J$-$V$ curve. The fill factor can be represented via Equation 1.

$$FF = \frac{P_{\text{max}}}{I_{\text{sc}} \times V_{\text{oc}}}$$  \hspace{1cm} \text{Equation 1}

Ideally, the fill factor should be one, but losses due to transport and recombination normally results in values between 0.2-0.7. The linear ("ohmic") $J$-$V$ curve has a low $FF$ of 0.25. The optimized BHJ solar cell has a $FF$ of 0.61. The $\eta_{\text{eff}}$ of a solar cell is the ratio between $P_{\text{max}}$ and the power of incident light $P_{\text{in}}$ and can be represented by Equation 2. Optimised organic solar cells have a $\eta_{\text{eff}}$ in the range of 5-6%.\textsuperscript{30,31}

$$\eta_{\text{eff}} = \frac{P_{\text{max}}}{P_{\text{in}} \times 100} = \frac{J_{\text{sc}} \times V_{oc} \times FF}{P_{\text{in}} \times 100}$$ \hspace{1cm} \text{Equation 2}

The ideal OMARG-SHJ photosystem should have a high $FF$, a high $V_{oc}$ and a comparably high $J_{\text{sc}}$. The high $V_{oc}$ in OMARG-SHJ photosystems could be due to a large HOMO-LUMO energy difference in the redox gradients. The high $J_{\text{sc}}$ in OMARG-SHJ photosystems could be because the colored chromophores absorb light over the entire visible range.

The $J$-$L$ profile of a supramolecular photosystem describes the dependence of photocurrent density on the thickness of, or the number of layers
deposited on the conducting surface. A typical $J-L$ profile is depicted in Figure 7. Ideally, the light absorbance of the film increases with an increasing number of layers, generating more charges and therefore increasing the photocurrent. At the beginning, the $J_{sc}$ increases linearly with the increasing number of layers. The increasing photocurrent density is saturated at a critical thickness. At this point the photocurrent density is at its maximum ($J_{\text{max}}$). Further deposition of layers could flatten out or even decrease the photocurrent density (Figure 7 bold). The critical thickness indicates the distance that charges (holes and electrons) can travel without recombining. The critical thickness of the supramolecular photosystem could be increased with the addition of redox gradients in the $n$- and $p$-conducting channels.

![Figure 7: Linear (dashed) and bell-shaped (solid) $J-L$ curves with key parameters.](image)

The incident photon-to-current conversion efficiency (IPCE) or the external quantum efficiency of the synthetic supramolecular photosystem is defined as the number of electrons collected under short-circuit condition
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divided by the number of incident photons. The IPCE can be represented by following Equation 3. A plot of the IPCE versus the excitation wavelengths is termed a photocurrent action spectrum. From the photocurrent action spectrum the photocurrent generated by individual chromophores in the supramolecular photosystems can be quantified.

\[
\text{IPCE (\%)} = \frac{1240}{\lambda \text{ (nm)}} \times \frac{J_{\text{sc}}}{P_{\text{in}}}
\]

Equation 3

Surface roughness of the synthetic supramolecular photosystems can be measured by AFM. The smoother surfaces of artificial photosystems have been associated with highly ordered structure and thus high efficiencies.

1.3 Supramolecular n/p-Heterojunctions (SHJs) in Solution

Over several years of research a collection of electron-rich aromatic systems (e.g., \(\pi\)-basic hexabenzocoronenes (HBCs)) have been found to be capable of donating their HOMO aromatic electrons to the LUMO of electron-poor aromatics (e.g., \(\pi\)-acidic naphthalenediimides (NDIs)) after photoexcitation to allow charge separation and charge transfer. In the ideal SHJs assembly architecture the hole (h\(^+\)) and electron (e\(^-\)) conductors should be positioned co-axially and in close proximity. The creation of an ideal SHJs architecture is a big challenge because a programmed assembly such as 1 with h\(^+\) and e\(^-\) conducting \(\pi\)-stacks from \(\pi\)-basic and \(\pi\)-acidic aromatics is unfavourable (Figure 8). Iverson and co-workers have reported that the complementary \(\pi\)-acidic NDI and \(\pi\)-basic 1,5-dialkoxynaphthalene (DAN) aromatic oligomers 2 and 3 form charge transfer complexes such as the double helix 4 via aromatic donor acceptor interactions.
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Figure 8: Representation of the ideal programmed supramolecular n/p-heterojunction assembly architecture 1. Formation of the favourable double helix 4 from the π-acidic and π-basic oligomers 2 and 3.

Wasielewski and co-workers have demonstrated that the multichromophoric hybrid molecule 5 self-assembles into ordered nanoparticles 6 with SHJ-like characteristics (Figure 9). The multichromophoric hybrid 5 is composed of four peripheral perylene-3,4:9,10-teracarboxydiimide (PDI) electron-accepting chromophores attached to a central zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP) electron donor. The multichromophoric hybrid 5 self-assembles into the nanoparticles 6 via face-to-face π-stacks of PDIs from neighbouring monomers. The obtained PDI stacks are well known electron transporting channels. Photoexcitation of the nanoparticles 6 results in quantitative charge separation in 3.2 ps to form a ZnTPP⁺PDI⁻ radical ion pair. Charge recombination occurs more slowly (7.2 ns).
Figure 9: Structure of the multichromophoric hybrid molecule 5, self-assembled into the nanoparticles 6.

Würthner and co-workers have reported the first example of a supramolecular $n/p$-heterojunction assembly. The supramolecular trimer 7 was obtained from two oligo $p$-phenylene vinylene (OPV) donors and a core-substituted PDI acceptor (Figure 10). The trimer 7 self-assembles into
left-handed helices that further assembled into a right-handed nanometre-scale super coil. The well defined co-aggregated OPV-PDI-OPV exhibits photoinduced electron transfer on a subpicosecond time scale, thereby supporting the existing of SHJ architecture. Poor diode behaviour found upon spin coating of the trimer 7 on the conducting indium tin oxide (ITO) surface was attributed to the wrong lateral orientation of the helices relative to the surface.

![Figure 10: Structure of the supramolecular trimer 7.](image)

Aida and co-workers recently reported an elegant example of formal SHJ architecture in the formation of bilayer nanotubes 9. The bilayer nanotubes 9 were made from the self assembly of trinitrofluorenone (TNF) appended HBCs amphiphiles 8 (Figure 11). In the nanotubes 9, the electron accepting TNFs are situated at the inner and outer surface and form co-axial n-conducting channels next to the electron donating graphitic layers of the \( \pi \)-stacked HBC \( p \)-conducting channel. The HBC \( \pi \)-stacks rank among the best \( p \)-conductors. These formal SHJ architecture nanotubes generated photocurrent when spin-coated onto electrodes. Aida and co-workers also reported mixed nanotubes with reduced TNF functionality. In comparison to the formal SHJs of the homotropic nanotubes, mixed nanotubes generate higher photocurrents.
The active architecture of the nanotubes was also stabilized by covalent cross-linking using ring-opening metathesis polymerisation (ROMP).  

**Figure 11:** Structure of HBC-TNF amphiphile 8 self assembled into bilayer nanotubes 9.

### 1.4 Oriented Supramolecular $n/p$-Heterojunctions (SHJs) on Conducting Surfaces

The creation of supramolecular $n/p$-heterojunction architectures on conducting surfaces is much more challenging than producing self-assembled SHJ architectures that are formed in solution. For the creation of such oriented architectures on solid surfaces, the layer-by-layer (LBL) assembly is a classical
bottom-up approach. Reynolds and co-workers have fabricated LBL multilayer films for photovoltaic cells. In an example of this type of fabrication, conducting ITO electrodes were sequentially immersed into a dilute solution of the conjugated polyanions 10 and poly or dications such as 11 with a rinsing step in between. The resultant, charge-inverted bilayer ITO-10-11 was dipped repeatedly by following the same sequence as above in order to build up the multilayer film ITO-(10-11)_n LBL architecture (Figure 12). The obtained LBL architectures were used for photovoltaic cells, in which the phenylene ethylene based conjugated polymer 10 were used as an electron donor and the water soluble cationic fullerene C60 derivate 11 was used as an electron acceptor. The bell-shaped J-L curve of the ITO-(10-11)_n LBL architecture revealed an excellent critical thickness of ~100 layers. The J-V curve of the ITO-(10-11)_n LBL architecture revealed a power conversion efficiency of \( \eta_{\text{eff}} = 0.041\% \), claimed to be the best among LBL photosystems.
Recently, Shi and co-workers fabricated multilayer films of the electron donor oligopyrene 12 and the electron acceptor PDI 13 via LBL deposition (Figure 13). The resultant LBL architecture ITO-(12-13)_n shows prompt ON-OFF response to photocurrent generation with illumination. The J-L curve of the LBL architecture ITO-(12-13)_n revealed a critical thickness of 10 layers, which is significantly lower than that of the LBL architecture ITO-(10-11)_n. The roughness of the LBL deposited film increases from 2.6 to 4.7 nm (rms) with increasing thickness.

Figure 12: Supramolecular layer-by-layer assembly for donor-acceptor architectures.
In a seminal contribution, Guldi and co-workers recently reported an LBL photosystem. They introduced carbon nanotubes 15 as electron acceptors with the tetra phenyl porphyrin (TPP) 14 as an electron donor (Figure 14). The cationic pyrene donor 16 was used as a charged solubilizer for the carbon nanotubes via strong $\pi$-$\pi$ interactions. The resultant LBL photosystem ITO-(14-15/16)$_n$ exhibits a linear J-L curve up to 17 layers. The photoactivity of the porphyrin was confirmed by measuring the photocurrent action spectrum of the system.
1.5 Vertically Oriented SHJs on Conducting Surfaces

The all above reported LBL photosystems are easily accessible and formed supramolecular n/p-heterojunctions. The main limitations of these LBL photosystems are poor organization and horizontal orientation of the adjacent hole and electron conducting layers. In this case, holes or electrons generated in layers distant from electrode surface can not be efficiently transported to the respective electrodes. Polymer brushes appear as an ideal example to achieve the desired vertical alignment of transporting layers for efficient charge collection at the electrodes.47,48

Huck and co-workers presented a new approach to achieve vertical alignment of conductors by using surface-initiated polymerization. In the polymer brush synthesis, the triphenylamine acrylate monomer 18 was polymerized using atom transfer radical polymerization (ATRP) directly onto the transparent conducting ITO electrode modified with an initiator (ITO-17)
The obtained ITO-19 films of polyacrylate brushes with hole transporting triarylamine side groups were soaked in a solution of CdSe nanocrystals (20). The obtained substrates were annealed at 150 °C to replace some of the pyridine ligands of the CdSe nanocrystal acceptors with the triarylamine side groups of the polymer chain. The obtained structure ITO-19-20 gave distinct vertical pathways in each component for efficient transport of electrons and holes to the electrodes. The photocurrent density generated by the ITO-19-20 polymer device is up to three orders of magnitude higher than that of the corresponding spin-coated film. The ITO-19-20 polymer device also converts absorbed photons to electrons more efficiently than that of the spin-coated film. However, the standard photovoltaic characterisations of the ITO-19-20 polymer device are hindered due to high dark currents.

Figure 15: Polymer brushes for the creation of a notational supramolecular n/p-heterojunction.
Nesterov et al. and Armstrong et al. have each reported the electropolymerization as an alternative way to synthesize polymer brushes.\textsuperscript{49,50} The electropolymerization of thiophenes together with semiconductor nanoparticles produces a SHJ-type hybrid structure, which is very similar to that of the polymer device ITO-19-20.\textsuperscript{49}

Hupp and co-workers have reported an elegant approach towards a vertically oriented SHJ architecture.\textsuperscript{51} In the architecture formation, the zirconated ITO-21 surfaces were dipped in an aqueous solution of the porphyrin square 22 for the capture of four phosphonates at the bottom of the porphyrin square. The upper four phosphonates were then zirconated for further binding of subsequently added porphyrin squares. This ordered LBL process was repeated several times to get the porous multilayer film ITO-(21-22)_n. The pores in the obtained ITO-(21-22)_n film were filled by repetitive LBL addition of the PDI 23 and zirconium cations 21. While the PDIs infiltrated into the porphyrin squares, PDI acceptors were also captured on top of the porphyrin donors. In the obtained architecture ITO-(21-22)_n-(21-23)_n, the lower part exhibited formal SHJ properties (Figure 16). Replacement of the porphyrin square 22 with the porphyrin 24 gave a similar architecture. Both architectures gave linear J-L curves up to 8-10 layers. The photocurrent action spectrum revealed that both the PDIs and the porphyrins contributed to photocurrent generation.
Figure 16: Vertical oriented formal SHJ architecture obtained with a porous array of porphyrin donors filled with PDI acceptors.

Recently, Imahori and co-workers reported an excellent approach for the formation of a vertically oriented SHJ architecture. The assembly started with the mixed monolayer formation on a tin oxide electrode using the pyridylporphyrin acid donor and the C60 acid acceptor. Pyridine ligands of porphyrins in the obtained SnO$_2$-25/26 monolayers were coordinated with the palladium propagator 27. The obtained SnO$_2$-25/26-27 electrode was dipped into a solution of the dipyridine porphyrin 28 followed by addition of palladium 27 to give SnO$_2$-25/26-27-28-27. Repeated LBL incubation with the dipyridine porphyrin 28 followed by the palladium 27 created the supramolecular porphyrin brushes SnO$_2$-25/26-(27-28)$_n$. For infiltration, the obtained porphyrin brushes SnO$_2$-25/26-(27-28)$_n$ were immersed into a pyridine-C60 29 acceptor solution, in which the pyridine ligands of the Py-C60 29 were coordinated to the zinc porphyrins and incorporated into the porphyrin
array. In the obtained formal SHJ architecture \(\text{SnO}_2\text{-(25/26)-(27-28)-}_n\text{-29}\) the donor porphyrin array grew from the electrode surface and was lined by coaxial fullerene acceptor arrays (Figure 17). The \(J-L\) profile of the \(\text{SnO}_2\text{-(25/26)-(27-28)-}_n\text{-29}\) photosystem revealed a critical thickness of five layers with an IPCE of 21\% at \(J_{\text{max}}\). Photocurrent generation increased linearly up to five layers but further deposition of layers decreased it. This decrease of photocurrent generation after five layers has been ascribed inhibited growth of the system.

![Figure 17](image-url)

**Figure 17:** Vertical oriented SHJ architecture made from supramolecular porphyrin brushes.
1.6 Zipper Assembly for the Formation of a Vertically Oriented Organic SHJ Photosystem

For the creation of vertically oriented fully organic SHJ photosystems, Matile and co-workers introduced a zipper assembly of a rod-stack architecture such as Au-30-(31-32)-n.\textsuperscript{53} In the zipper assembly the first step was the formation of the self-assembled monolayer (SAM) with the short initiator POP-B 30 on a gold electrode (Figure 18). The short POP-B 30 initiator possesses a disulfide group at one end of the rod to bind covalently to the gold electrode and negatively charged blue NDIs along the POP scaffold to avoid non-specific interaction with the gold electrode. For the propagation of the zipper assembly, the resultant Au-30 monolayers were immersed into an aqueous solution of the cationic propagator POP-B 31. The lower half of the blue cationic NDIs of the propagator 31 were expected to interdigitate with the anionic NDIs of the initiator 30 due to $\pi-\pi$ stacking, interstack hydrogen bonding and interstack ion pairing.\textsuperscript{54,55} The upper half of the NDIs of propagator 31 remained free as a “sticky end” to zip up with the complementary blue anionic propagator POP-NDI 32. The repeated LBL incubation of the cationic propagator 31 followed by the anionic propagator 32 gave the formal zipper architecture Au-30-(31-32)-n.
Figure 18: Vertically oriented organic SHJ architecture made from a zipper assembly.

In the zipper assembly Au-30-(31-32)_n the electron conducting NDI stacks are aligned co-axially next to the hole conducting POP rod. However, in
the zipper assembly \( \text{Au-30-} \left( \text{31-32} \right)_n \) photoinduced charge separation (PCS) between NDI stacks and POP rods was not possible because the HOMO energy level of the blue NDIs is above that of the POP rods. The transient absorption (TA) measurement of the POP-B 31 propagator revealed that the photoinduced charge separation takes place in the NDI stacks to generate NDI\(^+\) and NDI\(^-\) ions with minimal loss of energy.\(^{55,56}\) In this kind of charge separation, the hole and electron generated in the zipper assembly \( \text{Au-30-} \left( \text{31-32} \right)_n \) would move in adjacent NDI stacks while the POPs serve only as a rigid-rod scaffold. The \( J-L \) curve of the zipper assembly \( \text{Au-30-} \left( \text{31-32} \right)_n \) shows photocurrent generation linearly up to 10 layers. The non-ohmic \( J-V \) curve is consistent with high organization of the zipper architecture \( \text{Au-30-} \left( \text{31-32} \right)_n \) and revealed a \( FF \) of 0.42. To evaluate the importance and presence of sticky ends for the growth of the zipper assembly, a capping experiment of the assembly \( \text{Au-30-} \text{31} \) using 30 was done.

Mini-zippers with biphenyl initiators and \( p \)-quaterphenyl propagators show less photocurrent generation than the corresponding original \( \text{Au-30-} \left( \text{31-32} \right)_n \) zipper. The mini-zipper revealed a bell-shaped \( J-L \) profile with a critical thickness of 10 layers, which is half that of the critical thickness of the original \( \text{Au-30-} \left( \text{31-32} \right)_n \) zipper.\(^{57}\) These results demonstrate the importance of oligomer effects in the rod-stack zipper assembly.

To achieve a formal rod-stack SHJ (POP-NDI) zipper architecture, where electrons are transported by the NDI π-stacks and holes are transported by the POP rods, Matile and co-workers introduced a red POP-Rcl donor-acceptor hybrid in the zipper assembly.\(^{58}\) The photoinduced charge separation (PCS) and generation of the NDI\(^-\) anion and POP\(^+\) cation radicals were evidenced by the transient absorption spectrum.\(^{56}\) The lifetime of the PCS with the red POP-Rcl propagator 33 is in the range of ns, which is due to the formation of a notational SHJ architecture. The \( J-V \) curve of the mixed zipper
Au-30-33-32-31 has high $V_{oc}$ and an excellent FF of 0.55, whereas the Au-30-31-32-33 zipper with reversed redox gradient in the NDI stacks has a lower $V_{oc}$ and a nearly ohmic FF of 0.31. The difference between the FF of the favoured and the reversed zipper assemblies provided experimental evidence for the existence of a redox gradient in POP-NDI zipper assemblies and significance for function. The presence of red and blue colored NDIs in the zipper architecture Au-30-33-32-31 could be considered as a minimalist prototype of an ideal OMARG-SHJ photosystem.

Figure 19: Vertically oriented yellow POP-NDI zipper architecture as a SHJ photosystem.

Recently, Matile and co-workers also reported the formation of the yellow POP-Y SHJ zipper architecture Au-34-(35-36)$_n$ (Figure 19). The optoelectronic matching of the yellow NDI acceptor with the POP donor in the
POP-Y propagator was successful in producing a long-lived photoinduced charge separation (2.6 ns) compared to the red POP-R, and the blue POP-B propagators. The zipper assembly generated higher photocurrent than the conventional LBL assembly and the blue zipper assembly. The J-V and J-L profiles of the zipper assembly revealed a high FF (FF = 0.53) and a high critical thickness (~ 20 layers). The high FF and critical thickness evidenced the existence of ordered and oriented rod-stack SHJ architectures. In the zipper architecture the presence of unsubstituted NDI acceptors near the gold surface completed a formal redox gradient in the electron conducting channels.

1.7 Redox Gradients in SHJ photosystems

In bioinspired, ideal OMARG-SHJ photosystems the n- and p-conducting channels would be equipped with antiparallel redox gradients for the efficient transport of electrons and holes in the opposite direction to their respective electrodes. This organization would lead to an increase in the photovoltaic properties of the system. In the literature, few examples of formal SHJ photosystems equipped with unidirectional redox gradients are reported. Top-down approaches have resulted in several systems with significant redox gradients.

Yang and co-workers have reported a trilayer photovoltaic cascade device that produced an enhanced $V_{oc}$. The device was constructed by vapour deposition of a tetraceno[2,3-b]thiophene donor layer followed by a copper phthalocyanine layer as sandwich material and then a fullerene acceptor layer. The HOMO and LUMO energy levels of the three materials form a cascade energy structure in the energy band diagram of the device. The enhancement of the $V_{oc}$ occurs only when the phthalocyanine layers are thicker than 5 nm.
increase in the $V_{oc}$ demonstrates that the $V_{oc}$ in the cascade photosystem was determined by maximal or neighbouring HOMO-LUMO difference instead of smallest HOMO-LUMO difference. Therefore, redox gradients could be considered as a promising approach to enhance the photovoltaic properties of the photosystems.

Figure 20: Self-assembled monolayer photosystem equipped with redox gradients.
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Covalently constructed redox gradients on conducting surfaces have been explored extensively by SAMs. Imahori and co-workers constructed wet-type photovoltaic cells using SAMs on gold electrodes. In these photovoltaic cells, well-oriented, mixed SAMs were created using the covalently linked fullerene-porphyrin-ferrocene molecular triad and the boron dipyridine as an energy donor (Figure 20). Through irradiation of the triad-modified gold electrode, efficient photocurrent generation was observed in the presence of electron carriers such as oxygen and methylviologen.

For the creation of SHJ photosystems equipped with redox gradients, a LBL assembly appeared as an ideal supramolecular approach despite the low molecular level organisation and relatively low charge mobility of the system. Guldi and co-workers have reported a pioneering supramolecular redox gradient LBL photosystem. In the creation of the supramolecular redox gradient LBL photosystem, the poly(diallyldimethylammonium chloride) (PDDA) coated ITO electrodes were covered with a layer of the negatively charged fullerene dendrimer. The obtained ITO-39 was further covered with a layer of the octacationic porphyrin acceptor, which in turn was covered with a layer of the anionic zinc porphyrin donor and finally with a layer of the cationic ferrocene donor (Figure 21). The photocurrent action spectra demonstrated that the photocurrent generated by the more complex systems ITO-39-40-14 and ITO-39-40-14-41 was enhanced 14-fold and 20-fold, respectively, over the simple system ITO-39-40. The incident photon to current conversion (IPC) value at the porphyrin absorbance of the most complex system ITO-39-40-14-41 (1.6%) is 108-times more than the simple bilayer system ITO-39-40. When the order of deposition of the components was reversed, the efficiency of photocurrent generation decreased. The reversed system ITO-40-39 generates 5-fold less photocurrent than ITO-39-40. This decrease in photocurrent was due to mismatches in the redox gradients. These results demonstrate that for achieving high efficiency of photocurrent
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generation the photosystems should be equipped with a well-ordered redox gradient.

Figure 21: Supramolecular layer-by-layer photosystems equipped with oriented redox gradients.

Thompson and co-workers have constructed an excellent LBL SHJ photosystem equipped with an oriented redox gradient. The construction of the LBL redox gradient photosystem began with the deposition of a layer of the dithiolated zinc porphyrin donor 42 on a gold electrode. The obtained Au-42
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was activated by coordination with Cu\(^{2+}\) (43) to enable the repetitive LBL donor domain Au-(42-43)\(_n\) to be built up. On the top of the donor domain Au-(42-43)\(_n\), a bifunctional domain was deposited by repetitive exposure to the dithiolate porphyrin acceptor 44 and Cu\(^{2+}\) (43). On the obtained Au-(42-43)\(_n\)-(44-43)\(_n\), the compound 45 that possesses a thiol at one end and a phosphonate at the other end was deposited. The resulting Au-(42-43)\(_n\)-(44-43)\(_n\)-45 with a free phosphonate was repetitively immersed in a solution of Zr\(^{4+}\) (46) and then a solution of the biphosphonated viologen acceptor 47 (Figure 22).

Figure 22: Supramolecular LBL metallo-photosystem equipped with ordered and oriented redox gradients.
The $J$-$V$ profile of the redox cascade photosystem $\text{Au-}(42$-$43)_{2}$-$45$-$46$-$47)_{3}$ shows outstanding characteristics compared to the similar photosystems $\text{Au-}(42$-$43)_{2}$-$45$-$46$-$47)_{3}$ and $\text{Au-}(44$-$43)_{2}$-$45$-$46$-$47)_{3}$. The weak redox gradient photosystem $\text{Au-}(44$-$43)_{2}$-$45$-$46$-$47)_{3}$ revealed a lower $FF$ ($FF = 0.37$) than the strong redox gradient photosystem $\text{Au-}(42$-$43)_{2}$-$45$-$46$-$47)_{3}$ ($FF = 0.58$). The $V_{oc}$ of the fully cascade photosystem $\text{Au-}(42$-$43)_{2}$-$45$-$46$-$47)_{3}$ is the same as that of the weak redox gradient system $\text{Au-}(44$-$43)_{2}$-$45$-$46$-$47)_{3}$ and larger than that of the photosystem $\text{Au-}(42$-$43)_{2}$-$45$-$46$-$47)_{3}$. The overall improvement of the $FF$ and photovoltaic performance in $\text{Au-}(42$-$43)_{2}$-$45$-$46$-$47)_{3}$ relative to $\text{Au-}(44$-$43)_{2}$-$45$-$46$-$47)_{3}$ suggests that there is a more efficient charge separation in the former. The charge separation quantum yield (3.5\%) of $\text{Au-}(42$-$43)_{2}$-$45$-$46$-$47)_{3}$ is larger than that of the systems $\text{Au-}(44$-$43)_{2}$-$45$-$46$-$47)_{3}$ (2.4\%) and $\text{Au-}(42$-$43)_{2}$-$45$-$46$-$47)_{3}$ (2.3\%).

Kobuke and co-workers reported an elegant approach of surface-initiated supramolecular polymerisation of multiporphyrin arrays for the construction of photosystems equipped with redox gradients.\textsuperscript{75,76} In these photosystems, multiporphyrin arrays are formed on conducting surfaces by coordination-directed ring closing metathesis (RCM). Creation of the photosystem started with the deposition of the dithiolated zinc porphyrin initiator 48 on a gold electrode. The SAM modified gold electrode $\text{Au-}48$ was immersed in a solution of the dimeric zinc porphyrin propagator 49. One methylimidazole ligand of the propagator 49 coordinates with the initiator zinc porphyrin 48. The methylimidazole ligand of the initiator 48 back coordinates to the zinc porphyrin of the propagator 49. This kind of double coordination provides oriented porphyrin arrays. The second zinc porphyrin and the methylimidazole ligand of the propagator 49 remain free at the surface of $\text{Au-}48$-$49$ to bind with the next propagator 49. Grubbs catalyst was added to the obtained porphyrin array $\text{Au-}48$-$49$ to crosslink all of the porphyrins by RCM. The deposition of the propagator 49 and subsequent RCM steps were repeated.
several times to get the multilayer porphyrin arrays $\text{Au}_{48}-(49)_n$. The obtained multilayer porphyrin systems $\text{Au}_{48}-(49)_n$ were terminated by coordinative capping with the porphyrin 50 that possesses a terminal fullerene acceptor (Figure 23). The fullerene terminated photosystems generate cathodic photocurrent three times more efficiently than the photosystems without modification by fullerene. These results demonstrate that the increase of photocurrent in fullerene terminated photosystems was due to the development of redox- and energy-cascades.

![Multilayered porphyrin photosystem constructed by the combination of surface-initiated supramolecular polymerisation and ring closing metathesis.](image)

**Figure 23:** Multilayered porphyrin photosystem constructed by the combination of surface-initiated supramolecular polymerisation and ring closing metathesis.
1.8 Stabilization of Preorganized Assemblies by Polymerization

π-Conjugated supramolecular materials have been used enormously in molecular optoelectronics, organic solar cells and sensing devices. However, the low mechanical strength and stability of these materials, which are organized by utilizing non-covalent bonds, impose limitations for certain applications. Most self-assembled materials are rather fragile and easily collapse or change structure when exposed to organic solvents or high temperatures. A method that has proven very successful to preserve the functional superstructure is the covalent cross-linking of self-assembled superstructures. Over the past decade, different approaches have been developed for the cross-linking of self-assembled superstructures such as click chemistry,77 diene metathesis,39,75,76,78-81 disulfide bond formation82 and photo-polymerization.83-88 The photo-polymerized diacetylene functional groups have been widely utilized to stabilize various structures such as gel fibers,89-93 self-assembled nanotubes,89,94-96 and self-assembled peptide assemblies.96,97,98 The photo-polymerized diacetylene (DA) functionality has also been widely used in the preparation of chemosensors,99-102 stable liposomes,103-108 and π-conjugated conducting materials in optoelectronics and organic solar cells.109-113

Recently Nakanishi and co-workers reported water-repellent materials made from cross-linking fullerene derivatives.114 The fullerene derivative 51 contains photo-polymerizable diacetylene functional groups in long alkyl chains (Figure 24). In the preparation of water-repellent materials, the fullerene derivative self-assembles into microparticles with a bilayer structure. The obtained microparticles were irradiated with ultraviolet light to cross-link the diacetylene groups. The obtained cross-linked flakelike particles show
remarkable resistivity to organic solvents and heat and are mechanically stable. The cross-liked particles also exhibit a water-repellent nature.

![Diagram](image)

**Figure 24:** a) Structure of the fullerene derivative 51 that contains a polymerizable diacetylene group. b) A schematic representation of the photo-polymerization in the bilayer structural subunit of the fullerene derivative 51.

Shinkai and co-workers have demonstrated that the porphyrin derivative 52 containing four photo-polymerizable diacetylene units at the periphery self-assembles into an organogelator (Figure 25 (a)). The formation of the gelator takes place by *H* aggregation of the porphyrins, in which a *π*-*π* stacking interaction between the porphyrins and a hydrogen-bonding interaction between amide groups are contributing factors. Upon photo irradiation with a 500 W high-pressure Hg lamp the diacetylene units in the obtained organogelator polymerize along the gel fibers and form a stable...
gelator. In a seminal contribution, Russell and co-workers determined that the lipid diacetylene 53 self-assembles into nanotubes. The dispersion of the self-assembled diacetylene nanotubes on glass surfaces undergoes efficient photo-polymerization by UV exposure (Figure 25 (b)). The obtained photo-polymerized nanotubes (PNT) were stable and resistant to chloroform and heat.

Hest and co-workers have also applied the photo-polymerization of diacetylene for the formation of stable β-sheet fibers.

Figure 25: a) Molecular structures of porphyrin-based gelator (52) containing a diacetylene unit. b) Photo-polymerization of self-assembled lipid diacetylene nanotubes.
Recently Kumar and co-workers have reported the utilization of photo-polymerized diacetylene units as a hole conducting material in a solid state dye-sensitized solar cell.\textsuperscript{112,113} In the device construction an amphiphilic diacetylene solution of 10,12-pentacosadiynoic acid (PCDA) was incorporated into a nanoporous TiO\textsubscript{2} film by solution casting. The PCDA soaked TiO\textsubscript{2} film was photo-polymerized into polydiacetylenes (PDA) (Figure 26). The resultant dye-sensitized solar cell demonstrated a short-circuit current density of 3.73 mA/cm\textsuperscript{2} and power conversion efficiency of 0.62%.

\[ R_1 = (\text{CH}_2)\text{\textsubscript{11}}-\text{CH}_3 \]
\[ R_2 = (\text{CH}_2)\text{\textsubscript{16}}-\text{COOH} \]

**Figure 26:** Chemical structure for the photo-polymerization of DA-PCDA to PDA-PCDA.

Kim and co-workers have also successfully utilized the PDA as a hole conducting material with electron conducting fullerene in a BHJ organic solar cell.\textsuperscript{110}
CHAPTER 2

OBJECTIVES

In molecular optoelectronics, such as BHJ organic solar cells, the transport of directional energy, electrons and holes along sophisticated redox/energy gradients to and from the active sites are essential. To tackle this key challenge, Matile and co-workers have introduced supramolecular zipper assemblies. They have synthesized a library of multichromophoric NDI-POP hybrids as propagators, with NDI-POP as an initiator for the zipper assemblies. In these zipper assemblies, NDI chromophores attached to rigid rod scaffolds are assembled step-by-step to build π-stacks by interdigitating aromatic planes from neighbouring scaffolds along strings of interdigitating rigid rods. The inter- and intralayer recognition motifs direct the co-axial alignment of electron transport NDI stacks next to hole transporting POP rods.

The main objective of this thesis is to use oligophenylethynylenes (OPEs) as an alternative and complementary rigid-rod scaffold to the original POPs and, moreover, to construct SHJ photosystems with oriented multicoloured antiparallel redox gradients (OMARG-SHJs).
2.1 Topologically Matching NBr-NDI-OPE Supramolecular n/p-Heterojunction Zipper Architectures

In this part of the thesis, we will discuss the replacement of the rigid rod scaffold POP with the rigid rod scaffold OPE, to design a topologically matching ordered and oriented supramolecular red OPE-R_{Br} zipper assembly on a solid substrate. For this purpose (electron deficient naphthalenediimide) NDI-OPE initiator and NBr-NDI-OPE propagators were synthesized. The zipper assembly is initiated with a short OPE initiator containing disulphide at one end of the OPE rod to covalently bind to the gold surface and negatively charged NDI acceptors along the rigid rod scaffold. The zipper assembly is then propagated by dipping the gold monolayers into a solution of the cationic NBr-NDI-OPE propagator. The lower half of the cationic NBr-NDIs of the propagator should interdigitate with the NDIs of the initiator by topologically matching π-π stacking, interstack hydrogen bonding and interstack ion pairing. The upper half of the cationic propagator will remain free as ‘‘sticky ends’’ to zip up with an anionic NBr-NDI-OPE propagator, which in turn can zip up with the cationic propagator and so on.

The obtained supramolecular OPE-R_{Br} zipper assembly shows the generation of photocurrent upon irradiation with light. The contribution of the specific architecture of the zipper assembly to the generation of current is evaluated by employing the following methods: (1) Cyclic voltammetry (CV) for characterisation of SAMs and to determine the frontier orbital energy of the zipper assembly. (2) Photocurrent measurements, J-L profiles, J-V profiles and action spectra to find the basic photophysics of the created nano-architectures. (3) Using a quartz crystal microbalance (QCM) to determine the amount of deposited NDI-OPEs on the metal surface.
Chapter 2 Objectives

The obtained OPE-R\textsubscript{Br} zipper assembly is compared with the conventional LBL assembly of the \textit{NBr}-NDI-OPE. Using this methodology, we would prove the presence of an ordered, oriented and high critical thickness structure in the zipper architecture. The necessity and presence of sticky ends for growth of zipper assembly is studied employing capping experiments.

2.2 Topologically Matching \textit{ON}-NDI-OPE Supramolecular n/p-Heterojunction Zipper Architectures

In this section, we will discuss the replacement of \textit{NBr}-NDIs with non-halogenated \textit{ON}-NDIs to design a red \textit{ON}-NDI-OPE zipper assembly. For this purpose \textit{ON}-NDI-OPE propagators were synthesized. The zipper assembly was initiated and propagated as described in the previous section by using \textit{ON}-NDI-OPE propagators. Applying this study we prove that \textit{ON}-NDIs compared to \textit{NBr}-NDIs are less sensitive towards topological mismatch.

2.3 Supramolecular n/p-Heterojunction with Oriented Multicolored Antiparallel Redox Gradients (OMARG-SHJ)

Matile and co-workers have reported a yellow \textit{OO}-NDI-POP zipper \textit{Au-34-(35-36)}\textsubscript{a} complimentary to the red \textit{NBr}-NDI-OPE zipper.\textsuperscript{27} In POP-Y zippers the optoelectronic matching of \textit{OO}-NDI acceptors with POP donors shows maximal photocurrent generation. In this section, we will discuss the formation of mixed zipper assemblies by placing red \textit{NBr}-NDI-OPE zipper on top of yellow \textit{OO}-NDI-POP zipper, which gives rise to formal OMRG-SHJs. The obtained mixed zipper assembly is evaluated using photocurrent measurements, \textit{J-L} profiles, \textit{J-V} profiles and action spectrum. Applying this study, we can prove that the critical thickness of the mixed zipper assembly is
much better than that of the $NBr$-NDI-OPE zipper and can generate antiparallel redox gradient supramolecular n/p heterojunctions.

For the creation of covalently bound zipper assemblies, we synthesized $ON$-NDI-OPE propagators, which have a diacetylene unit as covalent capture unit at the core of the NDIs.
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Design and Synthesis of Topologically Matching Red NBr-NDI-OPE Supramolecular \( n/p \)-Heterojunction Zipper Architectures

3.1.1 Design

Directing the flow of electrons and holes by appropriate supramolecular design is a challenging task. An ideal design should not only consist of a structurally robust motif based on multiple supramolecular interactions, but also be equipped with multicolored chromophores, which can facilitate efficient energy absorption from the solar light and energetically favourable cascade of electrons and holes. Zipper assemblies have been developed for the creation of vectorial SHJs and other applications in molecular optoelectronics.\(^{27,53,57,58,115}\) Zipper architectures are composed of electron transporting \( \pi \)-stacks aligned along hole transporting rigid rods and consequently act as synthetic photosystems. In zipper architectures, \( \pi \)-acidic NDIs have been selected as electron-transporting \( \pi \)-stacks and POPs as hole-transporting rigid rods.

NDIs are ideal for the formation of \( \pi \)-stacks in zipper architectures when compared to many other possible multicolored chromophores (e.g., PDIs, porphyrinoids, phthalocyanines, cyanines, Alexa Fluors, fluoresceins,
BODIPys\textsuperscript{116-125} because they unify the following properties (Figure 27): 1) NDIs are available in many different colors spanning the whole visible spectrum.\textsuperscript{126-132} 2) Their photophysical properties are relatively well known and can be tuned without global structural change. 3) Decoration of the aromatic core unit of NDIs with electron donating or withdrawing substituents can govern the HOMO-LUMO gap resulting in compounds with the desired spectral properties.\textsuperscript{27,55,126-129,131-133} 4) NDIs have been intensively studied as \textit{n}-type air stable semiconductors.\textsuperscript{34,134} 5) Their planarity and $\pi$- acidity are suitable for $\pi$-$\pi$ stacking.\textsuperscript{135} 6) Synthetic accessibility.\textsuperscript{78,126 127-129,131,132} 7) Compactness (‘‘atom efficiency’’).

\textbf{Figure 27:} Frontier orbital energy levels of the NDIs (general structure C$_2$-G) (solid lines, HOMO; dashed lines, LUMO); dashed arrows, absorption of light ($hv$) with wavelength (nm) of maximum absorption (top) and emission (bottom).\textsuperscript{27}

In all zipper architectures to-date, POP rigid rods have been used as the hole transporting pathway. No attempt has been undertaken to modulate the hole transporting pathway. However, the PCS, CR and hole mobility are
influenced by different electron donor molecules and these changes must be taken into account.

**Table 1**: Frontier orbital energy levels and spectroscopic data of π-conjugated electron donor molecules.

<table>
<thead>
<tr>
<th>Donor molecules</th>
<th>Abs. $\lambda_{\text{max}}$[nm]</th>
<th>Flu. $\lambda_{\text{max}}$[nm]</th>
<th>HOMO [eV]</th>
<th>LUMO [eV]</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>POP</td>
<td>320</td>
<td>389</td>
<td>-5.75</td>
<td>-2.35</td>
<td>27</td>
</tr>
<tr>
<td>OT</td>
<td>439</td>
<td>546</td>
<td>-5.08</td>
<td>-2.22</td>
<td>136</td>
</tr>
<tr>
<td>OPV</td>
<td>465</td>
<td>543</td>
<td>-5.03</td>
<td>-2.16</td>
<td>137</td>
</tr>
<tr>
<td>OPE</td>
<td>410</td>
<td>257</td>
<td>-5.60</td>
<td>-2.84</td>
<td>139</td>
</tr>
<tr>
<td>PDA</td>
<td>500</td>
<td>800</td>
<td>-5.50</td>
<td>-3.50</td>
<td>113</td>
</tr>
</tbody>
</table>

The excited state energy (i.e. LUMO), and the ionization potential (i.e. HOMO), of the π-conjugated electron donor chain are key parameters in the photoinduced electron transfer process. The HOMO and LUMO energy levels of different π-conjugated donors as compared to the POP donor are as shown in Table 1. The HOMO energies of π-conjugated donors lie above the POP HOMO energy. This difference clearly suggests that replacing the POP donor with other π-conjugated donors such as oligothiophene (OT), OPV, OPE or polydiacetylene PDA should improve the electron transfer, the charge separation, the hole mobility and ultimately enhance the efficiency of the resulting zipper architectures.

While the replacement of POP with OPV, PDA or OT could improve the photovoltaic performance of zipper architectures, it would sacrifice the
vectorial orientation and rigidity of zipper architectures. OPE, however, is a rigid molecule like POP which would give vectorial orientation and rigidity to any ensuing zipper architecture. Compared to POPs, OPEs are attractive because they are planarizable, better red-shifted fluorophores, better hole conductors and they absorb more visible light. Moreover, the repeating distance of the NDIs attached to the OPEs (~7 Å) match the ideal distance for \( \pi \)-stack repeats. The POP repeated mismatch of 10 Å has been shown to cause hyperboloidal collapse into more helical architectures. More relevant for hole transfer, the HOMO energy level of OPEs lies above that of POPs.

The initial model photophysical studies of blue \( NN \)-NDI-OPE and red \( NCl \)-NDI-OPE multichromophoric systems have been reported by Vauthey and co-workers. They have found ultrafast CS and slow CR with both the red and the blue systems. In the red system, electron transfer occurs from the OPE scaffold to the NDI unit, independently of whether the OPE or an NDI is initially excited. However, in the blue system, electron transfer occurs from the OPE scaffold to the NDI unit only when the OPE is excited initially. The average lifetime of the charge-separated state (CSS) in the red system is about 0.65 ns, whereas in the blue system it is 2.7 ns. Therefore, very different dynamics are observed with the blue and red systems. The different dynamics could originate from the different oxidation potentials of the respective NDIs (acceptors) that are higher and lower than that of the OPE (donor) scaffolds. With this in mind, it was envisioned to replace the hole transporting POP donor with the OPE donor in the zipper architectures.
Figure 28: Molecular structures of the OPE-NDI initiator 54 and propagators 55 & 56 and the expected supramolecular architecture of their topologically matched zipper assembly (Au-54-(55-56)_n-55).
Chapter 3: Results and Discussion

The creation of the zipper assembly Au-54-(55-56)ₙ-55 (Figure 28) requires at least three different components and it was designed as follows: The first component is the short OPE initiator 54 having a disulfide group at one terminus for covalent linkage to the gold surface and six anionic colorless, electron poor HH-NDIs along the OPE scaffold. The second component is the cationic OPE propagator 55 with ten cationic NBr-NDIs attached along the OPE scaffold. The third component is the anionic OPE propagator 56 with ten anionic NBr-NDIs attached along the OPE scaffold. The lower half of the cationic NBr-NDIs of the propagator 55 is expected to form π-stacks with the anionic HH-NDIs of the initiator 54 to give a zipper of the structure Au-54-55. The free upper half of the cationic propagator 55 remains as a sticky end to zip up with the anionic OPE propagator 56, which in turn can zip up with the cationic OPE propagator 55 to give Au-54-55-56-55, and so on. The existence of this sticky end was supported by inhibition of zipper assembly growth with the addition of the OPE terminator 54.

In the zipper assembly, we have introduced unsubstituted, colorless and electron-poor HH-NDIs (Figure 28) as electron acceptors near the gold surface. HH-NDIs have been extensively studied for many diverse purposes. HH-NDIs have a quadrupole moment (Q) of +14.7 B that is far beyond that of the π-acidic hexafluorobenzene, and thus ideal for π-stack zipper architecture. HH-NDIs have an energetically deep-lying LUMO (-3.9 eV) (Figure 29) that is near that of C₆₀ (-4.2 eV), the most commonly used acceptor in organic solar cells. HH-NDIs are also one of the few air stable and high charge mobility n-channel organic semiconductors. Using electron-poor HH-NDIs we wanted to set a formal redox gradient in the n-semiconducting channel.
In the zipper assembly we introduced NBr-NDIs attached to the OPE propagator as an electron acceptor. NBr-NDIs are red colored chromophores that fluorescence orange. The spectroscopic properties of NBr-NDIs ($\lambda_{\text{abs}} = 530$ nm, $\lambda_{\text{em}} = 570$ nm) are almost identical with NCl-NDIs. These properties make NBr-NDIs an ideal acceptor in the zipper assembly.

3.1.2 Retrosynthetic Approach to the HH-NDI-OPE Initiator

The key challenge in the construction of the HH-NDI-OPE initiator is the introduction of six electron poor noncore-substituted HH-NDIs onto the
OPE rigid rod scaffold. This OPE rigid-rod scaffold must also possess a disulfide group at one end.

Scheme 1: Retrosynthetic analysis of the initiator 54.

As outlined in Scheme 1, the introduction of the six NDIs can be achieved by preparing the OPE rod 57 bearing a disulfide group at one end and six carboxylic acids on three phenyl rings. To access the OPE rod 57, an
obvious disconnection would be at the central acetylene bond. This would afford two subunits, the first unit 58 would bear four carboxylate groups and a terminal acetylene unit, whereas second unit 59 would contain one amine and two carboxylate groups. The first unit 58 would be prepared starting from 1-bromo resorcinol (60) and 1,4-dimethoxy benzene (61). The second unit 59 would be synthesized from 4-iodoaniline (62) and 1,4-dimethoxy benzene (61).

3.1.3 Synthesis of the \textit{HH}-NDI-OPE Initiator 54

The synthesis of the anionic \textit{HH}-NDI-OPE initiator 54 was achieved by using a convergent approach. As outlined in the retrosynthetic analysis, the synthetic scheme consists of the preparation of two different subunits followed by the coupling of these two subunits to afford the final compound. Scheme 2 summarises the synthesis of the OPE rod 57.
Scheme 2:  
a) BrCH\textsubscript{2}COO-\textit{t}-Bu, Cs\textsubscript{2}CO\textsubscript{3}, acetone, 70 °C, 1h, 94%;  
b) Pd(PPh\textsubscript{3})\textsubscript{4}, CuI, DMF, TEA, 110 °C, 7d, 58%;  
c) TBAF, MeOH, THF, -10 to 0 °C, 3.5h, 72%;  
d) Li\textsubscript{2}CO\textsubscript{3}, AcOH, H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{2}O, 6h, 65% ;  
e) BBr\textsubscript{3}, DCM, -78 °C – rt, 20h;  
f) BrCH\textsubscript{2}COO-\textit{t}-Bu, Cs\textsubscript{2}CO\textsubscript{3}, acetone, 70 °C, 1h, 81%, 2 steps;  
g) PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, CuI, DCM:THF:TEA (1:1:2), rt, 16h, 20%;  
h) PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}, CuI, TEA, 8h, 55%;  
i) K\textsubscript{2}CO\textsubscript{3}, MeOH/DCM, 3h, 82%;  
j) Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, THF:TEA (1:1), 70 °C, 20h, 66%;  
k) TBAF, MeOH, THF, 0 °C, 15min, 67%;  
l) Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, THF:TEA (1:1), 60 °C, 16h, 48%;  
m) Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, CuI, THF:TEA (1:1), 70 °C, 20h, 52%;  
m) DCM, TEA, 0 °C – rt, 13h, 41%.

3.1.3.1 Synthesis of the First Fragment 58

The compound 66 was synthesized in three steps from commercially available 1-bromo resorcinol (60) (Scheme 3). Sequential ether formation via a Williamson\textsuperscript{160} reaction with tert-butyl protected bromoacetate afforded the
compound 63 in 94% yield. In the Williamson ether formation, the first step involves the formation of the aromatic alkoxide, which is obtained by treatment of the compound 60 with a mild base such as cesium carbonate in acetone. The tert-butyl protected bromoacetate undergoes $S_N$2 type halide displacement by the alkoxide nucleophile generating the ether compound 63. The compound 65 was prepared in 58% yield via a Hagihara-Sonogashira reaction,\textsuperscript{139,161-163} in which a C(sp$^2$)-C(sp) coupling of the bromo compound 63 and trimethylsilyl acetylene (64) takes place. In this reaction TEA acts as a solvent and, simultaneously, as a base to neutralize the hydrogen bromide formed in the reaction medium. The latter compound 65 was converted to the compound 66 in 72% yield via deprotection of the trimethylsilyl (TMS) protecting group with tetrabutylammonium fluoride in THF/MeOH.

Scheme 3: Synthesis of the compound 66.

With diester 66 in hand, the synthesis of the compound 69 was undertaken. The diiodo compound 67 was synthesized from commercially available 1,4-dimethoxybenzene 61 following a literature procedure.\textsuperscript{164} Exposure of the obtained diiodo compound 67 to BBr$_3$ (1 M in CH$_2$Cl$_2$) in CH$_2$Cl$_2$ at -78 °C for 20 h followed by quenching with ice-cold water afforded a white solid. Sequential Williamson ether formation in refluxing acetone, in the presence of cesium carbonate and tert-butyl protected bromoacetate, yielded compound 68 in 81% over two steps. The obtained diiodo compound
Chapter 3: Results and Discussion

68 was converted into compound 69 in 20% yield via an introduction of ethynyl group using Hagihara-Sonogashira methodology (Scheme 4).\textsuperscript{139,161-163}

![Scheme 4: Synthesis of compound 69.](image)

With compounds 66 and 69 in hand, the next step was the formation of the first fragment 58 (Scheme 5). In order to achieve this, compound 66 and compound 69 were coupled together via a Hagihara-Sonogashira coupling reaction that furnished compound 72 in 66% yield. The obtained compound 72 was subjected to TMS deprotection using tetrabutylammonium fluoride in THF/MeOH at 0°C, to yield the first fragment 58 in 67% yield.

![Scheme 5: Synthesis of compound 58.](image)
3.1.3.2 Synthesis of the Second Fragment 59

With the first fragment 58 in hand, the next target was the synthesis of the second fragment 59 (Scheme 6). Compound 71 was synthesised from commercially available 4-iodoaniline (62) in two steps following a literature method. The obtained compound 71 was coupled with the diiodo compound 68 by a Hagihara-Sonogashira coupling reaction to give the second fragment 59 in 48% yield.

![Scheme 6: Synthesis of compound 59.](image)

3.1.3.3 Synthesis of the OPE Rod 57

With both fragments in hand, the synthesis of the OPE rod 57 was the next target. The compound 74 was synthesised from commercially available lipoic acid following a previously reported procedure. The synthesis of the free amine OPE rod 73 was achieved via a Hagihara-Sonogashira coupling reaction between the compound 58 and the compound 59. The obtained free amine OPE compound 73 was then subjected to an amide coupling reaction with the compound 74 to afford the OPE rod 57 in 41% yield. The desired short OPE rod 57 contains six carboxylic acid groups on three phenyl rings and a disulfide group at one end of the OPE rod (Scheme 7). Thus, it represents a
perfect scaffold for the construction of the HH-NDI-OPE initiator 54. The compound 57 was characterized by ESI-MS, IR, $^1$H-NMR, $^{13}$C-NMR, 2D COSY and HSQC NMR.

**Scheme 7: Synthesis of the OPE rod 57.**

With the key compound 57 in hand, the remaining part of the synthesis involved a protocol for the ester deprotection and subsequent coupling of the formed carboxylic acid with six HH-NDIs. The following section briefly describes the synthesis of the anionic HH-NDI used in the synthesis of the NDI-OPE initiator 54.

**3.1.3.4 Synthesis of the Glu-NDI (HH-NDI) 79**

Synthesis of the Glu-NDI was carried out using the L-glutamate 75 and the ethylenediamine 77 (Scheme 8). The glutamate side chain was protected with a tert-butyl group and one of the amines of the ethylenediamine with a Cbz protecting group. The use of orthogonal protecting groups was
necessary for selective deprotection of the Cbz functionality in the presence of a tert-butyl ester. The resulting free amine was used to form an amide bond in a reaction with the OPE rod 80.

Scheme 8: Synthesis of H-en-NDI-Glu(t-Bu)-NH₂ 79. i) TEA, DMF, 140°C (microwave), 10 min, 65%; ii) MeOH:EtOAc (3:1), Pd(OH)₂/C, H₂, rt, 10 h, 69%.

The commercially available 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (76) was condensed with the Cbz-ethylenediamine 77 and H-Glu(t-Bu)-NH₂ 75 in DMF and TEA at 140 °C under microwave irradiation for 10 min. The reaction yielded 65% of the required asymmetrical product 78 together with a small amount of the two symmetrically substituted (one with glutamates and the other with ethylenediamines) side products. This result is in contrast with the reported standard methods for the synthesis of unsymmetrical naphthalenediimides that usually afford a statistical mixture. The obtained product 78 was purified by column chromatography. The deprotection of the Cbz protecting group was carried out via hydrogenolysis using Pd(OH)₂/C as a catalyst in the mixture of MeOH:EtOAc (1:3) to give compound 79. The clear brown solution turned to a black gel during the reaction and an excess of MeOH and EtOAc was used to dissolve the product to allow filtration through
celite. The synthesised pure NDI compounds 78 and 79 were characterized by NMR and mass spectrometry.

### 3.1.3.5 Synthesis of the Anionic \( HH \)-NDI-OPE Initiator 54

With the \( HH \)-NDI amine 79 and the OPE rod 57 in hand, the coupling of these two units was undertaken to afford the anionic \( HH \)-NDI-OPE initiator 54 (Scheme 9). The OPE rod 57 was treated with TFA for the deprotection of the tert-butyl group of the carboxylic acids along the rigid rod scaffold, thus converting it to the hexa-acid 80 in quantitative yield. The free hexa-acid compound 80 was coupled to the \( HH \)-NDI amine 79 in DMF in the presence of HATU as a coupling reagent, DTBP and TEA, to furnish the compound 81 in 53% yield. The obtained fully protected \( HH \)-NDI-OPE initiator 81 was purified by column chromatography and successive PTLCs. The compound was identified as being pure by HPLC. The fully protected \( HH \)-NDI-OPE initiator 81 was subjected to deprotection of the tert-butyl ester group via treatment with a 1:1 mixture of TFA/\( CH_2Cl_2 \) at room temperature. The desired product 54 was obtained as a brown solid, which was purified by washing with diethyl ether and \( CH_2Cl_2 \).
Scheme 9: Synthesis of HHH-NDI-OPE initiator 54. i) TFA/DCM (1:1), rt, 1 h, quant; ii) HATU, DTBP, TEA, DMF, rt, 16 h, 53 %, iii) TFA/DCM (1:1), rt, 2 h, quant.

ESI mass spectrometry was unsuccessful in the characterisation of the protected compound 81 and the deprotected compound 54. Therefore, the identity of the protected initiator 81 was confirmed using MALDI-MS and purity was checked by HPLC (Figure 30).
Once, the HHI-NDI-OPE initiator 54 was successfully synthesized we aimed to synthesize the cationic and anionic NBr-NDI-OPE propagators.

Figure 30: A) MALDI-MS (in ditranol) of 81; B) HPLC of 81 (YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 90:10, 1 ml/min, \( R_t = 7.80 \) min).

3.1.4 Synthesis of the Cationic NBr-NDI-OPE Propagator 55

The cationic red NBr-NDI amine 82 was synthesized from commercially available 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (76) in four steps by following previously reported procedures.\textsuperscript{159} The obtained NBr-NDI amine 82 was in 2,6- and 3,7-regioisomer and could not be separated by column chromatography and PTLCs. The NBr-NDI amine 82 was coupled with the readily available free deca-acid OPE rod 83 (the synthesis of this compound was recently reported\textsuperscript{168}) in DMF in the presence of HATU, DTBP and TEA to furnish the compound 84 in 51% yield. The obtained compound 84
was purified by column chromatography and successive PTLCs. The purity of the protected cationic $NBr$-NDI-OPE propagator $\textbf{84}$ was determined using HPLC and its identity was confirmed using MALDI-MS (Figure 31).

**Scheme 10:** Synthesis of the cationic $NBr$-NDI-OPE propagator $\textbf{55}$. i) HATU, DTBP, TEA, DMF, rt, 16 h, 51%. ii) TFA, thioanisole, pentamethyl benzene, 50 °C, 3 h, quant.
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The fully protected \(NBr\text{-NDI-OPE}\) propagator 84 was treated with TFA, a catalytic amount of thioanisole and pentamethyl benzene at 50 °C for 3 h affording the hydrophilic \(NBr\text{-NDI-OPE}\) propagator 55 as a red solid (Scheme 10). The purity of the final product 55 was checked using RP-HPLC and its identity was confirmed using MALDI-MS.

**Figure 31:** A) MALDI-MS (in ditranol) of the compound 84; B) HPLC of the compound 84 (YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 90:10, 1 ml/min, \(R_t = 7.06\) min).

With the anionic \(HH\text{-NDI-OPE}\) initiator 54 and the cationic \(NBr\text{-NDI-OPE}\) propagator 55 in hand, the next target was the synthesis of the anionic \(NBr\text{-NDI-OPE}\) propagator 56.
3.1.5 Synthesis of the Anionic \( NBr\)-NDI-OPE Propagator 56

Similar to the cationic \( NBr\)-NDI amine 82, the anionic \( NBr\)-NDI amine 85 was synthesised from commercially available 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (76) in four steps by following previously reported procedures. The \( NBr\)-NDI amine 85 was coupled with the readily available OPE rod 83 in DMF in the presence of HATU, DTBP and TEA to furnish the compound 86 in 53% yield. The compound 86 was purified using a combination of column chromatography and successive PTLCs. The purity and identity of the fully protected \( NBr\)-NDI-OPE propagator 86 was confirmed using HPLC and MALDI-MS, respectively (Figure 32).

The fully protected hydrophobic \( NBr\)-NDI-OPE propagator 86 was subjected to deprotection conditions (1:1 TFA/DCM, rt) for the removal of the tert-butyl protecting group (Scheme 11). After evaporation of the solvent the hydrophilic \( NBr\)-NDI-OPE propagator 56 was washed with diethyl ether and DCM to give a red solid. The final product 56 was identified using MALDI-MS.
Scheme 11: Synthesis of the anionic NBr-NDI-OPE propagator 56. i) HATU, DTBP, TEA, DMF, rt, 16 h, 53%, ii) TFA/DCM, 3 h, quant.
Figure 32: A) MALDI-MS (in ditranol) of 86. B) HPLC of 86 (YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 95:5, 1 ml/min, $R_t = 6.76$ min).
3.2 Topologically Matching Red NBr-NDI-OPE Zipper
Assembly Formation and Characterisation

Once the HH-NDI-OPE initiator 54 and cationic and anionic NBr-NDI-OPE propagators 55 and 56 were successfully synthesised, the frontier energy orbital levels of the NBr-NDI monomers and the OPE scaffolds were determined using CV and UV absorption spectroscopy.

3.2.1 Cyclic Voltammetry

![Chemical structure of 2,6- and 3,7-regioisomer of the NBr-NDI 87 and the OPE rod 88.]

In order to understand the electron transfer process for the generation of photocurrent, the frontier energy orbital levels of the compound must be known. The frontier energy orbital levels were determined by CV and absorption spectroscopy (3.2.3, Figure 36, Table 2). The oxidation process corresponds to the removal of the electrons from the HOMO level, whereas the reduction process corresponds to the filling of electrons into the LUMO level. Therefore, the onset oxidation and reduction potentials are closely related to the
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HOMO and LUMO levels of the organic molecule and provide information regarding the energy band gap.

The redox potential of the mixture of the 2,6- and 3,7-regioisomers of the NBr-NDI 87 (Figure, 33) were determined by CV in DCM, with the ferrocene/ferricenium couple (Fc/Fc⁺) as an external or internal standard. The first NDI/NDI and the second NDI/NDI⁺ reduction of the NBr-NDI monomer 87 were both fully reversible and detectable (Figure 34 (a)). The NDI/NDI reduction waves were relatively broad and exhibited two poorly separated maxima. This broadening originated presumably from the presence of both the 2,6- and 3,7-regioisomers. The electrochemical properties of NBr-NDI were nearly identical with the previously reported NCl-NDI (Table 2, entry 2). To calculate the LUMO energy level of the NBr-NDI against vacuum, the onset of the first NDI/NDI reduction potential \( E_{\text{red1 \ onset}} = -0.95 \, \text{V} \) was taken. Subtraction from the - 4.8 eV for the Fc/Fc⁺ 37,115 standard gave \( E_{\text{LUMO}} = -3.85 \, \text{eV} \) (Table 1, entry 1). This value was in agreement with reported values for similar compounds. 115 While the oxidation wave for the NDI/NDI⁺ oxidation of the NBr-NDI monomer 87 was very strong, the reduction wave was much weaker but still detectable. The onset of the NDI/NDI⁺ oxidation potential \( E_{\text{ox1 \ onset}} = +1.10 \, \text{V} \) corresponded to an \( E_{\text{HOMO}} = -5.90 \, \text{eV} \) (Table 2, entry 1). The electrochemical bandgap energy \( E_g^{\text{CV}} = +2.05 \, \text{eV} \) was obtained from the HOMO and LUMO energies. The obtained value compared well with the optical bandgap energy \( E_g^{\text{opt}} = +2.18 \, \text{eV} \) 115 obtained from the onset of the lowest energy absorption at \( \lambda_{\text{max1 \ onset}} = 570 \, \text{nm} \) (Table 2, entry 1; Figure 36).
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Figure 34: Cyclic voltammograms of (a) NBr-NDI monomer and (b) OPE compound using ferrocene/ferricenium (0 V) as internal standard in DCM with 100 mM Bu₄NPF₆ as supporting electrolyte at room temperature, working electrode: Pt disk, counter electrode: Pt wire, reference electrode: Ag/AgCl, Scan speed: 100 mV/s for (b) and 20 mV/s for (a).

The oxidation wave for the OPE/OPE⁺ oxidation of the OPE (Figure 33) was detectable, whereas a maximum for the reduction wave was much weaker but still clearly visible (Figure 34 (b)). The onset of the OPE/OPE⁺ oxidation potential \( E_{\text{ox1 onset}} = +0.80 \) gave \( E_{\text{HOMO}} = -5.6 \) eV (Table 2, entry 4). The alternative use of -5.1 eV for the Fc/Fc⁺ standard would reduce the value for OPEs correspondingly to \( E_{\text{HOMO}} = -5.90 \) eV. The optical bandgap energy \( E_g^{\text{opt}} = +2.76 \) eV was obtained from the onset of the lowest energy absorption at \( \lambda_{\text{max1 onset}} = 450 \) nm (Table 2, entry 4; Figure 36). Subtraction of \( E_g^{\text{opt}} = +2.76 \) eV and \( E_{\text{HOMO}} = -5.60 \) eV gave an approximate \( E_{\text{LUMO}} = -2.84 \) eV. Comparison of the HOMO energies of the NBr-NDI and
OPE revealed that of NBr-NDI to be 0.30 eV lower than OPE. This difference suggested that PCS in the NBr-NDI acceptor and the OPE donor should be favourable.

Table 2: Frontier orbital energy levels of the OPEs 88 and the NBr-NDI 87 from cyclic voltammetry (CV) and absorption spectroscopy in comparison to other NDIs (NCl-NDI, HH-NDI)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>cpd\textsuperscript{b}</th>
<th>(E_{\text{ox} \text{onset}}) ((V)\text{f})</th>
<th>(E_{\text{red} \text{onset}}) ((V)\text{f})</th>
<th>(\lambda_{\text{max} \text{onset}}) ((\text{nm})\text{f})</th>
<th>HOMO ((\text{eV})\text{f})</th>
<th>LUMO ((\text{eV})\text{f})</th>
<th>(E_{\text{g} \text{CV}}) ((\text{eV})\text{f})</th>
<th>(E_{\text{g} \text{opt}}) ((\text{eV})\text{f})</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NBr</td>
<td>1.10</td>
<td>-0.95</td>
<td>570</td>
<td>-5.90</td>
<td>-3.85</td>
<td>2.05</td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>NCl</td>
<td>1.11</td>
<td>-1.00</td>
<td>570</td>
<td>-5.91</td>
<td>-3.80</td>
<td>2.13</td>
<td>2.10</td>
<td>115</td>
</tr>
<tr>
<td>3</td>
<td>HH</td>
<td>nd</td>
<td>-0.8</td>
<td>405</td>
<td>-7.07\textsuperscript{c}</td>
<td>-4.01</td>
<td>nd</td>
<td>3.06</td>
<td>115</td>
</tr>
<tr>
<td>4</td>
<td>OPE</td>
<td>0.80</td>
<td>nd</td>
<td>450</td>
<td>-5.60</td>
<td>-2.84\textsuperscript{c}</td>
<td>nd</td>
<td>3.40</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}For original data and condition, see Figure 34 and reference 115. \textsuperscript{b}Measured by CV for NBr-NDI 87 and OPE 88 and compared to previously reported values for NCl-NDI and HH-NDI. \textsuperscript{c}Onset values of the first oxidation potential against Fc/Fc\textsuperscript{c}. \textsuperscript{d}Onset value of the first reduction potential against Fc/Fc\textsuperscript{c} measured in volts. \textsuperscript{e}Onset wavelength of the longest wavelength absorption. \textsuperscript{f}Energy of the highest occupied molecular orbital against vacuum, from -4.8 eV for Fc/Fc\textsuperscript{c} minus \(E_{\text{ox} \text{onset}}\). \textsuperscript{g}Energy of the lowest unoccupied molecular orbital against vacuum, from -4.8 eV for Fc/Fc\textsuperscript{c} minus \(E_{\text{red} \text{onset}}\). Comparison with LUMO levels calculated from HOMO energies plus optical bandgap shows the small differences expected from the intrinsic experimental uncertainties and the formally incorrect comparison of charged molecules with neutral excited ones. \textsuperscript{h}Electrochemical band gap \(E_{\text{g} \text{CV}}\) \((\text{eV}) = \) LUMO-HOMO. \textsuperscript{i}Optical band gap \(E_{\text{g} \text{opt}}\) \((\text{eV}) = 1240/\lambda_{\text{max} \text{onset}}\) (nm).

3.2.2 UV Spectroscopy of the HH-NDI-OPE Initiator 54

The UV absorption spectrum of the HH-NDI-OPE initiator 54 in CHCl\textsubscript{3}/MeOH shows two bands at 361 nm and 381 nm. These two absorption bands can be assigned as local NDI transitions (Figure 35). A third absorption
band at 411 nm is due to the local OPE scaffold transition. This absorption spectrum shows there is no ground state interaction between HH-NDIs and the OPE scaffold.

![Absorption spectra](image)

**Figure 35:** Absorption spectra of the HH-NDI-OPE initiator 54.

### 3.2.3 UV Spectroscopy of the NBr-NDI-OPE Propagator 55

The absorption spectra of the monomeric NBr-NDI 87, the tert-butyl protected OPE rod 88 and the cationic NBr-NDI-OPE propagator (55) in MeOH are shown in Figure 36. The first absorption band around 530 nm is due to a local NDI transition. The energy of this charge-transfer type transition depends on the electron-donating properties of the core substituents. The absorption band at around 530 nm of the NBr-NDI-OPE propagator 55 is substantially broader and slightly red shifted compared to that of the NBr-NDI monomer 87. Similar effects have already been observed with other NDIs on POP and OPE scaffolds, and have been ascribed to an excitonic interaction between the chromophoric units.
A second absorption band at around 408 nm is due to a local transition of the OPE. The shape and position of the band in the NBr-NDI-OPE propagator 55 matches the absorption band of the tert-butyl protected OPE 88. The absorption spectra of the NBr-NDI-OPE propagator 55 shows there is no ground state interaction between the NBr-NDIs and the OPE scaffold. The absorption at band around 360 nm can be seen with both the monomeric NBr-NDI 87 and the propagator 55 and is due to a $\pi-\pi^*$ transition involving the NDI centre.

![Absorption spectra of the monomeric NBr-NDI 87 (blue, dotted), OPE rod 88 (black, dotted) and the NBr-NDI-OPE propagator 55 (red, solid).](image)

**Figure 36:** Absorption spectra of the monomeric NBr-NDI 87 (blue, dotted), OPE rod 88 (black, dotted) and the NBr-NDI-OPE propagator 55 (red, solid).

### 3.2.4 Conformational Studies of the NBr-NDI-OPE Propagator 55

The absorption spectra of the cationic NBr-NDI-OPE propagator 55 in MeOH in the presence of one drop of TFA or TEA were different (Figure 37). The peak of the maximal OPE absorption under basic conditions ($\lambda_{\text{max}} = 410$ nm) was 4 nm red-shifted compared to the maximal OPE absorption, under acidic conditions ($\lambda_{\text{max}} = 406$ nm). Moreover, the relative NDI absorption...
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(compared to OPE = 1.00) ($\lambda_{\text{max}} = 534$ nm) under acidic conditions (1.43) was 16% stronger than under basic conditions (1.23). Bathochromic OPE absorption under basic conditions implied increasing OPE conjugation due to OPE planarization. Hypochromic NDI absorption under basic conditions implied increasing NDI stacking due to reduced charge repulsion between increasingly deprotonated ammonium cations. This interpretation suggests that in the $NBr$-NDI-OPE propagator 55, NDI side chain attraction and repulsion can be used to control the extent of planarization of the OPE scaffold.

Comparison of the result of the $NBr$-NDI-OPE propagator 55 with the $NN$-NDI-OPE and $NCl$-NDI-OPE suggests that OPEs that are highly deplanarized, poorly conjugated and are poor conductors absorb below 400 nm. OPEs that are highly planarized, well conjugated and are good conductors absorb at around 410 nm. This interpretation implies that side chains with two repulsive, electron-rich, almost $\pi$-basic isopropyl amino NDIs cause full OPE deplanarization, whereas the sticky, polarizable and halogen-bonding brominated NDI side chains in the propagator 55 give mostly planarized, conjugated and conducting OPEs. The OPE conformers with intermediate chlorinated NDI side chains have the highest pH sensitivity. Matching of the action spectrum of $NBr$-NDI-OPE zippers (Figure 48) with the absorption spectrum of $NBr$-NDI-OPE propagator 55 thus indicated that the OPEs in $NBr$-NDI-OPE zippers are mostly planarized (Figure 37). This interpretation was consistent with zipper design and important, because it suggested high conductivity of the $p$-semiconductor in the formal $n/p$-heterojunction.
Figure 37: Absorption spectra of the cationic NBr-NDI-OPE 55 in MeOH in the presence of acid (TFA, red, dotted) or base (TEA, blue, solid). Absorptions were normalized at the maximum OPE absorption at around 400-430 nm.
3.2.5 NBr-NDI-OPE Zipper and LBL Assembly Formation

Zipper assembly of the NBr-NDI-OPE architecture Au-$^{54-55,56}_n$ was initiated by deposition of the short, anionic HH-NDI-OPE initiator $^{54}$ on freshly cleaned gold electrodes (Figure 38 (A)). The disulfide group at one end of the initiator was expected to bind covalently to gold surfaces, the HH-NDI acceptors along the OPE scaffold were charged negatively to avoid non-specific interaction with gold. The formation of the SAM was followed by CV and photocurrent generation. The formation of the SAM was continued until saturation values were reached. The absence of redox waves for $\text{K}_3\text{Fe(CN)}_6$ (Figure 39) demonstrated that the final Au-$^{54}_n$ electrode does not contain large uncovered areas. The complete and ordered surface coverage was also shown by Huskens and co-workers via atomic force microscopy (AFM) measurements. $^{168}$

![Figure 38: Zipper (A) and LBL assembly (B) of NBr-NDI-OPE systems from 55 and 56 on gold initiated by HH-NDI-OPE 54 and lipoic acid 89, respectively. Suprastructures are speculative representations drawn with the intention to illustrate the concept.](image-url)
Figure 39: Cyclic voltammogram of aqueous K$_3$Fe(CN)$_6$ using a gold plate with/without initiator 54 as a working electrode. Red dotted line: without 54; blue solid line: with 54.

The obtained Au-54 monolayers were immersed into an aqueous solution of the cationic NBr-NDI-OPE propagator 55. Driven by topologically matching interdigitating $\pi-\pi$ stacking and supported and directed by intrastack hydrogen bonding and interstack ion pairing,$^{33,59}$ the lower half of the cationic NBr-NDIs of the propagator 55 were expected to $\pi$-stack with the colorless and anionic $HH$-NDIs of the initiator 54. The upper half of the propagator 55 remains free as a sticky end to zip up with the anionic NBr-NDI-OPE propagator 56. The formation of Au-54-55 was followed by the increasing ability to generate photocurrent and continued until saturation was reached. As the photocurrent reached a saturation point after about 24 h (Figure 40), the duration of the depositions of 55 was set for 24 h each for the following layers.

The obtained Au-54-55 bilayers were dipped into the aqueous solution of the anionic NBr-NDI-OPE propagator 56. The obtained Au-54-55-56 trilayer can zip up with cationic propagator 55, and so on. It was assumed that
in the zipper assembly the \( n \)-conducting NDI stacks orient parallel to the \( p \)-conducting OPEs and perpendicular to the gold surface. The close proximity of \( n \)-conducting \( \pi \)-stacks and \( p \)-conducting OPEs is essential for efficient charge separation and transport.

![Figure 40: Change in photocurrent as a function of deposition time (Au-54 to Au-54-55).](image)

The comparison of the zipper assembly with the conventional LBL assembly was essential to verify the existence of the vertical alignment of \( n \)-conducting and \( p \)-conducting pathways and the significance of the zipper assembly. The LBL assembly of the \( NBr \)-NDI-OPE architecture was initiated via deposition of the lipoic acid initiator 89 instead of the \( HH \)-NDI-OPE initiator 54 on freshly cleaned gold electrodes (Figure 38 (b)). The disulfide group at one end of the lipoic acid initiator was expected to bind covalently to gold surfaces while the anionic carboxylic group at other end would remain free to bind with the cationic \( NBr \)-NDI-OPE propagator 55. The complete surface coverage of the electrode by the Au-89 SAM was followed by CV. The absence of redox waves for \( K_3Fe(CN)_6 \) indicated that the final \textbf{Au-89} electrode did not contain significant uncovered area.
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The obtained Au-89 monolayers with an anionic surface were immersed into an aqueous solution of the cationic NBr-NDI-OPE propagator 55. Driven by hydrogen bonding and ion pairing, the cationic NBr-NDIs of the propagator 55 were expected to bind with the anionic lipoic acid 89 via hydrogen bonding and ion pairing and should produce cationic Au-89-55 bilayers. The obtained cationic Au-89-55 bilayers were dipped into the aqueous solution of the anionic NBr-NDI-OPE propagator 56 to form the trilayer Au-89-55-56. Alternating layers of the propagators 55 and 56 were sequentially repeated. The difference between the zipper assemblies Au-54-(55-56)_n and the LBL assemblies Au-89-(55-56)_n beyond the first layer were small but important. OPE interdigitiation was not essential for LBL assembly. However the main difference with the zipper assembly was the presence of intra- and interlayer recognition motifs introduced by the initiator 54 and propagators 55 and 56 to produce the OPE-NDI architecture.

3.2.6 Photocurrent Generation of the NBr-NDI-OPE Zipper and the LBL Assembly

The efficiency of the supramolecular structure can be judged only by efficient generation of the desired function. In the present case, a desirable outcome would be successful and efficient photocurrent generation based on charge separation followed by electron and hole mobility in antiparallel directions. To test this concept, the NBr-NDI-OPE zipper architecture Au-54-(55-56)_n was characterized by photocurrent generation, i.e. the conversion of light energy into electric current. A conventional three-electrode cell was used to measure the photocurrent generation (Figure 41). A platinum wire was used as a counter electrode (CE) and the Ag/AgCl electrode as a reference electrode (RE). A solution of 50 mM triethanolamine (TEOA, pH = 10) in 100 mM aqueous Na2SO4 was selected as the sacrificial electron donor in
all photocurrent measurements. The gold electrodes modified with OPE-NDI zipper assemblies were used as the working electrode (WE). The photocurrent generation by the zipper assemblies was measured while irradiating with 66 mW/cm² white light. A steady and rapid anodic photocurrent was produced as the irradiation of the zipper assembly was switched ON and OFF. The response to ON/OFF cycling was prompt and reproducible. Three cycles are shown in Figure 42. The origin of the slight decrease in photocurrent observed for more than four layers is unknown. Photobleaching is unlikely to be the major cause because of the almost complete recovery found after 20 second of resting time in the dark (Figure 42). An alternative possible explanation includes the temporal depletion of the electron donor (TEAO) near the film and facilitated bimolecular recombination due to a high concentration of charge carriers.

Figure 41: Experimental set-up for the photocurrent measurements.
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Figure 42: Photocurrent generation of NBr-NDI-OPE zipper assembly upon the repetitive irradiation of 66 mWcm$^{-2}$ white light.

The relation between photocurrent densities and the number of layers in the NBr-NDI-OPE zipper assembly (i.e., J-L profile) is shown in Figure 43. As shown in Figure 43 and Figure 44 the generation of photocurrent by the red NBr-NDI-OPE Au-$\text{54-(55-56)}_n$ zipper increased almost linearly upon the deposition of layers. The linear increase of photocurrent density shows saturation after around 20 layers (i.e. critical thickness, $\tau_c = 20$). Two factors may contribute to the saturation of photocurrent around 20 layers: One possibility is the recombination of electrons and holes before reaching the electrodes. The other possibility is that the zipper assembly stops growing. QCM results show that the first possibility applies for the red NBr-NDI-OPE zipper Au-$\text{54-(55-56)}_n$ (see section 3.2.7). At $\tau_c = 20$ layers, the maximum
photocurrent density was $J_{\text{max}} = 101.6 \, \mu\text{Acm}^{-2}$. The analogous NBr-NDI-POP zipper architecture showed photocurrent saturation at around 10 layers and generated about 40% less photocurrent.\textsuperscript{168} The high photocurrent generation and double critical thickness of NBr-NDI-OPE zipper assembly compared with the analogous mismatched NBr-NDI-POP zipper could be due to the long-range ordered and oriented organization of topologically matching red NBr-NDI-OPE zipper architecture.

\textbf{Figure 43:} Current-layer ($J$-$L$) profiles of NBr-NDI-OPE architecture obtained by zipper assembly Au-54-55-56,\textsuperscript{55} (○), LBL assembly Au-89-55-56\textsuperscript{55} (□), LBL assembly with capping Au-89-55-54-55-56\textsuperscript{55} (●) and zipper assembly with capping Au-54-55-54-55-56\textsuperscript{55} (●). Error bars in quantitatively relevant $JL$ plots (○, □) indicate SE for at least two independent experiments.

The corresponding NBr-NDI-OPE LBL architecture Au-89-55-56\textsuperscript{n} generated significantly less photocurrent. The photocurrent density was

78
saturated after 8 layers, corresponding to the critical thickness of the \(NBr\)-NDI-OPE LBL architecture. The maximum photocurrent density generated by the LBL assembly at \(\tau_c = 8\) layers was \(J_{\text{max}} = 48.2\,\text{mA/cm}^2\) (Table 3, entry 2). The \(NBr\)-NDI-OPE LBL assembly generated less photocurrent and shows a lower critical thickness than the corresponding \(NBr\)-NDI-OPE zipper \((\tau_c = 20)\). The reasons for this decrease are as follows: i) The formation of a well ordered and oriented architecture in the zipper assembly, in comparison to the less ordered LBL assembly, maintains charge separation over a large distance. ii) The LBL assembly stops growing earlier than the zipper assembly.

![Figure 44: Photocurrent generation of the \(NBr\)-NDI-OPE zipper assembly \(Au-54-(55-56)_n\).](image)

The existence and relevance of the sticky ends for the vectorial growth of the zipper assembly was verified by a capping experiment. The \(Au-54-55\) bilayers were immersed into an aqueous solution of the \(HH\)-NDI-OPE \(54\). Repeated incubation of the capped \(Au-54-55-54\) with cationic propagator \(55\) and then the anionic propagator \(56\) did not increase the photocurrent density of...
the system (Figure 43). This experiment proved that the presence of sticky ends is essential for the vectorial growth of the zipper assembly. In sharp contrast, a tentative capping experiment in LBL assembly was unsuccessful, i.e., the LBL assembly Au-\textbf{89-55-54-(55-56)}_n continued generation of photocurrent.

### 3.2.7 Quartz Crystal Microbalance (QCM) Measurements

After successful characterisation of the zipper and LBL assemblies via photocurrent generation, the next target was to examine the assembly formation process. The zipper and LBL assemblies were therefore studied using a (QCM).

![Figure 45: Time course of quartz crystal frequency change upon exposure of Au-54 to the cationic propagator 55.](image)

**Figure 45**: Time course of quartz crystal frequency change upon exposure of Au-54 to the cationic propagator 55.
The mass deposited per layer of the NBr-NDI-OPE zippers and of the LBL assemblies were determined electromechanically using QCM (Figure 46). The results obtained from the QCM measurements were consistent with the activity measured by photocurrent generation. As noted in the photocurrent measurements (Figure 40), very slow deposition of the layers in the zipper and LBL assemblies were also observed using QCM measurements (Figure 45). This unusual kinetic behaviour was interpreted to originate from a slow post-adsorption conformational change as reported previously. The deposition of mass in the zipper and LBL assemblies were found in equal quantities. The mass deposition in the zipper and LBL assemblies were measured up to 30 layers. Both the LBL and zipper assemblies showed no saturation in mass deposition indicating continuous growth of the surface assembly.

![Figure 46: Frequency changes as a function of number of OPE zipper (○) or OPE LBL layers (□).](image-url)
The QCM measurements suggest that the saturation of photocurrent in the zipper and LBL assemblies was due to the charge recombination before it reaching the electrodes and not because the growth of the assemblies stops. The higher critical thickness of the zipper assembly in comparison to the LBL assembly suggests that the topologically matching long-range organisation of the zipper assembly translates into improved charge carrier mobilities and contributes to the strong relative photocurrents found.

We further studied the surface morphology of the NBr-NDI-OPE zipper and LBL assemblies by AFM measurements in collaboration with the group of Professor Huskens from the University of Twente. AFM images of the NBr-NDI-OPE zipper assembly were smoother than those of the LBL assemblies, control NBr-NDI-POP zippers¹⁶⁸ and the LBL and BHJ photosystems found in the literature.²²,⁴⁴,⁵² The low surface roughness has been proposed to be the key to significant function in organic photovoltaic and molecular optoelectronics.²²

3.2.8 Photocurrent-Voltage Curves (J-V Profile) of NBr-NDI-OPE Zipper and LBL Assemblies

With information regarding the assembly formation, the photocurrent generation and the surface morphology of the zipper and LBL assemblies in hand the photovoltaic performance of the assemblies was measured. The measurement of the J-V curve is an easy and useful method for the evaluation of the photovoltaic properties of the zipper and LBL assemblies. J-V curves were measured to determine following four key parameters (Figure 47): i) short circuit photocurrent density ($J_{sc}$), ii) open-circuit potential ($V_{oc}$), iii) fill factor (FF) and iv) solar energy to current conversion efficiency ($\eta$). The fill factor relates to the maximum power output divided by the product of the short circuit current density and open-circuit voltage. A good fill factor benefits from well
organised surface architectures, and is a very important parameter for determining the device efficiency.\textsuperscript{173}

The $J-V$ curve of the $\text{NBr-NDI-OPE zipper } \text{Au-54-(55-56)}_{55}$ (Figure 47 (solid line)) revealed $FF$ of 0.61 (Table 3 entry 1). The obtained $FF$ of the zipper assembly was the same as that of the LBL assembly ($FF = 0.61$) and as good as the optimized BHJ organic solar cells documented in the literature.\textsuperscript{22} This $FF$ is consistent with high charge mobility. The $FF$ found for the $\text{NBr-NDI-OPE zipper Au-54-(55-56)}_{55}$ compared very well with the $\text{OO-NDI-POP zippers } (FF = 0.53)$\textsuperscript{27} and that of the $\text{NN-NDI-OPE zipper architecture } (FF = 0.52)$.\textsuperscript{174}

![Figure 47: Current-voltage profile of the $\text{NBr-NDI-OPE zipper assembly Au-54-(55-56)}_{55}$ (solid line) and the $\text{NBr-NDI-OPE LBL assembly Au-89-(55-56)}_{55}$ (dotted line).](image)

The $J_{sc}$ generated by the $\text{NBr-NDI-OPE zipper architecture Au-54-(55-56)}_{55}$ ($J_{sc} = 78.7 \, \mu\text{Acm}^{-2}$) was almost double that of the $\text{NBr-NDI-OPE LBL assembly Au-89-(55-56)}_{55}$ ($J_{sc} = 46.8 \, \mu\text{Acm}^{-2}$), whereas the $V_{oc}$ obtained by both assemblies were almost the same. The obtained solar energy to current conversion efficiency ($\eta = 0.035\%$) for the $\text{NBr-NDI-OPE zipper assembly Au-54-(55-56)}_{55}$ was appreciated better considering a
reported 280-fold quenching via energy transfer to gold surfaces.\textsuperscript{175} The device efficiency of the NBr-NDI-OPE zipper architecture (\(\eta = 0.035\%\)) was higher than that of the LBL assembly Au-\textsuperscript{89}(55-56)_\textsubscript{n}-55 (\(\eta = 0.021\%\)) and the analogous mismatch NBr-NDI-POP zipper assembly (\(\eta = 0.022\%\)). The key photovoltaic parameters for the topologically matching NBr-NDI-OPE zipper architecture were therefore much better than those of the NBr-NDI-OPE LBL and the mismatch NBr-NDI-POP zipper assemblies.

Table 3: Characteristics of the NBr-NDI-OPE\textsuperscript{a} zipper and LBL and analogous NBr-NDI-POP zipper photosystems.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Assembly</th>
<th>Example</th>
<th>(\tau) (layers)\textsuperscript{f}</th>
<th>(J_{\text{max}}) ((\mu\text{Acm}\text{m}^2))</th>
<th>(J_{oc}) ((\mu\text{Acm}\text{m}^2))</th>
<th>(V_{oc}) (V)</th>
<th>FF\textsuperscript{g}</th>
<th>(\eta)\textsuperscript{h} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OPE Zipper</td>
<td>Au-54- (55-56)\textsubscript{55}</td>
<td>20</td>
<td>101.6</td>
<td>78.7</td>
<td>-0.48</td>
<td>0.61</td>
<td>0.035</td>
</tr>
<tr>
<td>2</td>
<td>OPE LBL</td>
<td>Au-\textsuperscript{89}(55-56)\textsubscript{n}-55</td>
<td>8</td>
<td>48.2</td>
<td>46.8</td>
<td>-0.49</td>
<td>0.61</td>
<td>0.021</td>
</tr>
<tr>
<td>3</td>
<td>POP Zipper</td>
<td>10</td>
<td>53.6</td>
<td>-0.44</td>
<td>0.61</td>
<td>0.022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}J-V data for the OPE systems are given for \(n = 14\). \textsuperscript{b}Data from ref.\textsuperscript{168} \textsuperscript{c}Critical thickness in \(J\)-L curves of OPE system are from Figure 43. \textsuperscript{d}Maximum photocurrent density in \(J\)-L curves, from Figure 43 (measured at input power \(P_{\text{in}} = 66\text{ mW cm}^2\)). \textsuperscript{e}J-V data, from Figure 47 (measured at input power \(P_{\text{in}} = 66\text{ mW cm}^2\)). \textsuperscript{f}Maximum photocurrent density in \(J\)-L curves, from Figure 43 (measured at input power \(P_{\text{in}} = 66\text{ mW cm}^2\)). \textsuperscript{g}Fill factor \(FF = \frac{P_{\text{max}}}{V_{oc} \times J_{oc}} = \frac{(V_{oc} \times J_{oc})}{(V_{oc} \times J_{oc})}\). \textsuperscript{h}Open circuit voltage. \textsuperscript{i}Efficiency of the photosystems \(\eta = \frac{P_{\text{max}}}{a \times P_{\text{in}}}\), \(a = \) the irradiated area of the electrode in the electrolyte solution (cm\textsuperscript{2}).
3.2.9 Action Spectrum and Possible Photoinduced Electron Transfer Mechanism

The photocurrent-action spectrum of the NBr-NDI-OPE zipper assembly Au-(55-56)x-55 was measured to quantify the photocurrent generated by the OPE scaffold and the NBr-NDI chromophores. The action spectrum revealed a strong peak at 540 nm that almost coincides with the NBr-NDI absorption maximum (Figure 48). The ratio IPCE_{540}/IPCE_{350} = 0.71 indicates that the maximal IPCE accessible at 540 nm was approximately the same as that at high energy (at 350 nm). The action spectrum also shows a peak around 410 nm, which coincides with the absorption of the OPE scaffold. The ratio of IPCE_{410}/IPCE_{350} = 0.61 showed that the OPE scaffold in the zipper assembly not only donates electrons to the NDI chromophores but also harvests light energy efficiently and generates photocurrent. The observed bathochromic absorption of the OPE in the action spectrum implies a co-planar orientation of the phenyl rings. OPE planarization was expected for the zipper assembly, and should give rise to higher charge mobility of the p-semiconductors.\textsuperscript{133,142} The comparably high IPCE of the NBr-NDI was in excellent agreement with the favourable electron transfer from the OPE donor to the NDI acceptors (Figure 29)
The photoinduced electron transport and high photoactivity of the NBr-NDI-OPE 55 was studied via femtosecond fluorescence and transient spectroscopy. This measurement was done in collaboration with Professor Vauthy of the University of Geneva. It was found that very fast electron transfer takes place from the OPE scaffold to the NBr-NDI units, independently of whether the OPE or an NDI was initially excited. The lifetime of the formed charge-separated state (OPE\(^+\)-NDI\(^-\) pair) of the propagator 55 was about 270 ns. This finding was an important evidence for the presence of the OPE\(^+\)-NDI\(^-\) pair, i.e., a SHJ. The faster charge separation observed upon OPE excitation than upon NDI excitation further demonstrated that electrons rather than energy are transferred from the OPE to the NDI.
Figure 49: Possible electron transfer mechanism in the \(\text{NBr-NDI-OPE zipper}\) architecture. HOMO levels (solid lines) and LUMO levels (dashed lines) of \(\text{NBr-NDI}\) (red), \(\text{HH-NDI}\) (grey), OPE (black) and TEOA (green). Orange rectangle represents the gold electrode.

Figure 49 illustrates the possible electron transfer mechanism when light energy is converted to electrical energy in the \(\text{NBr-NDI-OPE zipper}\) assembly \(\text{Au-54-(55-56)}_n\). Upon light absorption and photoexcitation of the \(\text{NBr-NDI}\) (state A), the exciton (state B) is generated. The generated hole at the HOMO level of \(\text{NBr-NDI}\) would be filled by electron transfer from (or hole transfer to) the OPE scaffold to give a charge separated state with a radical anion on the \(\text{NBr-NDI}\) unit and radical cations on the OPE scaffolds (state C,
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via path a). Similarly, photoexcitation of the OPE (state \( D \)) could generate an exciton (state \( E \)) and subsequently transfer an electron to the LUMO level of the \( NBr\)-NDI acceptor instead of energy transfer (this was proved via femtosecond fluorescence and transient spectroscopy) and generate a charge separated state \( C \) (via path b). A hole at the HOMO level of the OPE (state \( C \)) should eventually be transferred to the sacrificial electron donor TEOA in solution, while the electron on the \( NBr\)-NDI should be injected to the gold electrode via \( HH\)-NDI and generate the final state \( G \).

3.3 Design and Synthesis of the Red ON-NDI-OPE

Supramolecular n/p-Heterojunction Zipper Architectures

3.3.1 Design

The topologically matching red \( NBr\)-NDI-OPE zipper assembly generates consistently more photocurrent and has higher critical thickness (\(~20\) layers) than the mismatched \( NBr\)-NDI-POP zipper assembly. This result shows that \( NBr\)-NDIs are sensitive towards topological mismatches. The reason for this is elusive and could be due to excessive hydrophobicity, missing dispersion contacts between stacks, or even competing halogen bonds.\(^{176,177}\) It was found that the photoinduced charge separation and charge recombination were complicated with halogenated NDIs because of contributions from triplet state, presumably favoured because of heavy atom effects.\(^{168}\)
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Figure 50: Frontier orbital energy levels of ON-NDI compared to other NDIs and OPEs (solid lines, HOMO; dashed lines, LUMO; dashed arrows, absorption of light, with wavelength of maximum absorption and emission).

Figure 51: Molecular structures and expected supramolecular architectures of OPE-NDI initiator (54) and propagators (90 & 91) and of their topologically matched zipper assembly Au-54-(90-91)n-90.
To better understand the importance of topological matching and the halogen atom effect, we decided to make a non-halogenated red ON-NDI-OPE zipper architecture Au-54-(90-91)ₙ (Figure 51). Compared to halogenated red NDIs, the HOMO energy level of red ON-NDI is 0.2 eV higher and the energy band gap is 0.1 eV smaller (Figure 50). ON-NDIs like NBr-NDIs and NCI-NDIs under photoexcitation could donate a hole (which has a lower HOMO level than OPE) to the OPE scaffold and generate photocurrent. To make the non-halogenated red ON-NDI-OPE zipper assembly on a gold surface, we prepared the cationic and anionic red ON-NDI-OPE propagators 90 and 91. The previously synthesised HH-NDI-OPE 54 initiator was used to initiate the zipper assembly.

### 3.3.2 Synthesis of the Cationic ON-NDI-OPE Propagator 90

The cationic Alloc-protected red ON-NDI 92 was synthesised from commercially available 1,4,5,8-naphthalenetetraacarboxylic acid dianhydride (76) in five steps by following recently reported procedures. The obtained ON-NDI compound 92 was subjected to selective deprotection of the Alloc group in the presence of the Cbz group by a palladium (Pd⁰) catalyzed cleavage using PhSiH₃ in DCM to give the desired ON-NDI amine 93. The impurities were removed from compound 93 by solid-liquid extraction with diethyl ether and DCM. The obtained ON-NDI amine 93 was subjected for coupling with the OPE acid rod 83 in freshly distilled DMF in the presence of HATU, DTBP and TEA to furnish the protected propagator 94 in 28% yield. The obtained compound 94 was purified by column chromatography and successive PTLCs. The identity and the purity of the ON-NDI-OPE propagator 94 were determined using MALDI-MS and HPLC respectively (Figure 52).
Scheme 12: Synthesis of the cationic ON-NDI-OPE propagator 90. i) Pd(PPh$_3$)$_4$, PhSiH$_3$, rt, 15 min, DCM; ii) HATU, DTBP, TEA, DMF, rt, 16 h, 28%, iii) TFA, thioanisole, pentamethyl benzene, 50 °C, 3 h, quant.

The benzyl protected hydrophobic ON-NDI-OPE propagator 64 was treated with TFA and a catalytic amount of thioanisole and pentamethyl benzene at 50 °C for 3 h to afford quantitatively the cationic hydrophilic ON-NDI-OPE propagator 90 as a red solid (Scheme 12). The purity of the final
deprotected hydrophilic product 90 was checked using RP-HPLC and the identity was determined using MALDI-MS.

**Figure 52:** A) MALDI-MS (in dithranol) of the compound 94. B) HPLC of the compound 94 (YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 92:8, 2 ml/min, \(R_t = 7.29\) min).

With the cationic ON-NDI-OPE propagator 90 in hand, the anionic ON-NDI-OPE propagator 91 was the next synthetic target.

### 3.3.3 Synthesis of the Anionic ON-NDI-OPE Propagator 91

Similar to the cationic ON-NDI amine 93, the anionic ON-NDI amine 96 was synthesised from commercially available 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (76) in six steps following previously reported procedures. The obtained ON-NDI amine 96 was coupled with the OPE acid rod 83 by the same procedure described above to
furnish the compound 97 in 43% yield. The compound 97 was purified through a combination of column chromatography and successive PTLCs. The identity and the purity of the fully protected ON-NDI-OPE propagator 97 were determined using MALDI-MS and the HPLC respectively (Figure 53).

Scheme 13: Synthesis of the anionic ON-NDI-OPE propagator 91. i) Pd(PPh₃)₄, PhSiH₃, rt, 15 min, DCM; ii) HATU, DTBP, TEA, DMF, rt, 16 h, 43%, iii) TFA/DCM, 3 h, quant.
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The tert-butyl groups of the fully protected hydrophobic ON-NDI-OPE propagator 97 were cleaved via a treatment with 1:1 mixture of TFA/DCM at room temperature (Scheme 13). The solvent was removed in vacuo and the anionic hydrophilic ON-NDI-OPE propagator 91 was washed with diethyl ether and DCM to get a red solid. The final product 91 was identified using MALDI-MS.

![Figure 53](image)

**Figure 53:** A) MALDI-MS (in ditranol) of the compound 97; B) HPLC of the compound 97 (YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 92:8, 1 ml/min, \( R_t = 6.98 \) min).

3.4 The Red ON-NDI-OPE Zipper Assembly Formation and Characterisation

With the anionic HH-NDI-OPE initiator 54, the cationic ON-NDI-OPE propagator 90 and the anionic ON-NDI-OPE propagator 91 in hand, the next
target was the formation and characterisation of the ON-NDI-OPE zipper assembly.

### 3.4.1 UV Spectroscopy of the ON-NDI-OPE Propagator 90

![Absorption spectra](image)

**Figure 54:** Absorption spectra of the monomeric ON-NDI 92 (blue, dotted), the OPE rod 88 (black, dotted) and the ON-NDI-OPE propagator 90 (red, solid).

The absorption spectra of the monomeric ON-NDI 92 and the cationic ON-NDI-OPE propagator 90 in MeOH in comparison with the tert-butyl protected OPE rod 88 are shown in Figure 54. The first absorption band at around 550 nm is due to a local NDI transition. This charge-transfer type band in the ON-NDI-OPE propagator 90 is substantially broader and slightly red shifted compared to that of the ON-NDI monomer 92. A second absorption band at around 408 nm is due to local transition of OPE. The shape and position of this band in the ON-NDI-OPE propagator 90 matches with the absorption band of the tert-butyl protected OPE rod 88. The absorption spectra of the ON-NDI-OPE propagator 90 shows there is no ground state interaction between the ON-NDI chromophores and the OPE scaffold. The absorption band at around 360 nm can be seen with the monomeric ON-NDI 92 and the propagator 90 and is due to a π-π* transition involving the NDI centre.
3.4.2 ON-NDI-OPE Zipper and LBL Assembly Formation

For the ON-NDI-OPE zipper and LBL assembly initiating, monolayers of the HH-NDI-OPE initiator 54 and lipoic acid (89) on freshly cleaned gold electrodes were prepared and characterized following the previously described procedure in Section 3.2.5. The ON-NDI-OPE zipper architecture Au-54-(90-91)$_n$ was prepared by successive and repetitive incubation of the Au-54 monolayers with an aqueous solution of the cationic ON-NDI-OPE propagator 90 followed by the anionic ON-NDI-OPE propagator 91.

The presumably less ordered conventional LBL ON-NDI-OPE assembly Au-89-(90-91)$_n$ was prepared for comparison with the well ordered ON-NDI-OPE zipper Au-54-(90-61)$_n$ assembly. The LBL assembly Au-54-(90-91)$_n$ was prepared analogously from the anionic Au-89 monolayers with the cationic and anionic ON-NDI-OPE propagators 90 and 91.

3.4.3 Photocurrent Generation

The photocurrent generation by the ON-NDI-OPE zipper Au-54-(90-91)$_n$ and LBL Au-89-(90-91)$_n$ photosystems were evaluated with a conventional three-electrode system, in which the electrode with the photosystem served as the working electrode, a Pt wire as the cathode and Ag/AgCl as a reference electrode. A solution of 50 mM TEOA (pH = 10) in 100 mM aqueous Na$_2$SO$_4$ was used as the electron donor. Photocurrent generation and termination by the zipper and LBL systems is instantaneous and the obtained currents were stable. The relationship between the photocurrent densities and number of layers in the ON-NDI-OPE zipper and LBL assemblies is shown in the Figure 55.
Figure 55: $J$-$L$ profiles of the ON-NDI-OPE zipper Au-$54$-(90-91)$_n$ (○) and the LBL assembly Au-$89$-(90-91)$_n$ (□).

The photocurrent generated by the ON-NDI-OPE zipper assembly Au-$54$-(90-91)$_n$ increased linearly with an increasing number of layers. (Figure 55, ○). The saturation of photocurrent generation was reached at a critical thickness of around 20 layers and a maximum photocurrent density of $J_{\text{max}} = 16.0 \ \mu\text{A/cm}^2$ (Table 4, entry 1). The analogous mismatch ON-NDI-POP zipper architecture showed photocurrent saturation at around 10 layers and generated much less photocurrent ($J_{\text{max}} = 3.8 \ \mu\text{A/cm}^2$) (Table 4, entry 3). The better performance of the ON-NDI-OPE zipper architecture Au-$54$-(90-91)$_n$ compared to the analogous ON-NDI-POP zipper has been observed previously in red NBr-NDI-OPE and blue NN-NDI-OPE zipper systems. The high performance of the OPE zipper compared with that of the POP zipper originates from several contributions including photocurrent...
generation by OPEs as well as topological matching. The ON-NDI-OPE zipper generates much less photocurrent than the NBr-NDI-OPE zipper system, likely due to the higher HOMO level of ON-NDI than the NBr-NDI. The conventional ON-NDI-OPE LBL assembly Au-89-(90-91)_n had the same critical thickness as the ON-NDI-OPE zipper but produced much less photocurrent ($J_{\text{max}} = 6.0 \ \mu{\text{A/cm}}^2$) (Figure 55, □, Table 4, entry 2).

### 3.4.4 Photocurrent-Voltage Curves (J-V Profile) of ON-NDI-OPE Zipper and LBL Assembles

To evaluate their photovoltaic properties, the $J$-$V$ curves of the ON-NDI-OPE zipper and LBL assemblies were measured. The $J$-$V$ profile of the ON-NDI-OPE zipper assembly Au-54-(90-91)_7-90 (●) and LBL assembly Au-89-(90-91)_7-90 (○).

![Figure 56: Current-voltage (J-V) profile of ON-NDI-OPE zipper assembly Au-54-(90-91)_7-90 (●) and LBL assembly Au-89-(90-91)_7-90 (○).](image)

To evaluate their photovoltaic properties, the $J$-$V$ curves of the ON-NDI-OPE zipper and LBL assemblies were measured. The $J$-$V$ profile of the ON-NDI-OPE zipper assembly Au-54-(90-91)_7-90 revealed a non-linear dependence of photocurrent generation on voltage (Figure 56, ●, Table 4, entry 1). The $FF$ of the ON-NDI-OPE zipper, a measure for the maximum power generated with light, was calculated to be $FF = 0.55$. The obtained $FF$ of ON-NDI-OPE zipper assembly was similar to that of the LBL assembly and is
as good as the ON-NDI-POP zipper. These comparably high $FF$ were in the range of those observed previously with OPE-NDI zippers ($NBr$-NDI-OPE, $FF = 0.61$; $NN$-NDI-OPE, $FF = 0.52$)\textsuperscript{168,174} and POP-NDI zippers ($NBr$-NDI-POP, $FF = 0.61$; $OO$-NDI-POP; $FF = 0.53$).\textsuperscript{27,168} The $J_{sc}$ generated by the ON-NDI-OPE zipper assembly $\text{Au-54-(90-91)$_9$-90}$ ($J_{sc} = 15.3 \, \mu \text{Acm}^{-2}$) was more than double that of the LBL assembly $\text{Au-89-(90-91)$_7$-90}$ ($J_{sc} = 5.2 \, \mu \text{Acm}^{-2}$), although much less than that of the $NBr$-NDI-OPE zipper assembly ($J_{sc} = 78.7 \, \mu \text{Acm}^{-2}$). The $V_{oc}$ of the ON-NDI-OPE zipper and LBL assemblies are almost the same. The $J$-$V$ characteristics can be interpreted as corroborative support for better organisation of OPE zippers than POP zippers.

Table 4: Characteristics of ON-NDI-OPE$^a$ zipper $\text{Au-54-(90-91)$_9$-90}$ and LBL $\text{Au-89-(90-91)$_7$-90}$ and analogous ON-NDI-POP zipper photosystems.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Assembly</th>
<th>$\tau_c$ (layers)$^c$</th>
<th>$J_{max}$ ($\mu \text{Acm}^{-2}$)$^d$</th>
<th>$J_{sc}$ ($\mu \text{Acm}^{-2}$)$^e$</th>
<th>$V_{oc}$ ($V$)$^f$</th>
<th>$FF$ $^{fn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OPE zipper</td>
<td>20</td>
<td>16.0</td>
<td>15.3</td>
<td>-0.40</td>
<td>0.55</td>
</tr>
<tr>
<td>2</td>
<td>OPE LBL</td>
<td>20</td>
<td>6.0</td>
<td>5.2</td>
<td>-0.39</td>
<td>0.54</td>
</tr>
<tr>
<td>3$^b$</td>
<td>POP zipper</td>
<td>10</td>
<td>3.8</td>
<td>3.8</td>
<td>-0.38</td>
<td>0.56</td>
</tr>
</tbody>
</table>

$^a$J-V data for ON-NDI-OPE systems are given for $n = 14$. $^b$Data from ref. 177. $^c$Critical thickness in $J$-$L$ curves of ON-NDI-OPE system are from Figure 55. $^d$Maximal photocurrent density in $J$-$L$ curves, from Figure 55 (measured at input power $P_n = 66 \, \text{mW cm}^{-2}$). $^e$J-V data, from Figure 56 (measured at input power $P_n = 66 \, \text{mW cm}^{-2}$). $^f$Short circuit current density. $^g$Open circuit voltage. $^h$Fill factor $FF = \text{maximum power} / (V_{oc} \times J_{sc}) = (V_m \times J_m) / (V_{oc} \times J_{sc})$, $V_m$ = voltage at maximal power $P_{max}$, $J_m$ = photocurrent density at $P_{max}$. 
3.4.5 Action Spectrum of the ON-NDI-OPE Zipper Assembly

![Graph showing action spectra](image)

**Figure 57:** Action spectrum of the ON-NDI-OPE zipper assembly Au-54-(90-91)-90 (●) with comparison to the action spectrum of NBr-NDI-OPE zipper assembly Au-54-(55-56)-55 (○). IPCE = incident photon-to-current efficiency, normalized to 1 at 350 nm.

The action spectrum of the red ON-NDI-OPE zipper assembly Au-54-(90-91),_h revealed that the ON-NDI chromophore (peak around 560 nm) is capable of generating photocurrent (Figure 57, ●). Photocurrent generation by the ON-NDI chromophores decreased in comparison with the NBr-NDI chromophores. This means that the photocurrent generated by OPE-NDI increased with decreasing HOMO energy of the NDI chromophore (Figure 58). This result suggests that photoinduced hole transfer from the NDI to the OPE is important for photocurrent generation. Blue NN-NDIs with HOMO levels above OPEs failed to generate photocurrent. Among the red NDIs ON and NBr, the higher HOMO of the ON was correctly reflected in a reduced ability to generate photocurrent (Figure 58). The perfect correlation of the NBr > ON >> NN series for decreasing photocurrent generation with increasing HOMO energies supported the importance of rod/stack PCS, i.e. SHJ, for photocurrent.
This was supported by transient absorption spectroscopy.\textsuperscript{168,174,178}

Figure 58: Energy levels with favourable (bold), possible (solid) and unfavourable (dotted) photoinduced rod/stack electron (e\textsuperscript{-}) and hole (h\textsuperscript{+}) transfers (arrows).

Photocurrent generation of the OPE scaffold occurred at around 400 nm (Figure 57). The transient absorption spectroscopy measurement suggests that it originates from ultrafast rod/stack electron transfer from the excited OPE donor to the NDI acceptors (Figure 58, top arrows).\textsuperscript{149,168,174,178} According to increasing literature precedence,\textsuperscript{27,53,56,58,115,149,168} it appears that the presence of many acceptors (NDIs) around a single donor (OPE) is favourable for very fast electron transfer rather than energy transfer from OPEs to the NDIs.
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3.5 Supramolecular n/p-Heterojunction with Oriented Multicolored Antiparallel Redox Gradients (OMARG-SHJ)

The topologically matching red $NBr$-NDI-OPE zipper assembly has been shown to generate more photocurrent and has a higher critical thickness (~ 20 layers) than the conventional $NBr$-NDI-OPE LBL assembly. The $NBr$-NDI-OPE zipper assembly has a high $FF$ of 0.61, a very smooth surface, and responds positively to control experiments such as capping with the $HH$-NDI-OPE terminator. The optoelectronic matching of the $NBr$-NDI acceptors with the OPE donor in the $NBr$-NDI-OPE zipper is reflected in an increased photocurrent generation compared to the less favourable red $ON$-NDI-OPE and blue $NN$-NDI-OPE zippers. The action spectrum of the $NBr$-NDI-OPE zipper indicates that the OPEs (planarized donor) and the $NBr$-NDIs (acceptor) contribute to photocurrent generation. In the $NBr$-NDI-OPE zipper assembly the photoinduced rod/stack charge separation needed for a SHJ was proven by transient absorption spectroscopy, where the OPE excitation was followed by electron (rather than energy) transfer to the $NBr$-NDI acceptors on a femtosecond time scale.

The main limitation of the $NBr$-NDI-OPE zipper and other NDI-OPE zipper assemblies is the saturation of photocurrent when the critical thickness is reached. The following factors may contribute to the photocurrent saturation at the critical thickness: i) The probability increases that electrons and holes recombine before reaching the electrodes because the layer thickness becomes larger than the exciton diffusion length limit. ii) The zipper assembly may stop growing after reaching its critical thickness or form a disordered structure. iii) With increasing thickness of the zipper assembly, the absorbance may become so high such that only very few photons may reach the chromophores close to
the electrode. To tackle this key challenge, two different strategies were introduced.

The first strategy involved the formation of antiparallel redox gradients in the $n$- and $p$-conducting channels of the zipper assembly. It was shown by Matile and co-workers that the introduction of redox gradients in the $n$-semiconducting NDI channel of POP-NDI zipper assemblies has two different outcomes. In the case of a favourable redox gradient, a high $V_{oc}$ and a high $FF$ of 0.55 was observed. In the unfavourable POP-NDI zipper with reversed redox gradients in the $n$-conducting NDI channel, a low $FF$ of 0.35 and a very low $V_{oc}$ was observed. This demonstrates that the formal redox gradient and reversed redox gradient in the POP-NDI zipper architectures influence function. Therefore the introduction of an antiparallel redox gradient in the $n$- and $p$-conducting channels of a zipper assembly could increase the critical thickness, photovoltaic properties and absorb light over a large section of the visible range. The second strategy was the design and synthesis of a NDI-OPE zipper architecture, which can be polymerized after zipper assembly formation. This strategy could enable the formation of a well-ordered structure thereby increasing the critical thickness and photovoltaic properties of the zipper assembly.

### 3.5.1 Design of Oriented Multicolored Antiparallel Redox Gradient (OMARG) Zipper Assemblies

For the creation of an oriented multicolored antiparallel redox gradient (OMARG) zipper assembly, the yellow $OO\text{-NDI-POP zipper Au-34-(35-36)_{n}}$ appeared to be ideal to complement the red $NBr\text{-NDI-OPE zipper}$. In $OO\text{-NDI-POP zipper assemblies}$ the optoelectronic matching of $OO\text{-NDI acceptors with POP donors}$ shows large photocurrent generation, long-lived charge separation, a high $FF$ of 0.53 and a high critical thickness
The $HH$-NDI acceptors near the gold surface in both the $NBr$-NDI-OPE and $OO$-NDI-POP zipper assemblies have a formal redox gradient in the $n$-conducting channel. The placement of the $NBr$-NDI-OPE zipper on top of the $OO$-NDI-POP zipper would give a mixed zipper assembly of oriented multicolored antiparallel redox gradients and would generate the SHJ. The $OO$-NDI (lower HOMO level) acceptors in the $n$-conducting channel would accept electrons from the $NBr$-NDI (higher HOMO level) donors and direct them to the bottom of the multilayer zipper assembly. In contrast, the OPEs (higher HOMO level) in the $p$-conducting channel would accept holes from POPs (lower HOMO level) and direct them to the top of the multilayer zipper assembly (Figure 59).

$\text{Figure 59:}$ Energy levels with favourable photoinduced rod/stack electron ($e^-$) and hole ($h^+$) transfers (arrows) in the OMARG zipper assembly.
3.5.2 Formation of Oriented Multicolored Antiparallel Redox Gradient (OMARG) Zipper Assemblies

The mixed zipper assembly of a formal OMARG SHJ architecture was initiated by the deposition of the short anionic \( HH\)-NDI-POP initiator 34 on freshly cleaned gold electrodes. The deposition was characterised by the previously reported procedure.\(^{27}\) The obtained Au-34 monolayers were immersed sequentially into an aqueous solution of the cationic and then the anionic \( OO\)-NDI-POP propagators 35 and 36. The obtained zipper assemblies Au-34-(35-36)\(_n\)-35 were further immersed sequentially into an aqueous solution of the anionic and then the cationic \( NBr\)-NDI-OPE propagators 56 and 55 to get the formal OMARG zipper architecture Au-34-(35-36)\(_n\)-35-(55-56)\(_n\). The photocurrent generation of the mixed zipper assembly was measured after each deposition. The sequential deposition was continued until saturation of photocurrent generation was reached.

The reversed OMARG zipper assembly Au-54-(55-56)\(_n\)-55-(36-35)\(_n\) was prepared for comparison and verification of the existence of antiparallel redox gradients in the \( n \) and \( p \)-conducting channels of the formal OMARG zipper assembly. The reversed OMARG zipper assembly was initiated with the short anionic \( HH\)-NDI-OPE initiator 54 and propagated with \( NBr\)-NDI-OPE propagators 55 and 56 until ten layers by previously described procedure in the Section 3.2.5. The obtained \( NBr\)-NDI-OPE zipper assembly Au-54-(55-56)\(_n\)-55 was further immersed sequentially into an aqueous solution of the anionic and then the cationic \( OO\)-NDI-POP propagators 36 and 35 to get the reversed OMARG zipper assembly Au-54-(55-56)\(_n\)-55-(36-35)\(_n\).
3.5.3 Photocurrent generation

The mixed OMARG zipper architectures Au-34-(35-36)_n-35-(56-55)_n and Au-54-(55-56)_n-55-(36-35)_n were evaluated by photocurrent generation as described previously in the Section 3.2.6. The J-L profiles of the OMARG zipper architecture Au-34-(35-36)_n-35-(56-55)_n and the reversed OMARG zipper architecture Au-54-(55-56)_n-55-(36-35)_n are shown in Figure 60. The photocurrent generated by the formal OMARG zipper architecture Au-34-(35-36)_n-35-(56-55)_n (Figure 60, ●, ■) increased with an increasing number of layers. The favourable architecture showed that the increase in photocurrent density was saturated at around 38 layers (critical thickness \( \tau_c = 38 \) layers). The architecture Au-34-(35-36)_n-35-(56-55)_n generated a maximum photocurrent density of \( J_{\text{max}} = 85.5 \mu\text{A/cm}^2 \).

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**Figure 60:** Current-layer (J-L) profiles of formal OMARG zipper assembly architecture Au-34-(35-36)_n-35-(56-55)_n (●, ■) and reversed OMARG zipper architecture Au-54-(55-56)_n-55-(36-35)_n (○, □), lines are added to guide the eye.
The first nine layers of the \textit{OO}-NDI-POP propagators generated photocurrent to a similar degree as it was reported in the literature.\textsuperscript{27} Further addition of the \textit{NBr}-NDI-OPE propagators generated photocurrent quite linearly up to 38 layers. The high critical thickness of the OMARG zipper architecture Au-\textit{34}-\textit{(35}-\textit{36})\textit{a}-\textit{35}-\textit{(56}-\textit{55})\textit{a}, was almost double that of \textit{NBr}-NDI-OPE zipper assembly Au-\textit{54}-\textit{(55}-\textit{56})\textit{a} (\textapprox{} 20 layers). The unfavourable OMARG zipper assembly Au-\textit{54}-\textit{(55}-\textit{56})\textit{a}-\textit{55}-\textit{(36}-\textit{335})\textit{a}, (Figure 60, ○, □) consists of nine layers of the \textit{NBr}-NDI-OPE propagators 55 and 56 which show a linear increase in photocurrent generation. Further addition of the \textit{OO}-NDI-POP propagators 36 and 35 caused a decrease and saturation of the photocurrent density. This decrease could be due to the reverse redox gradients (i.e. mismatches in the redox gradients) formed after addition of the \textit{OO}-NDI-POP propagators 36 and 35. The difference between the abilities for photocurrent generation of the favoured and the reversed OMARG zipper assemblies provided experimental evidence that OMARG’s exist in zipper assemblies and matters for function.
3.5.4 Photocurrent-Voltage Curves (J-V Profile) of the OMARG Zipper Assembles

The current-voltage (J-V) curves of the OMARG zipper architecture Au-34-(35-36)_4-35-(56-55)_26 were measured to evaluate its photovoltaic properties. The J-V profile of the OMARG zipper architecture Au-34-(35-36)_4-35-(56-55)_26 (Figure 61) revealed an $V_{oc}$ of -0.39 V, $J_{sc}$ of 68 $\mu$Acm$^{-2}$ and a $FF$ of 0.54 (Table 5, entry 1). The obtained photovoltaic properties are comparatively less than those obtained for the NBr-NDI-OPE zipper architecture Au-54-(55-56)_6-55 ($V_{oc}$ = -0.48 V, $J_{sc}$ = 78.7 $\mu$Acm$^{-2}$, $FF$ = 0.61). Efforts towards optimizing the OMARG zipper assembly by varying the numbers of OO-NDI-POP and NBr-NDI-OPE propagators and using other conducting materials are ongoing.
Table 5: Characteristics of the OMARG zipper assembly $\text{Au-}^{34-}(35-36)_{4}-35-(56-55)_{10}$ compared with those of the $NBr$-NDI-OPE zipper assembly $\text{Au-}^{54-(55-56)_{4}}-55$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Assembly</th>
<th>$\tau_c$ (layers)</th>
<th>$J_{\text{max}}$ ((\mu\text{A/cm}^2))</th>
<th>$J_{\text{sc}}$ ((\mu\text{A/cm}^2))</th>
<th>$V_{\text{oc}}$ (V)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OMARG-SHJs Zipper</td>
<td>38</td>
<td>85.5</td>
<td>68.0</td>
<td>-0.39</td>
<td>0.54</td>
</tr>
<tr>
<td>2</td>
<td>$NBr$-NDI-OPE Zipper</td>
<td>20</td>
<td>101.6</td>
<td>78.7</td>
<td>-0.48</td>
<td>0.61</td>
</tr>
</tbody>
</table>

*J-V data for $NBr$-NDI-OPE system are taken from section 3.2.8.

3.5.5 Action Spectra of the OMARG Zipper Assemblies

The action spectrum of the favourable OMARG zipper assembly $\text{Au-}^{34-}(35-36)_{4}-35-(56-55)_{10}$ (Figure 62, ●) almost coincides with the action spectrum of the normal $NBr$-NDI-OPE zipper assembly $\text{Au-}^{54-(55-56)_{4}}-55$ (see Section 3.2.9) and revealed that $NBr$-NDIs (acceptor) and OPEs (donor) harvest light efficiently and contribute to the photocurrent generation. The action spectrum of $\text{Au-}^{34-}(35-36)_{4}-35-(56-55)_{10}$ also revealed that the OO-NDIs contribute very little to the photocurrent generation. The less contribution could be due to the increasing thickness of the OMARG zipper assembly. The absorbance of the $NBr$-NDI-OPE layers may become so high such that only very few photons may reach the OO-NDI-POP layers close to the electrode. The action spectrum of the unfavourable OMARG zipper assembly $\text{Au-}^{54-(55-56)_{4}}-55-(36-35)_{10}$ (Figure 65, ○) revealed that OO-NDIs and $NBr$-NDIs are contributing to the generation of photocurrent. To understand the different results of favourable and unfavourable OMARG zipper assemblies in action...
spectrum, more detailed studies including QCM and AFM measurements are ongoing.

![Figure 62: Comparison of action spectrum](image)

**Figure 62:** Comparison of the action spectrum of the favourable OMARG zipper assembly $\text{Au-34-(35-36)_4-35-(36-35)_10}$ (●) with the action spectrum of the unfavourable OMARG zipper assembly $\text{Au-54-(55-56)_4-55-(36-35)_10}$ (○). IPCE normalized to 1 at 350 nm.

3.6 Design and Synthesis of Oriented Covalent Capture

*ON-NDI-OPE Zipper Assemblies*

3.6.1 Design

As mentioned in Section 3.5, the main limitation of the $\text{NBr-NDI-OPE}$ and $\text{ON-NDI-OPE}$ zipper assemblies is the saturation of photocurrent at a low critical thickness. This could be due to the formation of disordered structures at the critical thickness. To test this hypothesis, we proposed a NDI-OPE zipper architecture that can be photo-polymerized after assembly formation by intra and inter-assembly cross linking. The cross-linking may provide high physical
stability to the entire morphology and could increase the critical thickness and the photovoltaic properties of the supramolecular zipper assembly.

Figure 63: Frontier orbital energy levels of ON-NDI compared to HH-NDIs, OPEs and PDAs (solid lines, HOMO; dashed lines, LUMO; dashed arrows, absorption of light, with wavelength of maximum absorption and emission).

Over the past decade several different approaches have been utilized for the cross-linking of self-assembled supramolecular assemblies including click chemistry,\textsuperscript{77} diene metathesis\textsuperscript{39,75,76,79} and photo-polymerization.\textsuperscript{91,95,98} In an attempt to enable the preservation of the zipper assembly, photo-polymerizable diacetylene units were incorporated into the ON-NDI-OPE zipper assembly. Upon ultraviolet light irradiation the diacetylene units in the zipper assembly could effectively be cross-linked to form PDAs. The obtained PDAs may give stability to the zipper assembly to increase photocurrent.
generation and enhance the photovoltaic properties. The frontier orbital energy levels of polydiacetylene\textsuperscript{110,112,113} are in the range of electron donor materials and may also act as an additional electron donor moiety in the zipper assembly (Figure 63).

To make the polymerized red \textit{ON}-NDI-OPE zipper assembly on a gold surface that contains the cationic and the anionic red \textit{ON}-NDI-OPE propagators \textit{98} and \textit{99} polymerizable diacetylene units were prepared (Figure 64). The previously synthesised \textit{HH}-NDI-OPE initiator \textit{54} would be used to initiate the zipper assembly.

![Figure 64: Molecular structures of \textit{ON}-NDI-OPE propagators \textit{98} and \textit{99}.](image-url)
3.6.2 Synthesis of the Cationic ON-NDI-OPE Propagator 98

3.6.2.1 Synthesis of the Cationic ON-NDI 118 with a Polymerizable Diacetylene Unit

Scheme 14: a) i) KOH, Isopropanol, 80 °C, 20 h, ii) Acetic acid, 80 °C, 36 h, 36%; b) DCM, rt, 16 h; c) HATU, TEA, DMF/CHCl₃ (2:1), rt, 12 h, 67%; d) SnCl₂, PhOH, DMF (acetic acid), 50 °C, 1 h, 87%.

Synthesis of the ON-NDI amine 118 is summarised in Scheme 14. The synthesis of compound 100 was achieved in two steps from commercially available 1,4,5,8-napthalenetetracarboxylic acid dianhydride (76) using a previously reported procedure. The obtained compound 100 was hydrolyzed with KOH in isopropanol to give the tetra acid, which reacted with the Pnz (p-
nitro benzyl) protected ethylenediamine 111 and the Cbz protected L-lysine amide 112 in acetic acid at 80 °C for 36 h. The reaction yielded the asymmetrical yellow OO-NDI chromophore 113 in 36% along with the two symmetrically substituted side products. The asymmetrical yellow OO-NDI 113 was purified by column chromatography.

The obtained asymmetrical yellow OO-NDI 113 was subjected to nucleophilic aromatic core substitution with the ethylenediamine 114 under mild conditions to afford the red ON-NDI chromophore 115. The ON-NDI chromophore 115 was subsequently coupled with 10,12-pentacosadiynoic acid (PCDA) 116, using HATU as a coupling reagent and TEA as a base in a DMF/CHCl₃ (2:1) mixture at room temperature for 12 h to afford the ON-NDI chromophore 117 in 67% yield. The selective deprotection of the Pnz protecting group in the presence of the Cbz group was carried out through a stannous chloride (SnCl₂) catalyzed cleavage in the presence of acidic DMF at 50 °C for 1 h to give the desired ON-NDI amine 118 in 87% yield.

### 3.6.2.2 Synthesis of the Cationic ON-NDI-OPE Propagator 98

The obtained ON-NDI amine 118 was coupled with the readily available OPE acid rod 83 using HATU, DTBP and TEA in freshly distilled DMF at room temperature for 16 h. The reaction furnished the Cbz protected cationic ON-NDI-OPE propagator 119 in 43% (Scheme 15). The obtained ON-NDI-OPE propagator 119 was purified by column chromatography and successive PTLCs. The identity of the Cbz protected cationic ON-NDI-OPE propagator 119 confirmed using MALDI-MS (Figure 65). To achieve the synthesis of the desired cationic ON-NDI-OPE propagator 98, the deprotection of the Cbz protecting groups is ongoing.
Scheme 15: Synthesis of the ON-NDI-OPE propagator 119. a) HATU, DTBP, TEA, DMF, rt, 16 h, 43%.
3.6.3 Synthesis of the Anionic ON-NDI-OPE Propagator 99

3.6.3.1 Synthesis of the Anionic ON-NDI 123 with a Polymerizable Diacetylene Unit

The anionic red ON-NDI amine 123 substituted with a polymerizable diacetylene unit at the core was synthesised in six steps in a similar manner to the cationic ON-NDI amine 118 (Scheme 16). The compound 110 was hydrolyzed with base and subsequently reacted with the Phz protected ethylenediamine 111 and the tert-butyl protected L-glutamate 75 to yield the asymmetrical yellow OO-NDI 120 in 28%.
Scheme 16: a) i) KOH, Isopropanol, 80 °C, 20 h, ii) Acetic acid, 80 °C, 36 h, 28%; b) DCM, rt, 16 h; c) HATU, TEA, DMF/CHCl₃ (2:1), rt, 12 h, 64%; d) SnCl₂, PhOH, DMF (acetic acid), 50 °C, 1 h, 74%.

The obtained **OO-NDI 120** was subjected to core substitution with ethylenediamine **114** under mild conditions to give the red **ON-NDI compound 121**, which was further coupled with PCDA (116), using HATU and TEA in a DMF/CHCl₃ (2:1) mixture to afford the anionic **ON-NDI 122** in 64% yield. The obtained **ON-NDI 122** was subjected to orthogonal deprotection of the Pnz protecting group in the presence of the tert-butyl protecting group using a stannous chloride (SnCl₂) in acidic DMF to give the desired red **ON-NDI amine 123** in 74% yield.

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3.6.3.2 Synthesis of the Anionic ON-NDI-OPE Propagator 99

Scheme 17: Synthesis of the anionic ON-NDI-OPE propagator 124. a) HATU, DTBP, TEA, DMF, rt, 16 h, 33%.

The synthesis of the protected anionic ON-NDI-OPE propagator 124 was achieved analogous to the protected cationic ON-NDI-OPE propagator 119. The ON-NDI amine 123 was coupled with the OPE acid rod 83 using HATU, DTBP and TEA in DMF and furnishing the tert-butyl protected anionic ON-NDI-OPE propagator 124 in 43% yield (Scheme 17). The identity of the fully protected anionic ON-NDI-OPE propagator 124 was confirmed using MALDI-MS (Figure 66). The synthesis of the desired red anionic ON-NDI-OPE propagator 99 via cleavage of the tert-butyl protecting groups is ongoing.
3.7 Summary

In this work, three different bioinspired approaches have been introduced to build up vertically oriented SHJ photosystems via a zipper assembly mechanism. Firstly, the halogenated red \( NBr-NDI-OPE \) zipper architecture \( Au-54(55-56)_n \) was assembled from the anionic \( HH-NDI-OPE \) initiator 54 and the cationic and anionic \( NBr-NDI-OPE \) propagators 55 and 56 on a gold electrode (Figure 67). The \( HH-NDI-OPE \) initiator 54 was synthesized in 21 steps from commercially available materials. The cationic and anionic \( NBr-NDI-OPE \) propagators 55 and 56 were synthesized in 6 steps from commercially available materials.

Figure 66: MALDI-MS (in dithranol) of the fully protected anionic \( ON-NDI-OPE \) propagator 124.
Figure 67: Chemical structures of the HH-NDI-OPE initiator 54 and the propagators 55, 56, 90, 91, 119 and 124 and the expected supramolecular architecture of their topologically matched zipper assemblies e.g. Au-54-(55-56)n-55.
The successful construction of the NBr-NDI-OPE zipper assembly was confirmed by positive inhibition of zipper growth in capping experiments. Comparison of the highly organized NBr-NDI-OPE zipper assembly with a less organized layer-by-layer assembly (Figure 68) and a zipper assembly using NBr-NDI-POPs revealed superior properties of the NBr-NDI-OPE zipper assemblies, i.e. a high photocurrent (101.6 µA/cm² vs 48.2 µA/cm² and 70.0 µA/cm²), higher critical thickness (20 layers vs 8 layers and 10 layers) and high efficiency (0.033% vs 0.021 % and 0.022%).

Figure 68: J-L profiles of the NBr-NDI-OPE architecture obtained by the zipper assembly Au-54-(55-56)ₙ,55 (◇), the LBL assembly Au-89-(55-56)ₙ,55 (◇), the LBL assembly with capping Au-89-55-54-(55-56)ₙ (□) and the zipper assembly with capping Au-54-55-54-(55-56)ₙ (●).
Chapter 3: Results and Discussion

The action spectra of the \( NBr\)-NDI-OPE zipper assembly indicated that OPEs are planarized and contribute to light harvesting and photocurrent generation with the electron acceptor \( NBr\)-NDIs. Photoinduced charge separation in the \( NBr\)-NDI-OPE propagator 55 was evidenced by transient absorption spectroscopy in collaboration with the Vauthey group. QCM measurements of the \( NBr\)-NDI-OPE zipper and LBL assemblies proved that growth of assemblies continues beyond their critical thickness determined by photocurrent measurements. This result suggests that photocurrent saturation occurs not because of stopped growth, but rather by recombination of the separated charges.

Secondly, the non-halogenated \( ON\)-NDI-OPE zipper assembly \( Au\)\(54\)-(90-91)\(n\) was introduced. The synthesis of the cationic and anionic \( ON\)-NDI-OPE propagators 90 and 91 were accomplished in 8 steps from the easily available OPE rod and the commercially available 1,4,5,8-naphthalenetetracarboxylic acid dianhydride. Compared with the halogenated \( NBr\)-NDI-OPE zipper less photocurrent and same critical thickness was observed. The lower photocurrent was attributed to the higher HOMO energy of the \( ON\)-NDI than the \( NBr\)-NDI (Figure 69). This conclusion was further corroborated by a less significant contribution of the \( ON\)-NDI to the photocurrent action spectra.
Figure 69: Action spectrum of the ON-NDI-OPE zipper assembly Au-54-(90-91)-90 (●) with comparison to the action spectrum of NBr-NDI-OPE zipper assembly Au-54-(55-56)-55 (○).

To overcome the shortcoming of the NBr-NDI-OPE and the ON-NDI-OPE zipper assemblies, the concept of antiparallel redox gradients was introduced. This was achieved by placing the red NBr-NDI-OPE zipper assembly on top of the yellow OO-NDI-POP zipper. The obtained OMARG-SHJ architecture Au-34-(35-36)ₙ-35-(56-55)ₙ generates approximately the same photocurrent and double critical thickness (38 layers) than the NBr-NDI-OPE zipper assembly. The reversed OMARG-SHJ zipper architecture Au-54-(55-56)ₙ-55-(36-35)ₙ generated less photocurrent and has a lower critical thickness than the formal OMARG-SHJs zipper (Figure 70). This decrease in photocurrent was proven to be a result of the mismatched redox gradients in n-conducting and p-conducting pathways of reversed OMARG-SHJs zipper. This result demonstrated that OMARG-SHJs exist in zipper architectures and matter for function.
Figure 70: $J\text{-}L$ profiles of the formal OMARG zipper assembly architecture $\text{Au-34-(35-36)_{\text{Au}}-35-(56-55)_n}$ (●, ■) and the reversed OMARG zipper architecture $\text{Au-54-(55-56)_{\text{Au}}-55-(36-35)_n}$ (○, □).

In a separate approach to increase the photovoltaic properties and to increase the critical thickness of the zipper assemblies, covalent cross-linking has also been envisaged. To form a zipper architecture with the potential for covalent cross-linking, the synthesis of the cationic and anionic protected $\text{ON-NDI-OPE}$ propagators 119 and 124 were successfully carried out in seven steps. The $\text{ON-NDI}$s in the propagators 119 and 124 were equipped with a photo-polymerizable diacetylene moiety (Figure 67).
CHAPTER 4

EXPERIMENTAL SECTION

4.1 General

4.1.1 Reagents, Solvents and Equipment

Reagents for synthesis were, if not otherwise specified, purchased from Aldrich, Fluka or Acros. Amino acid derivatives were from Novabiochem. The coupling reagent HATU (O-(7-azabenzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate) was from Applied Biosystem. Naphthalene tetracarboxylicbis-anhydride, ethylenediamine, allylchloroformate, benzylchloroformat, triethylamine, triethanolamine, trifluoroacetic acid, 2,2,2-trifluoroethanol, acetic acid and N,N-dimethylformamide were from Fluka or Aldrich. 

BBr$_3$, boron tribromide, (1M solution in methylene chloride) was from Acros and only used when the solution was colourless to slightly brown in colour. All buffers and salts were from Sigma or Fluka-Aldrich.

All reactions were carried out under argon or nitrogen, with magnetic stirring. Dry DMF and TEA used for synthesis were distilled over CaH$_2$. Other solvents such as toluene, tetrahydrofurane, diethyl ether, acetonitrile and dichloromethane were carried out using solvent purification system from Solv-tek (216 Lewisville Road, Berryville VA 22611 USA). Solvents were evaporated using a R-200 Rotavapour from Buchi, equipped with a vacuum
controller PVK 610 from MLT Labortechnik AG or with a Vacuubrand MZ 2C model and heating bath from Buchi. Water used in all experiments was always bidistilled.

All glassware used for synthesis was washed with soap solution, water, and acetone and dried in oven to assure complete dryness. Glassware used for final products was cleaned with base and acid baths, several times with water, bi-distilled water and dried in oven to complete dryness.

### 4.1.2 Chromatographic Methods

Column chromatography was carried out using silica gel 60 (40-63 µm) from Fluka. Analytical thin layer chromatography (TLC) was done using aluminium sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck, aluminium foils (20x20 cm) covered with nano-silica gel from Fluka and plastic plates coated with polygram alox. N UV254 from Macherey-Nagel. Preparative thin layer chromatography (PTLC) for amounts ≤ 5 mg was carried out using a glass plates (20x20 cm) coated with silica gel 60 F254 (0.2 mm) from Merck. For amounts ≤50 mg glass plates (20x20 cm) coated with silica gel 60 F254 (1 mm) from Analteck were used. Described in the text as follows: (eluent, retention factor).

UV-active compounds were detected with a UV-lamp from CAMAG at wavelength λ = 254 or 366 nm. Amines were stained with ninhydrin (0.2% ninhydrin in ethanol), acids and esters were detected using bromocresol green [bromocresol green (0.1 g), sodium hydroxide 0.1M (5 mL) and ethanol(500 mL)] and poorly UV-active substances were detected using a cesium-molybdenum staining reagent made of Ce(SO4)2 (2 g), H3PMo12O40 (4 g) and H2SO4 (40 g) in 160 mL of water.
Analytical and preparative high performance liquid chromatography (HPLC) was performed using either Jasco HPLC system (PU-980, UV-970, FP-920) or an Agilent 1100 series apparatus with a photo diode array detector. Spectra were evaluated using the software Borwin Version 1.21.07 or 1.50. Columns were from YMC for normal and reverse phase separation. Description in the text: (reverse phase RP-HPLC) (column, length x diameter, eluent, flow rate, retention time \( t_R \)).

4.1.3 Equipment for Product Characterisation

UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 °C) using quartz cells with a pathlength of 1 cm and are reported as maximal absorption wavelength \( \lambda \) in nm (extinction coefficient \( e \) in nM\(^{-1}\) cm\(^{-1}\)).

Optical rotation measurements were carried out at room temperature on a Perkin-Elmer 241 Polarimeter using a sodium lamp (\( \lambda = 587 \text{ nm} \)) in water thermostatized quartz cells of 10 cm length. Abbreviation in the text [a]\(^{20}\) D = (c = concentration in g/100 mL in solvent).

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate, unless stated) at room temperature. Intensities of the vibrational bands are reported as w = weak, m = medium, s = strong. Abbreviation in the text: IR (medium): v (intensity) (cm\(^{-1}\)).

Melting points were measured on a heating microscope from Reicher (Austria) and are given in degrees Celsius. Abbreviation in the text: Mp.: temperature range °C.

\(^1\)H and \(^{13}\)C NMR spectra were recorded on Bruker 300, 400 or 500 MHz Specrometer and were processed by WinNMR software. Chemical shifts
δ are reported in ppm downfield relative to TMS internal reference in the solvent. Spin multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), quint (quintet) or multiplet (m) and coupling constants are given in Hz. Resonance were assigned with the aid of 2D NMR spectra (H-COSY, HSQC, HMBC).

ESI-MS (Electron Spray Ionization Mass Spectroscopy) was performed on a Finnigan MAT SQ 7000, or (only for ESI) on a spectrometer from Applied Biosystems API 150 EX LC/MS system equipped with an automatic injector HTS PLA from CTC. Analytics and a Shimadzu HPLC system composed of a system controller SCL-10A VP, a liquid chromatograph LC-10AD VP and a solenoid valve FCV-10AL VP. High Resolution Mass Spectroscopy (HR-MS) was done on a VG analytical 7070E. Abbreviation in the text MS (ESI, solvent): m/z [interpretation], in case of high resolution (HR-MS) mass spectra: HR-MS: m/z (interpretation, C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}I\textsubscript{w}charge, calculated value). MALDI-TOF MS (Matrix Assisted Laser Disorption Ionization Time OF Flight Mass Spectroscopy) was carried out on a Axima CFP\textsuperscript{+} (Shimadzu). Abbreviation in the text as MALDI matrix, m/z [interpretation].

4.1.4 Equipment Used During Experiments

Autoclavable micropipettes from Nichiriy (Japan), Socorex (Switzerland), Brand (Germany) and Vaudoux-Eppendorf (Switzerland) calibrated for amount 0-10 µL, 20-200 µL, 100-1000 µL were used to prepare stock solutions or transfer solution.

pH Values were determined using either a Piccolo Plus pH-meter from HANNA instruments or a Consort C832 multi-parameter analyzer, calibrated with Titrisol solution from Merck at pH 4.00 and 7.00.
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’s were measured upon monochromatic light excitation (150 W XE lamp with Oriel 1/8 m monochromator).

The quartz crystal microbalance (QCM) measurements were conducted using Q-sense E4 device with flow cells at constant temperature 23.3 °C.
Figure 71: Numbering Scheming for oligophenylethynylene rod 57.
4.2 Synthesis

4.2.1 Synthesis of OPE Initiator Scaffold

2,5-Di[Gla-Or-Bu]-1-bromo benzene 63. To a solution of 2-bromobenzene-1,4-diol 60 (1.0 g, 5.3 mmol) in acetone (30 mL) was added Cs$_2$CO$_3$ (5.2 g, 16 mmol). The resulting suspension was stirred at rt for 30 min before addition of tert-butyl bromoacetate (3.1 ml, 21 mmol). The reaction mixture was stirred at 70 °C for 1 h. The reaction mixture was then allowed to cool down and the remaining solid filtered off and washed with ethyl acetate (70 mL). The filtrate was washed with water and brine and dried over anhydrous Na$_2$SO$_4$. After evaporating the solvent under reduced pressure, 63 was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1), yielding a colorless solid (2.0 g, 94%).

Mp = 103 - 104 °C; IR (neat): 2983 (w), 2917 (w), 1739 (s), 1489 (s), 1434 (m), 1399 (w), 1367 (m), 1281 (w), 1144 (s), 1080 (s); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): 7.18 (d, $^3J$ (H, H) = 2.4 Hz, 1H, 1$^1$H$_6$), 6.90 - 6.81 (m, 2H, 1H$_3$-4), 4.57 (s, 2H, 1$^2$CH$_2$CO), 4.50 (s, 2H, 1$^5$CH$_2$CO), 1.53 (s, 9H, 1$^2$CH$_3$-but), 1.51 (s, 9H, 1$^5$CH$_3$-but); $^{13}$C NMR (100 MHz, CDCl$_3$): 167.5 (s, 1$^2$C$_O$), 167.2 (s, 1$^5$C$_O$), 154.0 (s, 1C$_2$), 151.7 (s, 1C$_3$), 120.2 (d, 1C$_6$), 115.0 (d, 1C$_4$), 114.7 (d, 1C$_3$), 113.0 (s, 1C$_1$), 82.8 (s, 1$^2$C$_3$-but), 82.7 (s, 1$^5$C$_3$-but); MS (ESI, +ve, CH$_2$Cl$_2$/MeOH): 852 (50, [2M + NH$_4]^+$), 436 (90, [M + NH$_4]^+$), 380 (20, [M + NH$_4$ - C$_4$H$_8$]), 363 (50, [M - C$_8$H$_8$ + 2H$^+$]), 307 (20, [M - C$_8$H$_6$ + 3H$^+$]); HR-MS (ESI, +ve): Calcd for C$_{18}$H$_{30}$O$_6$Br$: 434.1172, Found: 434.1180.
2,5-Di(Gla-Or-Bu)-1-trimethylsilyethyne benzene 65. A solution of 63 (1.5 g, 3.6 mmol), trimethylsilylacetylene 64 (5.0 ml, 36 mmol), Pd(PPh3)4 (100 mg, 0.9 mmol) and CuI (21 mg, 0.11 mmol) in a dry and degassed mixture of DMF (20 mL) and TEA (20 mL) was placed in a sealed Schlenk tube and stirred at 110 °C for 7 days. After cooling down, the reaction mixture was diluted with DCM (200 mL) and washed with water (40 mL x 5) and dried over anhydrous Na2SO4. After evaporating the solvent under reduced pressure, 65 was purified by silica gel column chromatography (petroleum ether/ethyl acetate 19:1), yielding 65 as a pale yellow solid (900 mg, 58%).

Mp = 102 - 103 °C; IR (neat): 2978 (w), 2970 (w), 1739 (s), 1495 (s), 1434 (w), 1360 (m), 1149 (s), 1078 (s); 1H NMR (400 MHz, CDCl3, 25 °C): 6.95 (d, 4J (H,H) = 3.0 Hz, 1H, 1H6), 6.84 (dd, 4J (H,H) = 3.0 Hz, 3J (H,H) = 9.1 Hz, 1H, 1H4), 6.76 (d, 3J (H,H) = 9.1 Hz, 1H, 1H3), 4.55 (s, 2H, 12CH2CO), 4.45 (s, 2H, 15CH2CO), 1.48 (s, 18H, 12CH3t-but, 15CH3t-but), 0.25 (s, 9H, 18CH3TMS); 13C NMR (100 MHz, CDCl3, 25 °C): 168.0 (s, 12CO), 167.9 (s, 15CO), 154.0 (s, 1C2), 152.4 (s, 1C3), 119.5 (d, 1C6), 117.0 (d, 1C5), 115.6 (d, 1C4), 114.3 (s, 1C1), 100.6 (s, 1C8), 99.3 (s, 1C7), 82.4 (s, 15CH3t-but), 82.2 (s, 12CH2CO), 67.7 (t, 12CH3CO), 66.5 (t, 15CH3CO), 28.1 (q, 12CH3t-but), 28.0 (q, 15CH3t-but), 0.0 (q, 18CH3TMS); MS (ESI, +ve, CH2Cl2/MeOH): 886 (70, [2M + NH4]+), 452 (95, [M + NH4]+), 379 (95, [M - C4H8 + H]+), 323 (20, [M - C4H8 + H]+).
2,5-Di[Gla-Or-Bu]-ethyne benzene 66. To a solution of 65 (845 mg, 1.9 mmol) in dry THF (20 mL) was added MeOH (1.0 mL, 29 mmol), TBAF (0.7 mL of a 1 M solution in THF, 0.7 mmol). The resulting mixture was stirred at -10 °C to 0 °C for 3.5 h. The reaction was quenched by the addition of saturated aqueous ammonium chloride. The product was extracted with DCM, dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate 10:1), to give 66 as a pale yellow solid (500 mg, 72%).

$\text{M}p = 75 - 76 \degree \text{C}; \text{IR (neat): } 3297 \ (\text{w}), 2980 \ (\text{w}), 2917 \ (\text{w}), 1745 \ (\text{s}), 1500 \ (\text{s}), 1439 \ (\text{m}), 1368 \ (\text{m}), 1220 \ (\text{s}), 1145 \ (\text{s}), 1079 \ (\text{s}); ^1\text{H NMR} (400 \text{MHz, CDCl}_3, 25 \degree \text{C}): 7.00 \ (d, ^2J (\text{H, H}) = 3.0 \text{ Hz, } 1\text{H}, 1\text{H}_6), 6.87 \ (dd, ^3J (\text{H, H}) = 3.0 \text{ Hz, } 1\text{H}, 1\text{H}_i), 6.74 \ (d, ^3J (\text{H, H}) = 9.1 \text{ Hz, } 1\text{H}, 1\text{H}_i), 4.57 \ (s, 2\text{H}, 1\text{CO}_2), 4.46 \ (s, 2\text{H}, 1\text{CO}_2), 3.31 \ (s, 1\text{H}, 1\text{CH}_3), 1.48 \ (s, 9\text{H}, 1\text{CH}_3-t\text{-but}), 1.46 \ (s, 9\text{H}, 1\text{CH}_3-t\text{-but}); ^13\text{C NMR} (100 \text{MHz, CDCl}_3, 25 \degree \text{C}): 167.9 \ (s, 1\text{CO}), 167.8 \ (s, 1\text{CO}), 154.2 \ (s, 1\text{C}_5), 152.2 \ (s, 1\text{C}_5), 119.8 \ (d, 1\text{C}_6), 117.0 \ (d, 1\text{C}_3), 114.1 \ (d, 1\text{C}_5), 112.8 \ (s, 1\text{C}_1), 82.5 \ (s, 1\text{CO}_2), 82.4 \ (s, 1\text{CO}_2), 81.8 \ (s, 1\text{C}_7), 79.5 \ (d, 1\text{C}_5), 67.1 \ (t, 1\text{CH}_2), 66.4 \ (t, 1\text{CH}_2), 28.1 \ (q, 1\text{CH}_3-t\text{-but}, 1\text{CH}_3-t\text{-but}); \text{MS (ESI, +ve, CH}_3\text{Cl}_2/\text{MeOH): 743 (70, [2M + NH}_4^+], 686 (20, [2M - C}_4\text{H}_8 + \text{H}]^+), 380 (100, [M + NH}_4^+], 324 (20, [M - C}_4\text{H}_8 + \text{NH}_4]^+), 307 (15, [M - C}_4\text{H}_8 + \text{H}]^+), 251 (30, [M - C}_4\text{H}_6 + \text{H}]^+).$

2,5-diiodo-dimethoxybenzene 67 This compound was prepared following a literature procedures.$^{164}$
2,5-Di[Gla-Ot-Bu]-1,4-diiodo benzene 68. A solution of 67 (5.0 g, 13 mmol) in dry DCM (60 mL) was cooled down to -78 °C, then BBr₃ (64 mL, 1 M in DCM) was added dropwise. The resulting mixture was stirred at rt for 20 h. Then the reaction was cooled down to 0 °C and water was added carefully. The resulting precipitate was filtered and dried in vacuo.

The solid was then dissolved in acetone (120 mL) and Cs₂CO₃ (11.6 g, 35.6 mmol) was added, the resulting suspension was stirred at rt for 30 min. Then, tert-butyl bromoacetate (5.7 mL, 29 mmol) was added and the mixture was refluxed for 1 h. After cooling down and filtering off the solid, the solution was diluted with ethyl acetate, washed with water, dried over Na₂SO₄ and dried under vacuum. The residue was purified by silica gel column chromatography (with DCM only), yielding 68 as a light yellow solid (6.2 g, 81%).

Mp = 175 - 176 °C; IR (neat): 2978 (w), 2928 (w), 1736 (s), 1476 (s), 1434 (s), 1367 (m), 1352 (s), 1256 (m), 1218 (s), 1146 (s), 1078 (s), 1039 (m); ¹H NMR (400 MHz, CDCl₃, 25 °C): 7.17 (s, 2H, ¹H₃, ¹H₆), 4.56 (s, 4H, ¹₂CH₂CO, ¹₅CH₂CO), 1.54 (s, 18H, ¹₂CH₃t-but, ¹₅CH₃t-but); ¹³C NMR (100 MHz, CDCl₃, 25 °C): 167.1 (s, ¹₂CO, ¹₅CO), 152.6 (s, ¹₂C, ¹₅C), 123.2 (d, ¹Cl, ¹₅C), 85.8 (s, ¹Cl, ¹₅C), 82.8 (s, ¹₂C-t-but, ¹₅C-t-but), 67.5 (t, ¹₂CH₂CO, ¹₅CH₂CO), 28.1 (q, ¹₂CH₃t-but, ¹₅CH₃t-but); MS (ESI, CH₂Cl₂-MeOH): 1198 (50, [2M + NH₄]+), 608 (100, [M + NH₄]+), 552 (60, [M-C₆H₆ + NH₄]+), 535 (60, [M-C₆H₆ + H]+), 496 (30,[M-C₄H₆ + NH₄]+), 479 (5, [M-C₆H₆ + H]+), 408 (85, [M-C₆H₆-I]+), 352 (100, [M-C₆H₆-I]+).
2,5-Di[Gla-Or-Bu]-4-timethylsilylethynyl-iodo benzene 69. A solution of 68 (500 mg, 0.847 mmol), trimethylsilylacetylene 64 (30 µL, 0.21 mmol), Pd(PPh₃)₂Cl₂ (59.5 mg, 10 mol%) and CuI (16.1 mg, 0.087 mmol) in a mixture of dry and degassed DCM/THF/TEA (10:10:20, 40 mL) was stirred at rt for 16 h. The solvent was evaporated under reduced pressure and 69 purified by column chromatography (petroleum ether/ethyl acetate 19:1), yielding a white solid (135 mg, 28%).

Mp = 63 - 64 °C; IR (neat): 2956 (w), 1744 (s), 1731 (w), 1481 (s), 1385 (w), 1253 (m), 1209 (m), 1157 (s), 1070 (m); ¹H NMR (400 MHz, CDCl₃, 25 °C): 7.25 (s, 1H, 1H₆), 6.77 (s, 1H, 1H₃), 4.54 (s, 2H, 1₂CH₂CO), 4.51 (s, 2H, 1₅CH₂CO), 1.49 (s, 18H, 1₂CH₃t-bu), 1.26 (s, 9H, 1₈CH₃TMS); ¹³C NMR (100 MHz, CDCl₃, 25 °C): 167.5 (s, 1₂CO), 167.2 (s, 1₅CO), 154.0 (s, 1C₂), 151.7 (s, 1C₅), 125.6 (d, 1C₆), 116.9 (d, 1C₇), 114.2 (s, 1C₄), 100.7 (s, 1C₈), 100.1 (s, 1C₉) 87.1 (s, 1Cl), 82.7 (s, 1₂C₇t-bu), 82.5 (s, 1₅C₇t-bu), 67.7 (t, 1₂CH₂CO), 67.4 (t, 1₅CH₂CO), 28.1 (q, 1₂CH₃t-bu), 28.1 (q 1₅CH₃t-bu), 0.1 (q, 1₈CH₃TMS); MS (ESI, +ve, CH₂Cl₂-MeOH): 1138 (25, [2M + NH₄⁺]), 578 (90, [M + NH₄⁺]), 506 (75, [M - C₆H₄+ 2H⁺]), 449 (100, [M - C₆H₄+ 3H⁺]).
1\(^{1}\),1\(^{2}\),2\(^{2}\),2\(^{5}\)-Tetra[Gla-Ot-Bu]-1\(^{4}\)-phenyltrimethylsilylethynedi(phenyleneethynylene) 72. A solution of 69 (130 mg, 0.267 mmol), 66 (90 mg, 0.25 mmol), and Pd(PPh\(_{3}\))\(_{4}\) (46 mg, 0.026 mmol) in a mixture of dry and degassed TEA (15 mL) and THF (15 mL) was stirred at 70 °C for 20 h. The solution was allowed to cool down and the solvent evaporated. The residue was purified by column chromatography (petroleum ether/ethyl acetate 10:1), yielding 72 as a pale yellow solid (140 mg, 66%).

\[\text{mp } = 116 - 117 ^\circ \text{C; IR (neat): 2978 (w), 1753 (s), 1492 (m), 1440 (w), 1366 (m), 1253 (w), 1209 (w), 1144 (s), 1072 (s); }^{1}\text{H NMR (400 MHz, CDCl}_3, 25 ^\circ \text{C): 7.12 (d, } J (\text{H,H}) = 3.0 \text{ Hz, 1H, 1H6), 7.05 (s, 1H, 2H6), 6.96 (s, 1H, 2H6), 6.91 (dd, } J (\text{H,H}) = 3.0 \text{ Hz, 3J (H,H) = 9.1 Hz, 1H, 1H4), 6.84 (d, 3J (H,H) = 9.1 Hz, 1H, 1H3), 4.66 (s, 2H, 1H2CH2CO), 4.65 (s, 2H, 2H2CH2CO), 4.62 (s, 2H, 1H5CH2CO), 4.53 (s, 2H, 2H5CH2CO), 1.56 (s, 9H, 1H5CH3t-but), 1.53 (s, 18H, 1H2CH3t-but), 1.51 (s, 9H, 2H5CH3t-but), 0.3 (s, 9H, 2H8CH3-TMS); }^{13}\text{C NMR (100 MHz, CDCl}_3, 25 ^\circ \text{C): 168.1 (s, 1H2CO), 168.0 (s, 2H2CO), 167.8 (s, 1H5CO), 153.8 (s, 1C2), 153.5 (s, 2C5), 153.1 (s, 2C3), 152.2 (s, 1C5), 119.0 (d, 1C8), 118.9 (d, 2C6), 118.4 (d, 2C3), 117.0 (d, 1C1), 115.1 (d, 1C3), 114.9 (s, 1C1), 114.2 (s, 2C4), 114.1 (s, 2C1), 110.0 (s, 2C7), 100.5 (s, 2C8), 91.7 (s, 1C7, 1C8), 82.4 (s, 2C1-t-but), 82.3 (s, 2C2-t-but, 1C1-t-but), 82.2 (s, 1C5-t-but), 67.5 (t, 2C1H2CO), 67.4 (t, 2C2H2CO), 67.4 (t, 1C7H2CO), 66.4 (t, 1C8H2CO), 28.1 (q, 1C21H3-t-but, 1C15H3-t-but, 2C15H3-t-but, 2C16H3-t-but), -0.03 (q, 2C18H3-TMS); MS (ESI, +ve, CH3Cl2): 813 (100, [M + NH4]\(^{+}\)), 627 (20, [M - C12H24 + H]\(^{+}\)), 572 (70, [M - C16H34 + H]\(^{+}\)), 544 (90, [2M + H + 2NH4]\(^{3+}\)).} \]
1,1',2',2'-Tetra[Gla-Ot-Bu]-1'-phenylethynyl-di(phenyleneethynylene) 58.

To a solution of 72 (570 mg, 0.717 mmol) in THF (20 mL) was added MeOH (0.5 mL, 8 mmol), TBAF (0.1 mL of a 1M solution in THF, 0.1 mmol). The resulting reaction mixture was stirred at rt for 15 min. Reaction was quenched by the addition of saturated aqueous ammonium chloride and extracted with DCM, dried over anhydrous Na$_2$SO$_4$ and solvent was evaporated in vacuo. The residue was purified on silica gel column chromatography (petroleum ether/ethyl acetate 5:1), yielding 58 as a pale yellow solid (336 mg, 67%).

Mp = 108 - 109 °C; IR (neat): 3278 (w), 2924 (w), 1747 (s), 1647 (s), 1504 (s), 1492 (s), 1367 (s), 1147 (s), 1075 (m); $^1$H NMR (400 MHz, CDCl$_3$, 25 °C): 7.08 (d, $^4$J (H,H) = 3.0 Hz, 1H, 1H$_6$), 7.00 (s, 1H, 2H$_6$), 6.96 (s, 1H, 2H$_3$), 6.87 (d, $^4$J (H,H) = 9.1 Hz, 1H, 1H$_4$), 6.79 (d, $^3$J (H,H) = 9.1 Hz, 1H, 1H$_3$), 4.62 (s, 4H, 2CH$_2$CO, 2CH$_2$CO), 4.60 (s, 2H, 2CH$_3$CO), 4.49 (s, 2H, 1CH$_3$CO), 3.40 (s, 1H, 2CH$_3$), 1.49 (s, 18H, 1CH$_3$-but, 2CH$_3$-but), 1.48 (s, 9H, 2CH$_3$-but), 1.47 (s, 9H, 1CH$_3$-but); $^{13}$C NMR (100 MHz, CDCl$_3$, 25 °C): 168.1 (s, 1CO), 168.0 (s, 2CO), 167.8 (s, 2CO), 167.5 (s, 1CO), 153.8 (s, 1C$_2$), 153.7 (s, 2C$_2$), 153.0 (s, 2C$_5$), 152.4 (s, 1C$_5$), 119.3 (d, 1C$_6$), 119.0 (d, 2C$_6$), 117.3 (d, 2C$_3$), 117.0 (d, 1C$_3$), 115.4 (s, 1C$_1$), 115.1 (d, 1C$_4$), 114.1 (s, 2C$_4$), 112.8 (s, 2C$_4$), 91.8 (s, 1C$_7$), 89.6 (s, 1C$_8$), 83.1 (s, 2C$_4$), 82.5 (s, 1C$_{3\text{-but}}$), 82.4 (s, 2C$_{3\text{-but}}$), 82.4 (s, 2C$_{1\text{-but}}$), 82.2 (s, 1C$_{3\text{-but}}$), 79.4 (d, 2C$_8$), 67.5 (t, 2CH$_2$CO), 67.4 (t, 2CH$_2$CO), 66.9 (t, 2CH$_2$CO), 66.4 (t, 1CH$_3$CO), 28.1 (q, 1C$_{3\text{-but}}$), 28.1 (q, 1C$_{3\text{-but}}$), 28.1 (q, 1C$_{1\text{-but}}$); MS (ESI, +ve, CH$_2$Cl$_2$): 741 (100, [M + NH$_4$]$^+$), 499 (10)
1-ethyne, 4-amino benzene 71. This compound was prepared following a literature procedure.\(^{165}\)

\(1^2,1^5\)-Di[Gla-Ot-Bu]-1^4-iodo-2^4-aminophenyl-phenyleneethynylene 59. A solution of 71 (100 mg, 0.85 mmol), 68 (1.006 g, 1.70 mmol), CuI (3.2 mg, 20 mol%), and Pd(PPh\(_3\))\(_2\)Cl\(_2\) (6 mg, 10 mol%) in a mixture of dry and degassed TEA (10 mL) and THF (10 mL) was stirred at 60 °C for 16 h. The solution was allowed to cool down and the solvent evaporated. The product was purified by column chromatography (petroleum ether/ethyl acetate 10:3, \(R_f = 0.4\)) yielding 59 as a pale yellow solid (212 mg, 48%).

Mp: 158 - 159 °C; IR (neat): 2920 (w), 2511 (w), 1722 (s), 1512 (m), 1424 (s), 1274 (s), 1193 (s), 1079 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C): 7.40 (d, \(^3\)J (H,H) = 8.8 Hz, 2H, 2\(_H^2\), 2\(_H^6\)), 7.31 (s, 1H, 1\(_H^3\)), 6.87 (s, 1H, 1\(_H^6\)), 6.69 (d, \(^3\)J (H,H) = 8.8 Hz, 2H, 2\(_H^3\), 2\(_H^5\)), 4.62 (s, 2H, 1\(_H^2\)CO), 4.58 (s, 2H, 1\(_H^5\)CO), 3.89 (s, 2H, 2\(_H^4\)NH), 1.54 (s, 18H, 1\(_H^2\)CH\(_3\)t-but, 1\(_H^5\)CH\(_3\)t-but); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 25 °C): 167.9 (s, 1\(_H^2\)CO), 167.5 (s, 1\(_H^5\)CO), 153.6 (s, 1\(_C^4\)), 152.0 (s, 1\(_C^1\)), 147.1 (s, 2\(_C^3\)), 133.3 (d, 2\(_C^2\), 2\(_C^6\)), 125.6 (d, 1\(_C^7\)), 116.3 (d, 1\(_C^5\)), 115.3 (s, 2\(_C^1\)), 114.9 (d, 2\(_C^6\), 2\(_C^2\)), 112.5 (s., 1\(_C^1\)), 96.2 (s, 1\(_C^8\)), 85.8 (s, 1\(_C^4\)), 82.9 (s, 1\(_C^7\)), 82.8 (s, 1\(_C^3\)t-but), 82.7 (s, 1\(_C^5\)t-but), 67.9 (t, 1\(_H^2\)CO), 67.6 (t, 1\(_H^5\)CO), 28.3 (q, 1\(_H^2\)CH\(_3\)t-but, 1\(_H^5\)CH\(_3\)t-but); MS (ESI, +ve): 597 (65, [M + NH\(_4^+\)]\(^+\)), 524 (75, [M + H - \(t\)-Bu\(^+\)]\(^+\)), 468 (100, [M + 2H - 2\(t\)-Bu\(^+\)]\(^+\)).
73. A solution of 59 (79 mg, 0.10 mmol), 58 (70 mg, 0.12 mmol), CuI (2 mg, 0 mol%), and Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (7.6 mg, 10 mol%) in a mixture of dry and degassed TEA (10 mL) and THF (10 mL) was stirred at 60 °C for 16 h. The solution was allowed to cool down and the solvent evaporated. The crude product was purified by column chromatography (petroleum ether/ethyl acetate 7:3, \(R_f = 0.3\)) to yield 73 (45 mg, 52%) as a pale yellow solid.

Mp: 63 - 64 °C; IR (neat): 2979 (w), 2932 (w), 2202 (w), 1748 (s), 1519 (m), 1415 (m), 1367 (m), 1207 (m), 1147 (s), 1073 (s); \(^1\text{H}\) NMR (400 MHz, CDCl\textsubscript{3}, 25 °C): 7.35 (d, \(J_{(H,H)} = 8.0\) Hz, 2H, 4\(_2\)H\textsubscript{2}, 4\(_6\)H\textsubscript{6}), 7.09 (d, \(J_{(H,H)} = 3.0\) Hz, 1H, 1\(_{11}\)H\textsubscript{11}), 7.04 (s, 2H, 2\(_3\)H\textsubscript{3}, 2\(_6\)H\textsubscript{6}), 6.93 (s, 1H, 3\(_6\)H\textsubscript{6}), 6.87 (dd, \(J_{(H,H)} = 3.0\) Hz, \(J_{(H,H)} = 9.1\) Hz, 1H, 1\(_4\)H\textsubscript{4}), 6.79 (d, \(J_{(H,H)} = 9.1\) Hz, 1H, 1\(_3\)H\textsubscript{3}), 6.62 (d, \(J_{(H,H)} = 8.0\) Hz, 2H, 4\(_3\)H\textsubscript{3}, 4\(_5\)H\textsubscript{5}), 4.63 (s, 4H, 1\(_2\)CH\textsubscript{2}CO, 3\(_2\)CH\textsubscript{2}CO), 4.62 (s, 4H, 2\(_2\)CH\textsubscript{2}CO, 2\(_5\)CH\textsubscript{3}CO), 4.50 (s, 4H, 2\(_H\)H\textsubscript{2}, 2\(_H\)H\textsubscript{2}), 4.48 (s, 2H, 1\(_5\)H\textsubscript{5}), 3.88 (br s, 2H, 4\(_4\)NH\textsubscript{2}), 1.47 (s, 45H, 1\(_2\)CH\textsubscript{3}t\text{but}, 2\(_2\)CH\textsubscript{3}t\text{but}, 2\(_5\)CH\textsubscript{3}t\text{but}, 3\(_2\)CH\textsubscript{3}t\text{but}, 3\(_5\)CH\textsubscript{3}t\text{but}), 1.45 (s, 9H, 1\(_5\)CH\textsubscript{3}t\text{but}); \(^1\text{C}\) NMR (100 MHz, CDCl\textsubscript{3}, 25 °C): 168.3 (s, 1\(_2\)CO), 168.2 (s, 3\(_5\)CO), 168.0 (s, 1\(_{15}\)CO), 167.9 (s, 2\(_3\)CO, 2\(_3\)CO, 2\(_5\)CO), 153.9 (s, 1\(_C\)), 153.5 (s, 3\(_C\)), 153.4 (s, 3\(_C\)), 152.9 (s, 2\(_C\), 2\(_C\)), 152.6 (s, 1\(_C\)), 147.2 (s, 4\(_C\)), 133.3 (d, 4\(_C\), 4\(_C\)), 119.0 (s, 1\(_C\)), 118.4 (d, 2\(_C\), 2\(_C\)), 118.2 (d, 3\(_C\)), 118.1 (d, 3\(_C\)), 117.1 (d, 1\(_C\)), 115.7 (s, 1\(_C\)), 115.4 (d, 1\(_C\)), 114.8 (d, 4\(_C\), 4\(_C\)), 114.6 (s, 4\(_C\)), 114.4 (s, 3\(_C\)), 113.7 (s, 2\(_C\)), 112.6 (s, 2\(_C\), 3\(_C\)), 97.1 (s, 3\(_C\)), 92.0 (s, 3\(_C\)), 91.9 (s, 1\(_C\)), 91.5 (s, 1\(_C\)), 90.2 (s, 2\(_C\), 2\(_C\)), 83.5 (s, 1\(_C\)t\text{but}), 82.6 (s, 3\(_C\)t\text{but}), 82.5 (s, 3\(_C\)t\text{but}), 82.4 (s, 2\(_C\)t\text{but}, 2\(_C\)t\text{but}), 82.3 (s, 1\(_C\)t\text{but}), 67.8 (t, 1\(_C\)t\text{but}), 67.6 (t, 3\(_C\)t\text{but}).
Chapter 4: Experimental Section

67.5 (t, 2\(^2\)CH\(_2\)CO, 2\(^2\)CH\(_2\)CO), 67.4 (t, 3\(^3\)CH\(_2\)CO), 66.6 (t, 1\(^1\)CH\(_3\)\text{-}\text{but}, 3\(^3\)CH\(_3\)\text{-}\text{but}), 28.3 (q, 2\(^2\)CH\(_3\)\text{-}\text{but}, 2\(^3\)CH\(_3\)\text{-}\text{but}), 28.2 (q, 3\(^3\)CH\(_3\)\text{-}\text{but}, 1\(^1\)CH\(_3\)\text{-}\text{but}); MS (ESI, +ve): 1192 (100, [M + NH\(_4\)]\(^+\)), 1175 (20, [M + H]\(^+\)).

DL-\(\alpha\)-lipoxy chloride. 74 This compound was prepared following a literature procedure.

\(1^1,1^2,2^1,2^2,3^1,3^2\text{-}\text{Hexa[Gla-Ot-Bu]-4^4\text{-}(DL-\(\alpha\)-lipoamide)phenyl-tri(phenyleneethynylene) 75. To a solution of 73 (25 mg, 0.021 mmol) in dry DCM (2 mL), TEA (14 \(\mu\)L, 0.10 mmol) and 74 (12 mg, 0.052 mmol) in DCM (1 mL), were added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and at rt for 12 h in the dark. Then, the reaction mixture was diluted with 50 mL DCM, washed with aqueous NaHCO\(_3\) and brine. The organic layer was dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. The crude product was purified by column chromatography (DCM/acetone 10:1, \(R_f = 0.4\)) to yield 75 as a pale yellow oil (12 mg, 41%).

\(^1\)H NMR (400 MHz, CDCl\(_3\), 25 °C):

- 7.52 (br s, 4H, 4\(^1\)H, 4\(^2\)H, 4\(^3\)H, 4\(^4\)H), 7.11 (d, \(^4\)J (H,H) = 3.0 Hz, 1H, 1\(^{16}\)H), 7.10 (s, 2H, 2\(^1\)H, 2\(^2\)H), 7.07 (s, 1H, 3\(^3\)H), 6.97 (s, 1H, 3\(^4\)H), 6.90 (dd, \(^4\)J (H,H) = 3.0 Hz, \(^3\)J (H,H) = 9.0 Hz, 1H, 1\(^{16}\)H), 6.81 (d, \(^3\)J (H,H) = 9.0 Hz, 1H, 1\(^{16}\)H), 4.65 (s, 6H, 1\(^2\)CH\(_2\)CO, 3\(^2\)CH\(_2\)CO, 2\(^2\)CH\(_2\)CO), 4.64 (s, 2H, 2\(^3\)CH\(_2\)CO), 4.62 (s, 2H, 3\(^3\)CH\(_2\)CO), 4.50 (s, 2H, 1\(^3\)CH\(_2\)CO), 3.62 - 3.56 (m, 1H, 4\(^4\)CH), 3.22 - 3.09 (m, 2H, 4\(^2\)CH\(_2\)), 2.52 - 2.50 (m, 1H, 4\(^4\)CH), 2.38 (t, \(^3\)J (H,H) = 7.0 Hz, 2H, 140
4(CH$_2$CO), 1.98 - 1.96 (m, 1H, 4(CH$_2$CO), 1.78 - 1.40 (m, 6H, 2(CH$_3_3$-but, 2(CH$_3_3$-but), 3(CH$_3_3$-but, 3(CH$_3_3$-but)), 1.49 (s, 9H, 1(CH$_2$-CH$_3$)), 1.48 (s, 36H, 2(CH$_3_3$-but, 2(CH$_3_3$-but), 3(CH$_3_3$-but, 3(CH$_3_3$-but)), 1.46 (s, 9H, 1(CH$_2$-CH$_3$)), 13C NMR (100 MHz, CDCl$_3$, 25 °C): 173.2 (s, 4(NH$_2$)), 168.3 (s, 1(CO)), 168.2 (s, 3(CO)), 168.0 (s, 1(CO)), 167.9 (s, 3(CO)), 167.8 (s, 2(CO)), 167.0(s, 2(CO)), 154.0(s, 1(C)), 153.4 (s, 3(C), 3(C)), 153.3 (s, 2(C)), 153.2 (s, 2(C)), 152.6 (s, 1(C)), 138.2 (s, 4(C)), 132.8 (d, 4(C), 4(C)), 119.4 (d, 4(C), 4(C)), 111.8 (d, 4(C)), 118.9 (s, 4(C)), 118.4 (d, 2(C)), 118.3 (d, 2(C)), 118.1 (d, 3(C)), 117.2 (d, 1(C)), 115.6 (d, 1(C)), 114.9 (s, 1(C)), 114.8 (s, 2(C)), 114.5 (s, 3(C)), 114.4 (s, 2(C), 3(C)), 95.7 (s, 3(C)), 92.0 (s, 3(C)), 91.8 (s, 1(C), 1(C)), 90.2 (s, 2(C), 2(C)), 82.6 (s, 1(C)-but, 3(C)-but), 82.5 (s, 3(C)-but, 2(C)-but), 82.4 (s, 2(C)-but, 1(C)-but), 67.8 (t, 1(C)), 67.6 (t, 3(C)), 67.5 (t, 2(C)), 67.4 (t, 2(C)), 67.3 (t, 3(C)), 66.6 (t, 1(C)), 56.6 (d, 4(C)), 40.5 (t, 4(C)), 38.7 (t, 4(C)), 37.7 (t, 4(C)), 34.8 (t, 4(C)), 29.0 (t, 4(C)), 28.4 (q, 1(C)-but, 3(C)-but, 2(C)-but), 28.3 (q, 3(C)-but, 5(C)-but, 1(C)-but), 25.4 (t, 4(C)), MS (ESI, +ve): 1380 (100, [M + NH$_4$]$^+$).

4.2.2 Synthesis of the HH-NDI-OPE Initiator 54

![Diagram](image)

Figure 72: Nomenclature for the HH-NDI-OPE initiator synthesis. Numbering of amines and protecting groups.
**Cbz-en-NDI-Glu(tert-Bu)-NH₂ 78.** NDA 76 (200 mg, 0.746 mmol) and Cbz-ethylendiamine 77 (174 mg, 0.746 mmol) were suspended in dry 10 mL of DMF in a pressure-tight 20-mL microwave vial. To this suspension was added 0.1 mL of dry TEA. The suspension was sonicated until the mixture became homogeneous. The reaction mixture was heated for 5 min at 140 °C under microwave irradiation using Biotage Initiator™ microwave synthesizer. Once the solution was cooled to rt, H-Glu(r-Bu)-NH₂ 75 (150 mg, 0.746 mmol) and an additional 0.1 mL of dry TEA were added, and the mixture was sonicated for 15 min. The reaction mixture was heated for additional 5 min at 140 °C under microwave irradiation. After evaporation of solvent under reduced pressure the crude material was purified by column chromatography (DCM/MeOH 25:1) to give 78 (320 mg, 65%) as a brown solid.

\[ \alpha_{20}^D = -25.6 \ (c = 1.00 \text{ in CH}_2\text{Cl}_2); \text{Mp} = 117 - 118 \ ^\circ \text{C}; \text{IR: 3355 (w), 2978 (w), 1704 (s), 1659 (s), 1581 (m), 1519 (m), 1453 (m), 1330 (s), 1244 (s), 1148 (s), 1012 (m), 768 (s); } ^1\text{H NMR (400 MHz, CDCl}_3/\text{MeOD 5:1, 25 °C):} \]

- 8.70 (d, \( ^3J (H,H) = 7.8 \text{ Hz}, 2H, C(Naph)H)\)
- 8.65 (d, \( ^3J (H,H) = 7.8 \text{ Hz}, 2H, C(Naph)H)\)
- 7.27 - 7.17 (m, 5H, C(2, 3, 4-Cbz)H)
- 6.37 (br s 1H)
- 5.61 (dd, \( ^3J (H,H) = 8.8 \text{ Hz}, ^3J (H,H) = 5.0 \text{ Hz}, 1H, Cα(Glu)H)\)
- 4.90 (s, 2H, C(Cbz)H)\)
- 4.35 (t, \( ^1J (H,H) = 5.6 \text{ Hz}, 2H, Cα(en)H)\)
- 3.61 - 3.59 (m, 2H, Cβ(en)H)
- 2.55 - 2.48 (m, 2H, Cγ(Glu)H)\)
- 2.35 - 2.26 (m, 2H, Cα(Glu)H)\)
- 1.34 (s, 9H, C(t-Bu)H)\)

\[ ^13\text{C NMR (100 MHz, CDCl}_3, 25 ^\circ \text{C):} \]

- 172.1 (s, CONH₂-Glu)
- 171.0 (s, CO-O-Bu), 163.2 (s x 2, CO-Naph), 163.0 (s x 2, CO-Naph), 156.8 (s, CO-Cbz), 136.5 (s, C₁-Cbz), 131.5 (d x 2, CH-Naph), 131.3 (d x 2, CH-Naph), 128.6 (d x 2, C₁-Cbz), 128.2 (s, C₁-Cbz), 128.1 (d x 2, C₂-Cbz), 127.0 (s x 2, C-Naph), 126.6 (s x 2, C-Naph), 126.5 (s x 2, C-Naph), 81.2 (s, C³-Bu), 66.7 (t, CH₂-Cbz), 54.7 (d, Cγ-Glu), 40.6 (t, Cα-en), 40.0 (t, Cβ-en), 32.6 (t, Cγ-Glu), 142

**H-en-NDI-Glu(tert-Bu)-NH₂ 79.** To a solution of 78 (250 mg, 0.39 mmol) in methanol/ethyl acetate (15:5 mL), Pd(OH)₂/C (5 mg) was added. The suspension was degassed and set under H₂ atmosphere for 10 h at rt. The reaction mixture was filtered through celite and concentrated *in vacuo*. Purification of the residue by column chromatography (first with DCM/MeOH 10:1, then DCM/MeOH/TEA 100:10:1) yielded pure 79 (140 mg, 69%) as a brown solid.

 Mp = 126 - 127 °C; IR: 3315 (w), 2977 (m), 1706 (s), 1657 (s), 1580 (s), 1500 (m), 1453 (s), 1331 (s), 1248 (s), 1149 (m), 1091 (m), 767 (s); ¹H NMR (400 MHz, CDCl₃/MeOD 5:1, 25 °C): 8.78 (s, 4H, C(Naph)H), 5.67 (dd, 3J (H,H) = 4.3 Hz, 3J (H,H) = 4.5 Hz, 1H, Cα(Glu)H), 4.53 (t, 3J (H,H) = 5.5 Hz, 2H, Cα(en)H₂), 3.39 (t, 3J (H,H) = 5.5 Hz, 2H, Cα(en)H₂), 2.65 - 2.57 (m, 1H, Cβ(Glu)H₂), 2.50 - 2.41 (m, 1H, Cβ(Glu)H₂), 2.33 - 2.30 (m, 2H, Cγ(Glu)H₂), 1.32 (s, 9H, C(t-Bu)H₃); MS (ESI, +ve): 495 (100, [M + H⁺]), 478 (30, [M + H - NH₂]⁺), 439 (10, [M + H - 'Bu']⁺).
1,1',2,2',5,5'-Hexa[Gla-en-NDI-Glu(tert-Bu)-NH2]-4'-((DL-α-lipoamide)phenyl-tri(phenyleneethynylene)81.

To a solution of 57 (6 mg, 4.4 µmol) in DCM (1 mL) and TFA (1 mL) was stirred for 1 h at rt, and then concentrated in vacuo to give 80 (6 mg, quant). The crude 80 (4 mg, 3.8 µmol) was dissolved in DMF (1 mL), and HATU (13 mg, 34 µmol), DTBP (61 µL, 273 µmol), 79 (45 mg, 91 µmol), and TEA (25 µL, 182 µmol) were successively added. After stirring for 16 h at rt, the solvent was evaporated under reduced pressure. A preliminary purification by column chromatography (DCM/MeOH 10:1), followed by two PTLCs (first DCM/MeOH 10:1.2, Rf = 0.5, then DCM/MeOH 10:0.5, Rf = 0.2) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 90:10, 1 ml/min, Rf = 7.80 min) 81 (8 mg, 53%) as a brown solid.

1H NMR (400 MHz, CDCl3/CD3OD 1:1, 25 °C): 8.65 - 8.41 (m, 24H, C(Naph)H), 6.97 (d, J(H,H) = 8.0 Hz, 2H, 4CH, 4′CH), 6.79 (d, J(H,H) = 8.0 Hz, 2H, 4CH, 4′CH), 6.70 (s, 1H, 1 NH), 6.48 (s, 2H, 2H, 2H, 3 NH), 6.19 (br s, 2H, 3 NH, 3 NH), 5.64 - 5.48 (m, 6H, Cα(Glu)H), 4.62 - 4.21 (several m, 24H, C(triphenyleneethynylene)H2 [12H], Cα(en)H2 [12H]), 3.90 - 3.75 (m, 13H, Cα(en)H2 [12H], 4′CH), 3.10 - 3.08 (m, 2H, 4′CH), 2.56 - 2.26 (m, 26H, Cα(Glu)H2 [12H], Cα(Glu)H2 [12H], 4′CH), 1.96 - 1.87 (m, 2H, 4′CH),
1.78 - 1.40 (m, 6H, 4^3CH_2, 4^9CH_2, 4^13CH_2), 1.28 - 1.23 (m, 54H, C(Bu)_2); MS (MALDI, +ve linear, dithranol): 3925 (100, [M + K]^+).

\( 1^1,1^2,2^1,2^2,3^1,3^2,3^3,3^4\)-Hexa[Glu-en-NDI-Glu-NH_2]-4\(^4\)-(DL-\(\alpha\)-lipoamide)phenyltri(phenyleneethynylene)\(54\).

To a solution of 81 (5 mg, 1.2 mmol) in TFA (1 mL), and DCM (1 mL) was stirred for 2 h. After this time the solution was evaporated to dryness under reduced pressure. Impurities were removed by solid-liquid extraction with ether (3 x 2 mL) and DCM (3 x 2 mL) leaving 54 (4.8 mg, quantitative) as a brown solid.

\(^1\)H NMR (400 MHz, CDCl_3/TFA 9/1, 25 °C): 8.87 - 8.72 (m, 24H, C(Naph)H), 7.24 - 7.19 (m, 4H, 4^3CH, 4^9CH, 4^12CH, 4^13CH), 6.98 - 6.82 (m, 7H, 1^3H, 2^2H, 2^5H, 3^2H, 3^5H, 1^1H, 1^4H), 5.94 - 5.88 (m, 6H, C_9(Glu)H), 4.72 - 4.41 (several m, 24H, C(triphenyleneethynylene)H_2 [12H], C_9(en)H_2 [12H]), 3.90 - 3.75 (m, 13H, C_9(en)H_2 [12H], 4^3CH), 3.45 - 3.44 (m, 2H, 4^12CH), 2.68 - 2.43 (m, 26H, C_9(Glu)H_2 [12H], C_9(Glu)H_2 [12H], 4^3CH), 2.03 - 1.92 (m 2H, 4^12CH), 1.83 - 56 (m, 6H, 4^3CH, 4^9CH, 4^13CH).
4.2.3 Synthesis of the Cationic NBr-NDI-OPE Propagator 55

Figure 73: Nomenclature for the cationic NBr-NDI-OPE propagator synthesis. Numbering of amines and protecting groups.

H-en-[N, Br]-NDI-Lys(Z)-NH_2 82 This compound was prepared in four steps following previously reported procedure.\textsuperscript{159,168}

1^2,1^3,2^2,2^3,3^2,3^3,4^2,4^3,5^2,5^3-Deac[Gla-en-N,Br-NDI-Lys(Z)-NH_2]-penta(phenyleneethynylene) 84.

To a solution of 83 (1.5 mg, 1.2 µmol), 82 (33 mg, 47 µmol), HATU (7 mg, 18 µmol), DTBP (32 µL, 144 µmol) and TEA (13 µL, 96 µmol) in distilled and...
degassed DMF (1 mL) was stirred at rt for 16 h. DMF was removed under high vacuum. A preliminary purification by column chromatography (DCM/MeOH 9:1) followed by PTLC (DCM/MeOH 9:1, $R_f = 0.5$) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 90:10, 1 ml/min, $R_t = 7.06$ min) 84 (4.9 mg, 51%) as a red solid.

$^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 1:1, 25 °C): 8.67 - 8.09 (m, 20H, C(Naph)H), 7.19 - 7.16 (several m, 50H, C$_{\alpha}$(Cbz)H), 6.89 - 6.66 (m, 12H, C$_{\alpha}$(penta phenyleneethynylene)H), 5.61 - 5.47 (m, 10H, C$_{\alpha}$(Lys)H), 4.97 - 4.88 (m, 20H, C(Cbz)H$_2$), 4.45 - 3.92 (several m, 50H, C(penta phenyleneethynylene)H$_2$ [20H], C$_{\alpha}$(en)H$_2$ [20H], C$_{\alpha}$(Isopropyl)H [10H]), 3.61 - 3.54 (m, 20H, C$_{\beta}$(en)H$_2$), 3.05 - 2.98 (m, 20H, C$_{\epsilon}$(Lys)H$_2$), 2.31 - 2.17 (m, 20H, C$_{\beta}$(Lys)H$_2$), 1.56 - 1.49 (m, 20H, C$_{\gamma}$(Lys)H$_2$), 1.41 - 1.28 (several m, 80H, C$_{\gamma}$(Lys)H$_2$ [20H], C$_{\epsilon}$(Isopropyl)H$_3$ [60H]); MS (MALDI, +ve linear, HABA): 8138 (100, [M + Na]$^+$).
1\textsuperscript{1},1\textsuperscript{2},2\textsuperscript{1},2\textsuperscript{2},2\textsuperscript{3},3\textsuperscript{1},3\textsuperscript{2},3\textsuperscript{3},4\textsuperscript{1},4\textsuperscript{2},4\textsuperscript{3},5\textsuperscript{1},5\textsuperscript{2},5\textsuperscript{3}-Deac\{Gla-\textit{en}-N,Br-NDI-Lys-NH\textsubscript{2}\} penta(phenyleneethynylene) 55.

Thioanisole (14 µL) and a catalytic amount of pentamethyl benzene were added to a solution of 84 (2 mg, 0.2 µmol) in TFA (1 mL), and this red solution was stirred for 3 h at 50 °C. After this time, the red solution was evaporated to dryness under reduced pressure. Impurities were removed by solid-liquid extraction with ether (3 x 2 mL) and DCM (3 x 2 mL), to yield analytically pure (RPHPLC, Nucleosil 100-7 c18 250 x 8 mm, MeOH (with 1% TFA)/H\textsubscript{2}O 85:15, 1 ml/min, R\textsubscript{f} = 6.51 min) 55 (2 mg, quantitative) as a red solid. 

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}/CD\textsubscript{3}OD 1:1, 25 °C): 8.79 - 7.96 (m, 20H, C(Naph)H), 7.11 - 6.69 (m, 12H, C\textsubscript{A}(penta phenyleneethynylene)H), 5.66 - 5.48 (m, 10H, C\textsubscript{d}(Lys)H), 4.56 - 3.98 (several m, 50H, C(penta phenyleneethynylene)H\textsubscript{2} [20H], C\textsubscript{d}(en)H\textsubscript{2} [20H], C\textsubscript{d}(Isopropyl)H [10H]), 3.75 - 3.52 (m, 20H, C\textsubscript{d}(en)H\textsubscript{2}), 2.97 - 2.98 (m, 20H, C\textsubscript{d}(Lys)H\textsubscript{2}), 2.39 - 2.05 (m, 20H, C\textsubscript{d}(Lys)H\textsubscript{2}), 1.80 - 1.65 (m, 20H, C\textsubscript{d}(Lys)H\textsubscript{2}), 1.50 - 1.30 (several m, 80H, C\textsubscript{d}(Lys)H\textsubscript{2} [20H], C\textsubscript{d}(Isopropyl)H\textsubscript{3} [60H]); MS (MALDI, +ve linear, HABA): 6795 (100, [M + Na\textsuperscript{+}]).
4.2.4 Synthesis of the Anionic NBr-NDI-OPE Propagator 56

![Figure 74: Nomenclature for the anionic NBr-NDI-OPE propagator synthesis. Numbering of amines and protecting groups.]

H-en-[N, Br]-NDI-Glu(tert-Bu)-NH2 85. This compound was prepared in four steps following previously reported procedure.159,168

1^1,2^1,2\text{a},3^3,3\text{a},4^4,4\text{a},5^5,5\text{a}-Deac[Gla-en-N,Br-NDI-Glu(tert-Bu)-NH2]-penta(phenyleneethynylene) 86.

To a solution of 83 (1.5 mg, 1.2 µmol), 85 (30 mg, 47.5 µmol), HATU (7 mg, 18.4 µmol), DTBP (32 µL, 144 µmol) and TEA (13 µL, 96 µmol) in distilled and degassed DMF (1 mL) was stirred at rt for 16 h. DMF was removed under
A preliminary purification by column chromatography (DCM/MeOH 90:10) followed by PTLC (DCM/MeOH 90:10, $R_t = 0.5$) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 95:5, 1 ml/min, $R_t = 6.76$ min) 86 (4.6 mg, 53%) as a red solid.

$^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 1:1, 25 °C): 8.69 - 8.13 (m, 20H, C(Naph)H), 6.96 - 6.71 (m, 12H, C$_a$(pentaphenyleneethynylene)H), 5.60 - 5.54 (m, 10H, C$_a$(Glu)H), 4.45 - 4.06 (several m, 50H, C(pentaphenyleneethynylene)$_2$[20H], C$_a$(en)$_2$[20H], C$_1$(Isopropyl)H[10H]), 3.71 - 3.64 (m, 20H, C$_a$(en)$_2$H$_2$), 2.55 - 2.30 (m, 40H, C$_a$(Glu)$_2$[20H], C$_2$(Glu)$_2$[20H]), 1.43 - 1.30 (m, 150H, C$_2$(Isopropyl)$_2$H$_3$[60H], C$_3$(Bu)$_2$H$_3$[90H]); MS (MALDI, +ve linear, HABA): 7368 (100, [M + Na]$^+$).

$^{1,2,3,3',4,4',5,5'}$-Deac[Gla-en-N$_2$Br-NDI-Glu-NH$_2$]-penta(phenyleneethynylene) 56.

A solution of 86 (3 mg, 0.69 µmol) in TFA (1 mL) was stirred for 3 h at rt. After this time, the red solution was evaporated to dryness under reduced
pressure. Impurities were removed by solid-liquid extraction with ether (3 x 2 mL) and DCM (3 x 2 mL), leaving 56 (3 mg, quantitative) as a red solid.

$^1$H NMR (400 MHz, CDCl$_3$/TFA 9:1): 8.81 - 8.15 (m, 20H, C(Naph)H), 6.97 - 6.56 (m, 12H, C$_a$(penta phenyleneethynylene)H), 5.92 - 5.85 (m, 10H, C$_a$(Glu)H), 4.79 - 4.21 (several m, 50H, C(penta phenyleneethynylene)H$_2$[20H], C$_a$(en)H$_2$[20H], C$_b$(Isopropyl)H [10H]), 3.81 - 3.65 (m, 20H, C$_b$(en)H$_2$[20H]), 2.87 (m, 40H, C$_b$(Glu)H$_2$[20H], C$_y$(Glu)H$_2$[20H]), 1.47 - 1.45 (m, 60H, C$_2$(Isopropyl)H$_3$[60H]); MS (MALDI, +ve linear, HABA): 6807 (100, [M + Na]$^+$).

4.2.5 Synthesis of the Cationic ON-NDI-OPE Propagator 90

![Figure](image)

**Figure 75:** Nomenclature for the cationic ON-NDI-OPE propagator synthesis. Numbering of amines and protecting groups.

**Alloc-en-[O, N]-NDI-Lys(Z)-NH$_2$ 92.** This compound was prepared in five steps following previously reported procedure.$^{159,178}$
To a solution of compound 92 (80 mg, 0.105 mmol) in 20 mL DCM, was added Pd(PPh)$_3$ (7.2 mg, 0.0062 mmol) followed by PhSiH$_3$ (105µL, 0.845 mmol). The solution was stirred at rt and monitored by TLC. After 15 min, when the consumption of the reactant compound 92 was observed then the solvent was removed under vacuum at rt and impurities were removed by solid-liquid extraction with ether (3 x 10 mL) and DCM (3 x 10 mL), yielded compound 93 (71 mg, quantitative) as a red solid. A solution of compound 83 (3.2 mg, 2.6 µmol), compound 93 (69 mg, 0.102 mmol), HATU (15 mg, 39.4 µmol), DTBP (70 µL, 0.312 mol) and TEA (28 µL, 0.208 mol) in freshly distilled and degassed DMF (1 mL) was stirred at rt for 16 h. DMF was removed under high vacuum. A preliminary purification by column chromatography (DCM/MeOH 90:10) was followed by PTLC (DCM/MeOH 90:10, $R_t$ = 0.5) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 92:8, 2 ml/min, $R_t$ = 7.29 min) compound 94 (5.6 mg, 28%) as a red solid.
$^1$H NMR (500 MHz, CDC13/CD3OD 5:1, 25 °C): 9.57 (br.s, 10H, N(Isopropyl)H), 8.17 - 7.65 (m, 20H, C(Naph)H), 7.20 (br.s, 50H, C$_\alpha$(Cbz)H), 7.03 - 6.75 (m, 12H, C$_\alpha$(penta phenyleneethynylene)H), 5.55 - 5.51 (m, 10H, C$_\alpha$(Lys)H), 4.99 - 4.89 (br.s, 20H, C(Cbz)H$_2$), 4.47 - 3.99 (several m, 70H, C(penta phenyleneethynylene)H$_2$ [20H], C$_\alpha$(Ethoxy)H$_2$ [20H], C$_\alpha$(en)H$_2$ [20H], C$_\alpha$(Isopropyl)H [10H]), 3.72 - 3.61 (m, 20H, C$_\alpha$(en)H$_2$), 3.15 - 2.99 (m, 20H, C$_\alpha$(Lys)H$_2$), 2.26 - 2.14 (m, 20H, C$_\alpha$(Lys)H$_2$), 1.52 - 1.51 (m, 20H, C$_\alpha$(Lys)H$_2$), 1.34 - 1.24 (several m, 110H, C$_\alpha$(Lys)H$_2$ [20H]. C$_\alpha$(Ethoxy)H$_3$ [30H], C$_\alpha$(Isopropyl)H$_3$ [60H]); MS (MALDI, +ve linear, Dithranol): 7789 (penta phenyleneethynylene)H$_{20}$, C$_\alpha$(Ethoxy)H$_{20}$, C$_\alpha$(en)H$_{20}$, C$_\alpha$(Isopropyl)H$_{10}$, 7748 (M + Na$^+$), 7748 ([M – NH$_3$]$^+$)

1$^1$,1$^2$,2$^1$,2$^2$,3$^1$,3$^2$,3$^3$,4$^1$,4$^2$,4$^3$,5$^1$,5$^2$,5$^3$-Deac[Gla-en-O,N-NDI-Lys-NH$_2$]-penta(phenyleneethynylene) 90.

P-nitroanisole (14 µl) and a catalytic amount of pentamethyl benzene were added to a solution of compound 94 (2 mg, 0.2 µmol) in TFA (1 ml) and this red solution was stirred for 3 h at 50 °C. After this time, the red solution was evaporated to dryness under reduced pressure. Impurities were removed by solid-liquid extraction with ether (3 x 2 ml) and DCM (3 x 2 ml), to yield
analytically pure (RPHPLC, Nucleosil 100-7 c18 250 X 8 mm, MeOH (with 1% TFA)/H₂O 80:20, 1 ml/min, Rᵣ = 5.86 min) compound 90 (2 mg, quantitative) as a red solid.

¹H NMR (400 MHz, CDCl₃/CD₃OD 1:1): 8.51 – 8.43 (m, 20H, C(Naph)H), 6.81 – 6.63 (m, 12H, C₆(penta phenyleneethynylene)H), 5.88 - 5.67 (m, 10H, C₆(Lys)H), 4.58 – 4.40 (several m, 50H, C(penta phenyleneethynylene)H₂ [20H], C₁(Ethoxy)H₂ [20H], C₁(Isopropyl)H [10H]), 4.18 – 4.10 (m, 20H, C₁(en)H₂), 3.84 – 3.72 (m, 20H, C₆(en)H₂), 3.15 – 3.14 (m, 20H, C₁(Lys)H₂), 2.38 - 2.28 (m, 20H, C₈(Lys)H₂), 1.91 – 1.79 (m, 20H, C₈(Lys)H₂), 1.53 – 1.52 (several m, 50H, C₁(Lys)H₂ [20H], C₁(Ethoxy)H₃ [30H]), 1.42 – 1.40 (m, 60H, C₂(Isopropyl)H₃); MS (MALDI, +ve linear, HABA): 6443 (100, [M + NH₄]+).

4.2.6 Synthesis of ON-NDI-OPE Anionic Propagator 91

![Diagram](image)

**Figure 76:** Nomenclature for the anionic ON-NDI-OPE propagator synthesis. Numbering of amines and protecting groups.

**Alloc-en-[O, N]-NDI-Glu(tert-Bu)-NH₂ 95.** This compound was prepared in five steps following previously reported procedures.¹⁵⁹,¹⁷⁸
To a solution of compound 95 (67.6 mg, 0.099 mmol) in 20 mL DCM, was added Pd(PPh₃)₄ (6.8 mg, 0.0046 mmol) followed by PhSiH₃ (98 µL, 0.555 mmol). The solution was stirred at rt and monitored by TLC. After 15 min, when the consumption of the reactant compound 95 was observed then the solvent was removed under vacuum at rt and impurities were removed by solid-liquid extraction with ether (3 x 10 mL) and DCM (3 x 10 mL), yielded compound 96 (58 mg, quantitative) as a red solid. A solution of compound 83 (2.5 mg, 1.6 µmol), compound 96 (38 mg, 63.7 µmol), HATU (9.1 mg, 23.9 µmol), DTBP (43 µL, 0.192 mmol) and TEA (18 µL, 0.128 mmol) in freshly distilled and degassed DMF (1 mL) was stirred at rt for 16 h. DMF was removed under high vacuum. A preliminary purification by column chromatography (DCM/MeOH 90:10) was followed by PTLC (DCM/MeOH 90:10, Rₜ = 0.5) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, DCM/MeOH 92:8, 1 ml/min, Rₜ = 6.98min) compound 97 (5.1 mg, 43%) as a red solid.
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$^1$H NMR (500 MHz, CDCl3/CD3OD 9:1, 25 °C):  9.55 (br. s, 10H, N(Isopropyl)H), 8.19 - 7.70 (m, 20H, C(Naph)H), 6.96 - 6.65 (m, 12H, $C_6$α(penta phenyleneethynylene)H), 5.66 -5.60 (m, 10H, Cα(Glu)H), 4.56 - 3.95 (several m, 70H, C(penta phenyleneethynylene)H$_2$ [20H], C1(Ethoxy)H$_2$ [20H], C$_2$(en)H$_2$ [20H], C$_3$(Isopropyl)H [10H]), 3.65 - 3.50 (m, 20H, C$_5$(en)H$_2$), 2.58 - 2.17 (several m, 40H, C$_β$(Glu)H$_2$ [20H], C$_γ$(Glu)H$_2$ [20H]), 1.46 - 1.31 (several m, 180H, C$_2$(Ethoxy)H$_3$ [30H], C$_3$(Isopropyl)H$_3$ [60H], C'(Bu)H$_3$ [90H]); MS (MALDI, +ve linear, HABA): 7021 (100, [M + Na]).

$^{11}$,1$^{2}$,2$^{3}$,2$^{4}$,3$^{5}$,3$^{6}$,4$^{7}$,4$^{8}$,5$^{9}$,5$^{10}$-Deac[Gla-en-O,N-NDI-Glu(tert-Bu)-NH$_2$]-penta(phenyleneethynylene) 91.

A solution of compound 97 (3.5 mg, 0.5 µmol) in TFA (1 mL) was stirred for 3 h at rt. After this time, the red solution was evaporated to dryness under reduced pressure. Impurities were removed by solid-liquid extraction with ether (3 x 2 mL) and DCM (3 x 2 mL), leaving compound 91 (3.3 mg, quantitative) as a red solid.
$^1$H NMR (400 MHz, CDCl$_3$/TFA 9:1): 8.49 - 8.31 (m, 20H, C(Naph)H), 7.22 - 6.96 (m, 12H, C$_u$(penta phenyleneethynylene)H), 6.09 - 5.85 (m, 10H, C$_v$(Glu)H), 4.81 - 4.75 (m, 20H, C(penta phenyleneethynylene)H$_2$), 4.54 - 4.39 (m, 30H, C$_1$(Ethoxy)H$_2$ [20H], C$_1$(Isopropyl)H [10H]), 4.19 - 4.17 (m, 20H, C$_a$(en)H$_2$), 3.83 - 3.73 (m, 20H, C$_b$(en)H$_2$), 2.73 - 2.51 (several m, 40H, C$_p$(Glu)H$_2$ [20H], C$_q$(Glu)H$_2$ [20H]), 1.60 - 1.53 (m, 30H, C$_2$(Ethoxy)H$_3$), 1.48 - 1.36 (m, 60H, C$_3$(Isopropyl)H$_3$); MS (MALDI, +ve linear, HABA): 6458 (100, [M + Na]$^+$), 6479 (50, [M + K]$^+$).

4.2.7 Synthesis of the Cationic ON-NDI-OPE Propagator

Figure 77: Nomenclature for the cationic ON-NDI-OPE propagator synthesis. Numbering of amines and protecting groups.

Tetraethyl 2,6-diethoxynaphthalene-1,4,5,8-tetracarboxylate (O,O-NTE) 100. This compound was prepared following previously reported procedure.$^{159}$
**Pnz-en-[2,6-diethoxy]-NDI-Lys(Z)-NH$_2$ 113.** A compound 100 (560 mg, 1.03 mmol) was added to 60 mL of a 1 M solution of KOH in isopropanol. The reaction mixture was refluxed for 20 h and then evaporated to dryness under vacuu. Then obtained residue was dissolved in 50 mL acetic acid giving a clear yellow solution. To this was added H-Lys(Cbz)-NH$_2$ 112 (289 mg, 1.03 mmol) and Pnz-ethylenediamine 111 (247 mg, 1.03 mmol) sequentially and the reaction mixture was heated for 12 h at 80 °C. H-Lys(Cbz)-NH$_2$ 112 (579 mg, 2.06 mmol) and pnz-ethylenediamine 111 (495 mg, 2.06 mmol) were added again to the reaction mixture and the mixture was heated further 24 h. The reaction mixture after that time was cooled down to rt and diluted with EtOAc (500 mL). The organic layer was washed with 1 M KHSO$_4$ (100 ml x 2), H$_2$O (100 mL), brine (50 mL) and finally dried over Na$_2$SO$_4$. The solvent was evaporated and the resultant residue was purified by column chromatography (CH$_2$Cl$_2$/MeOH 97:3; $R_f$ = 0.5 with CH$_2$Cl$_2$/MeOH 90:10) affording 113 (327 mg, 36%) as a yellow solid.

Mp: 184-185 °C; $^1$H NMR (400 MHz, CDCl$_3$/MeOD 5:1, 25°C): 8.44 (s, 1H, C(Nap)), 8.40 (s, 1H, C(Nap)), 8.00 (d, $^3$J(H,H) = 8.6 Hz, 2H, C$_3$(Pnz)), 7.40 (d, $^3$J(H,H) = 8.6 Hz, 2H, C$_5$(Pnz)), 7.27 – 7.22 (m, 5H, C(Cbz)), 5.66 (dd, $^3$J(H,H) = 9.1 Hz, $^1$J(H,H) = 5.3 Hz, 1H, C$_a$(Lys)), 5.06 (s, 2H, C(Pnz)), 4.95 (s, 2H, C(Cbz)), 4.46 (q, $^3$J(H,H) = 7.0 Hz, 4H, C(Ethoxy)), 4.33 – 4.30 (m, 2H, C(en)), 3.58 – 3.56 (m, 2H, C(en)), 3.10 – 3.09 (m, 2H, C$_6$(Lys)), 2.28 – 2.24 (m, 2H, C$_6$(Lys)), 1.61 (t, $^3$J(H,H) = 6.8 Hz, 6H, C$_2$(Ethoxy)), 1.54 – 1.48 (m, 2H, C$_6$(Lys)), 1.45 – 1.36 (m, 2H, C$_6$(Lys)); $^{13}$C NMR (100 MHz, CDCl$_3$/CD$_3$OD 5:1, 25 °C, N/N = regiosomeric equivalents): 173.2 (s, CONH$_2$-Lys), 163.0 (s, C-Naph), 162.9 (s, C-Naph), 161.7 (s, CO-Naph), 161.4 (s, CO-Naph), 160.6 (s, CO-Naph), 158
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160.4 (s, CO-Naph), 157.5 (s, CONH-Cbz), 157.1 (s, CONH-Pnz), 147.6 (s, C-Pnz), 144.9 (s, C1-Pnz), 136.9 (s, C1-Cbz), 128.7 (d x 2, C2-PNZ), 128.3 (d x 2, C2-Cbz), 128.1 (d, C2-Cbz), 128.0 (d x 2, C2-Cbz), 127.5 (s, C-Naph), 127.2 (s, C-Naph), 124.0 (s, C-Naph), 123.8 (s, C-Naph), 123.8 (d x 2, C3-Pnz), 120.2 (d, CH-Naph), 120.1 (d, CH-Naph), 111.0 (s, C-Naph), 110.8 (s, C-Naph), 66.8 (t x 2, C2-Ethoxy), 66.7 (t, C-Pnz), 65.2 (t, C-Cbz), 54.8 (d, Cα-Lys), 40.7 (t, Cγ-Lys), 40.4 (t, Cβ-en), 39.5 (t, Cε-Lys), 29.6 (t, Cγ-Lys), 28.2 (t, Cγ-Lys), 24.0 (t, Cβ-Lys), 14.9 (q, Cα-Ethoxy), 14.8 (q, Cε-Ethoxy); MS (ESI, +ve): 656 [M + NH4]+, 839 [M + H]+, 594 [M – NH3]+; HR-MS (ESI, +ve): Calcd for C25H32O13N5H+: 839.2888, Found: 839.2914.

Pnz-en-[O(ethoxy), N(2-amino)-10,12-pentacosadimate]-NDI-Lys(Z)-NH2 117.

A compound 113 (200 mg, 0.238 mmol) was dissolved in CHCl3 (25 mL) to this the ethylenediamine 114 (1.433 gm, 23.8 mmol) was added slowly at rt. The reaction mixture was stirred at rt and monitored by TLC. After 16 h, when the consumption of the reactant compound 113 was observed then the solvent was removed under vacuum at rt and impurities were removed by quick short column chromatography (CH2Cl2/MeOH 100:5 Rf = 0.3 with CH2Cl2/MeOH/TEA 100:10:0.5) yielded compound 115 as a red solid (90 mg).
A solution of compound \(116\) (40.8 mg, 0.109 mmol), HATU (36 mg, 0.094 mmol) and TEA (81 \(\mu\)l, 0.581 mmol) in distilled DMF/CHCl\(_3\) 2:3 (10 mL) was stirred at rt for 2 min. To this the compound \(115\) (62 mg, 0.072 mmol) was added and the resulting reaction mixture was stirred at rt for 12 h. The reaction mixture was diluted by CHCl\(_3\) (200 mL). The organic layer was washed with saturated solution of NaHCO\(_3\) (25 mL x 2), H\(_2\)O (50 mL), brine (25 mL) and finally dried over Na\(_2\)SO\(_4\). The solvent was evaporated and the resultant residue was purified by column chromatography (CH\(_2\)Cl\(_2\)/MeOH 100:3 \(R_f = 0.6\) with CH\(_2\)Cl\(_2)/MeOH 100:4) yielded compound \(117\) (70 mg, 67 %) as a red solid.

\(\text{Mp: 216-217 °C; } ^1\text{H NMR (400 MHz, CDCl}_3/\text{MeOD 5:1, 25°C, N/N = regioisomeric equivalents): 9.70-9.55 (m, N(en)H), 8.14/8.11 (s, 1H, C(Nap)H), 8.04 (s, 2H, C(Nap)H), 7.96 (d, } ^3\text{J(H,H) = 8.6 Hz, 2H, C}_3\text{(Pnz)H), 7.35/7.32 (d, } ^3\text{J(H,H) = 8.6 Hz, 2H, C}_3\text{(Pnz)H), 7.21 – 7.16 (m, 5H, C(Cbz)H), 5.82 – 5.81 (m, 1H, N(amide)H), 5.66/5.62 (dd, } ^3\text{J(H,H) = 9.1 Hz, } ^3\text{J(H,H) = 5.3 Hz, 1H, C}_6\text{(Lys)H), 5.02/4.99 (s, 2H, C(Pnz)H), 4.89/4.86 (s, 2H, C(Cbz)H), 4.30 -4.27 (m, 2H, C(Ethoxy)H), 4.10 – 4.09 (m, 2H, C(en)H), 3.61 – 3.60 (m, C_(DAA)H}_2), 3.53 – 3.52 (m, 2H, C_(DAA)H}_2), 3.42 – 3.36 (m, C_(en)H), 3.07 - 3.06 (m, 2H, C_(Lys)H), 2.32 - 2.27 (m, 1H, C_(Lys)H), 2.19 – 2.12 (m, 7H, C_(DAA)H}_2), C_8 & C_{13}, 1.56 – 1.48 (m, 7H, C_(Ethoxy)H), C_(Lys)H, C_(Ethoxy)H, C_(DAA)H}_2), 1.46 – 1.40 (m, 4H, C_7 & C_{14}, 1.32 – 1.20 (m, 28H, C_(Lys)H), C_15, C_16, C_17, C_18, C_19, C_20, C_21, C_22 & C_{23}, 0.82 (t, } ^3\text{J(H,H) = 6.5 Hz, 3H, C_(DAA)H}_2), 1^3\text{C NMR (100 MHz, CDCl}_3/CD}_3\text{OD 5:1, 25 °C, N/N = regioisomeric equivalents): 176.8 (s, CONH}_2-Lys), 166.8 (s, C-Naph), 164.1 (s, CO-Naph), 164.0 (s, CO-Naph), 162.8 (s, CO-Naph), 162.6 (s, CO-Naph), 159.5/159.4 (s, CONH-Cbz), 158.6 (s, CONH-DAA), 158.2 (s, CONH-Pnz), 152.0 (s, C-Naph), 148.7 (s, C_2-Pnz), 145.9 (s, C_1-Pnz), 138.0/137.9 (s, C_1-Cbz), 129.8 (d x 2, C_2-Pnz), 129.4 (d, C_3-Cbz), 129.3 (d, C_4-Cbz), 129.2 (d, C_5-Cbz), 129.1 (d, ...}
Cbz), 129.1 (d x 2, C2-Cbz), 128.5 (s, C-Naph), 128.0 (s, C-Naph), 126.4 (s, C-Naph), 125.8 (s, C-Naph), 124.9 (d x 2, C3-Pnz), 121.9 (d, CH-Naph), 119.4 (d, CH-Naph), 113.0 (s, C-Naph), 112.6 (s, C-Naph), 101.7 (s, C9-DAA), 101.3 (s, C12-DAA), 67.9 (t, C2-Ethoxy), 67.6/67.5 (t, C-Cbz), 66.7 (s x DAA), 66.6 (s, x 2, C11-DAA), 66.4 (t, C3-Pnz), 55.8 (d, Cα-Lys), 43.8 (t, Cα1-en), 42.0/41.9 (t, Cε-Lys), 41.5 (t, Ca-en), 40.5/40.4 (t, Cb-en), 40.2/40.1 (t, Cn1-DAA), 37.8/37.7 (t, C1-DAA), 33.4 (t, C22-DAA), 31.1(t, C17-DAA), 31.0 (t, C20-DAA), 30.9 (t, C18-DAA), 30.8 (t, C19-DAA), 30.6 (t, C1-DAA), 30.5 (t x 2, C3 & C16-DAA), 30.4 (t, C3-DAA), 30.3 (t, C17-DAA), 30.2 (t, C7-DAA), 29.9 (t, C14-DAA), 29.8 (t, C7-DAA), 29.4 (t, C8-Lys), 29.2 (t, C7-Lys), 27.3/27.2 (t, C2-DAA), 25.1 (t, C9-Lys), 24.1 (t, C23-DAA), 20.6 (t, C8-DAA), 20.5 (t, C13-DAA), 16.0 (q, C2-Ethoxy), 15.4 (q, C24-DAA); MS (ESI, +ve): 1232 (35, [M + Na]+), 1267 (100, [M + NH4]+), 1210 (50, [M + H]+), 1293 (20, [M − NH2]+); HR-MS (ESI, +ve): Calcd for C67H85O13N8+: 1209.6236, Found: 1209.6241.

**H-en-[O(ethoxy), N(2-amino)-10,12-pentacosadinamide]-NDI-Lys(Z)-NH2**

A compound 117 (70 mg, 0.057 mmol) was dissolved in acidic DMF (0.1 mmol acetic acid) (10 mL). To this SnCl2 (109.7 mg, 0.578 mmol) and phenol (0.21 mg, 2.315 µmol) were added. The resulting reaction mixture was stirred
at 50 °C and monitored by TLC. After 1 h when the consumption of the reactant compound 117 was observed, then the solvent was removed under vacuum at rt and the crude product was purified by column chromatography (CH\textsubscript{2}Cl\textsubscript{2}/MeOH 100:5) with CH\textsubscript{2}Cl\textsubscript{2}/MeOH/TEA 100:10:0.5. Compound 118 (52.3 mg, 87%) as a red solid. 

**Mp:** 170-171 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}/MeOD 5:1, 25°C, N/N = regioisomeric equivalents): 8.30 (s, 1H, C(Nap)\textsubscript{H}), 8.24 (s, 1H, C(Nap)\textsubscript{H}), 7.28 – 7.19 (m, 5H, C(Cbz)\textsubscript{H}), 5.69/5.64 (dd, \textsuperscript{3}J(H,H) = 9.1 Hz, \textsuperscript{3}J(H,H) = 5.3 Hz, 1H, C\textsubscript{a}(Lys)\textsubscript{H}), 4.91/4.89 (s, 2H, C(Cbz)\textsubscript{H}), 4.43 - 4.39 (m, 2H, C\textsubscript{1}(Ethoxy)\textsubscript{H}), 4.25 – 4.19 (m, 2H, C\textsubscript{4}(en)\textsubscript{H}), 3.67 – 3.64 (m, C\textsubscript{b1}(DAA)\textsubscript{H}), 3.55 – 3.52 (m, 2H, C\textsubscript{b2}(DAA)\textsubscript{H}), 3.10 – 3.07 (m, C\textsubscript{b}(en)\textsubscript{H}), 3.01 - 2.98 (m, 2H, C\textsubscript{a}(Lys)\textsubscript{H}), 2.32 - 2.27 (m, 1H, C\textsubscript{b}(Lys)\textsubscript{H}), 2.32 – 2.11 (m, 8H, C\textsubscript{a}(Lys)H\textsubscript{2}, C\textsubscript{1}, C\textsubscript{4} & C\textsubscript{13}(DAA)\textsubscript{H}), 1.60 - 1.51 (m, 7H, C\textsubscript{a}(Ethoxy)\textsubscript{H}, C\textsubscript{a}(Lys)\textsubscript{H}, C\textsubscript{a}(DAA)\textsubscript{H}), 1.49 – 1.43 (m, 4H, C\textsubscript{3} & C\textsubscript{14}(DAA)\textsubscript{H}), 1.35 – 1.22 (m, 28H, C\textsubscript{a}(Lys)\textsubscript{H}, C\textsubscript{3}, C\textsubscript{4}, C\textsubscript{5}, C\textsubscript{6}, C\textsubscript{15}, C\textsubscript{16}, C\textsubscript{17}, C\textsubscript{18}, C\textsubscript{19}, C\textsubscript{20}, C\textsubscript{21}, C\textsubscript{22} & C\textsubscript{23}(DAA)\textsubscript{H}), 0.86 (t, \textsuperscript{3}J(H,H) = 6.8 Hz, 3H, C\textsubscript{b2}(DAA)\textsubscript{H}). MS (ESI, +ve): 1053 (15, [M + Na]\textsuperscript{+}), 1031 (100, [M + H]\textsuperscript{+}), 1013 (10, [M – NH\textsubscript{3}]\textsuperscript{+}).
To a solution of 83 (1.5 mg, 1.2 µmol), 118 (33 mg, 49 µmol), HATU (7 mg, 18 µmol), DTBP (33 µL, 144 µmol) and TEA (14 µL, 96 µmol) in distilled and degassed DMF (1 mL) was stirred at rt for 16 h. DMF was removed under high vacuum. A preliminary purification by column chromatography (DCM/MeOH 9:1) followed by PTLC (DCM/MeOH 9:1, $R_f = 0.5$) yielded 119 (6 mg, 43%) as a red solid.

$^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 1:1, 25 °C): 8.12 – 7.83 (m, 20H, C(Naph)H), 7.21 - 7.20 (several m, 50H, C$_{\alpha}$(Cbz)H), 6.88 - 6.68 (m, 12H, C$_{\alpha}$(penta phenyleneethynylene)H), 5.66 - 5.48 (m, 10H, C$_{\alpha}$(Lys)H), 4.99 - 4.90 (br.s, 20H, C(Cbz)H$_2$), 4.45 - 3.12 (several m, 60H, C(penta phenyleneethynylene)H)
phenyleneethynylene)H₂ [20H], C₆(en)H₂ [20H], C₁(Ethoxy)H₂ [20H]), 3.71 - 3.43 (m, 60H, C₆(en)H₂ [20H], C₂(en)H₂ [20H], C₆(en)H₂ [20H]), 3.10 - 3.02 (m, 20H, C₆(Lys)H₂), 2.20 - 2.17 (m, 80H, C₁(Lys)H₂ [20H], C₁, C₈ & C₁₃(DAA)H₂ [60H]), 1.58 - 1.41 (several m, 110H, C₂(Ethoxy)H₃ [30H], C₆(Lys)H₂ [20H], C₁, C₇ & C₁₄(DAA)H₂ [60H]), 1.34 - 1.22 (several m, 280H, C₆(Lys)H₂ [20H], C₄, C₅, C₆, C₁₅, C₁₆, C₁₇, C₁₈, C₁₉, C₂₀, C₂₁, C₂₂ & C₂₅(DAA)H₂ [260H]), 0.86 – 0.83 (m, 30H, C₂₆(DAA)H₃); MS (MALDI +ve linear, Dithranol): 11360 (100, [M + NH₄]+).

4.2.7 Synthesis of the Anionic ON-NDI-OPE Propagator 99

**Figure 78:** Nomenclature for the anionic ON-NDI-OPE propagator synthesis. Numbering of amines and protecting groups.
**Pnz-en-[2,6-diethoxy]-NDI-Glu(tert-Bu)-NH$_2$ 120.** A compound 100 (520 mg, 1.031 mmol) was added to 55 mL of a 1 M solution of KOH in isopropanol. The reaction mixture was refluxed for 20 h and then evaporated to dryness under vacuu. Then obtained residue was dissolved in 50 mL acetic acid giving a clear yellow solution. To this was added H-Glu(OBu')-NH$_2$ 75 (208.6 mg, 1.031 mmol) and Pnz-ethylenediamine 111 (246.3 mg, 1.031 mmol) sequentially and the reaction mixture was heated for 12 h at 80 °C. H-Glu(OBu')-NH$_2$ 75 (417.3 mg, 2.062 mmol) and Pnz-ethylenediamine 111 (492.6 mg, 2.032 mmol) were added again to the reaction mixture and the mixture was heated further 24 h. The reaction mixture after that time was cooled down to rt and diluted with EtOAc (500 mL). The organic layer was washed with 1 M KHSO$_4$ (100 ml x 2), H$_2$O (100 mL), brine (50 mL) and finally dried over Na$_2$SO$_4$. The solvent was evaporated and the resultant residue was purified by column chromatography (CH$_2$Cl$_2$/MeOH 97:3; $R_f$ = 0.5 with CH$_2$Cl$_2$/MeOH 90/10) affording 120 (220 mg, 28 %) as a yellow solid.

Mp: more than 230 °C; $^1$H NMR (400 MHz, CDCl$_3$/MeOD 5:1, 25°C): 8.45 (s, 1H, C(Nap)H), 8.43 (s, 1H, C(Nap)H), 8.02 (d, $^3$J(H,H) = 8.6 Hz, 2H, C$_3$(Pnz)H), 7.41 (d, $^3$J(H,H) = 8.6 Hz, 2H, C$_2$(Pnz)H), 5.68 (dd, $^3$J(H,H) = 9.6 Hz, $^3$J(H,H) = 4.8 Hz, 1H, C$_a$(Glu)H), 5.07 (s, 2H, C(Pnz)H$_2$), 4.48 (q, $^3$J(H,H) = 7.0 Hz, 4H, C$_1$(Ethoxy)H$_2$), 4.35 (t, $^3$J(H,H) = 5.6 Hz, 2H, C$_a$(en)H$_2$), 3.60 – 3.56 (m, 2H, C$_b$(en)H$_2$), 3.48 – 3.40 (m, 4H, C$_b$ & C$_a$(Glu)H$_2$), 1.62 (t, $^3$J(H,H) = 7.0 Hz, 6H, C$_2$(Ethoxy)H$_3$), 1.33 (s, 9H, C(tBu)H$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$/CD$_2$OD 5:1, 25 °C): 173.9 (s, CONH$_2$-Glu), 173.7 (s, CO-OBu), 164.2 (s, C-Naph), 163.9 (s, C-Naph), 163.0 (s, CO-Naph), 162.5 (s, CO-Naph), 161.7 (s, CO-Naph), 161.6 (s, CO-Naph), 158.1 (s, CONH-Pnz), 148.7 (s, C$_a$-Pnz), 145.9 (s, C$_7$-Pnz), 129.3 (d x 2, C$_2$-Pnz), 128.7 (s, C-Naph), 128.4 (s, C-
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Naph), 125.2 (s, C-Naph), 125.0 (s, C-Naph), 124.9 (d x 2, C-Pnz), 121.3 (d, CH-Naph), 121.2 (d, CH-Naph), 112.2 (s, C-Naph), 111.9 (s, C-Naph), 82.5 (s, C-’Bu), 67.9 (t x 2, C-’Ethoxy), 66.4 (t, C-Pnz), 55.4 (d, C-Pz-Glu), 41.5 (t, C-’en), 40.8 (t, C-’en), 34.0 (t, C-Pz-Glu), 29.3 (q x 3, CH-’Bu), 25.0 (t, C-Pz-Glu), 16.1 (q, C-’Ethoxy), 16.0 (q, C-’Ethoxy); MS (ESI, +ve): 785 (20, [M + Na]+), 763 (80, [M + H]+), 746 (20, [M – NH2]+), 707 (30, [M – ’Bu]+), 690 (100, [M – O’Bu]+); HR-MS (ESI, +ve): Calcd for C_{33}H_{56}O_{13}N_{4}Na+: 784.2442, Found: 784.2406.

Pnz-en-[O(ethoxy), N(2-amino)-10,12-pentacosadimamide]-NDI-Glu(tert Bu)-NH₂ 122.

A compound 120 (180 mg, 0.236 mmol) was dissolved in CHCl₃ (25 mL). To this the ethylenediamine (1.42 gm, 23.6 mmol) was added slowly at rt. The reaction mixture was stirred at rt and monitored by TLC. After 16 h, when the consumption of the reactant compound 120 was observed then the solvent was removed under vacuum at rt and impurities were removed by quick short column chromatography (CH₂Cl₂/ MeOH 100:5 Rₜ = 0.3 with CH₂Cl₂/MeOH/TEA 100:10:0.5) yielded compound 121 as a red solid (70 mg). A solution of compound 116 (50 mg, 0.135 mmol), HATU (44 mg, 0.117 mmol) and TEA (100 µl, 0.721 mmol) in distilled DMF/CHCl₃ 2:3 (10 mL)
was stirred at rt for 2 min. To this the compound 121 (70 mg, 0.090 mmol) was added and the resulting reaction mixture was stirred at rt for 12 h. The reaction mixture was diluted by CHCl₃ (200 mL). The organic layer was washed with saturated solution of NaHCO₃ (50 mL x 2), H₂O (50 mL), brine (25 mL) and finally dried over Na₂SO₄. The solvent was evaporated and the resultant residue was purified by column chromatography (CH₂Cl₂/MeOH 100:3 Rf = 0.6 with CH₂Cl₂/MeOH 100:4) yielded compound 122 (65 mg, 64 %) as a red solid.

Mp: 189-190 °C; ¹H NMR (400 MHz, CDCl₃/CD₃OD 5:1, 25 °C, N/N = regioisomeric equivalents): 9.73-9.69 (m, N(en)H), 8.26 (s, 1H, C(Nap)H), 8.18/8.14 (s, 1H, C(Nap)H), 8.00/7.99 (d, ³J(H,H) = 8.6 Hz, 2H, C₃(Pnz)H), 7.39/7.38 (d, ³J(H,H) = 8.6 Hz, 2H, C₇(Pnz)H), 6.26 (br.s, 1H, N(amide)H), 6.08 (br s, 1H, N(amide)H), 5.71 – 5.63 (m, 1H, Cα(Glu)H), 5.06 (s, 2H, C(Pnz)H₂), 4.38 – 4.36 (m 2H, C₁(Ethoxy)H₂), 4.23 – 4.22 (m, Hz, 2H, C₁(Pnz)H₂), 3.68 – 3.64 (m, 2H, C₅(DAA)H₂), 3.55 – 3.47 (m, 4H, C₂₃(DAA)H₂, C₂₂(DAA)H₂), 2.64-2.56 (m, 1H, Cβ(Glu)H), 2.43 – 2.25 (m, 3H, Cγ(Glu)H₂, Cβ(Glu)H), 2.21 – 2.15 (m, 6H, C₂, C₈ & C₁₃(DAA)H), 1.58-1.55 (m, 5H, C₂(Ethoxy)H₃, C₅(DAA)H₃), 1.48-1.42 (m, 4H, C₇ & C₁₄(DAA)H₂), 1.32 - 1.21 (several m, 34H, C(tBu)H₃, C₃, C₄, C₅, C₆, C₁₅, C₁₆, C₁₇, C₁₈, C₁₉, C₂₀, C₂₁, C₂₂ & C₂₃(DAA)H₂), 0.85 (t, ³J(H,H) = 6.8 Hz, 3H, C₃₂(DAA)H); ¹³C NMR (100 MHz, CDCl₃/CD₃OD 5:1, 25 °C, N/N = regioisomeric equivalents): 176.7 (s, CONH₂-Glu), 174.0 (s, CO-O'Bu), 166.9 (s, C-Naph), 164.3 (s, CO-Naph), 164.2 (s, CO-Naph), 163.0 (s, CO-Naph), 162.5 (s, CO-Naph), 159.5 (s, CONH-DAA), 158.1 (s, CONH-Pnz), 152.2 (s, C-Naph), 148.7 (s, C₄-Pnz), 145.9 (s, C₁-Pnz), 129.4 (d, C₂-Pnz), 129.3 (d, C₂-Pnz), 128.6 (s, C-Naph), 128.2 (s, C-Naph), 126.5 (s, C-Naph), 125.3 (s, C-Naph), 124.9 (d x 2, C₃-Pnz), 121.9 (d, CH-Naph), 119.7 (d, CH-Naph), 113.2 (s, C-Naph), 112.8 (s, C-Naph), 101.8 (s x 2, C₆ & C₁₀-DAA), 82.4 (s, C₃-Bu), 67.6 (t, C₂-Ethoxy), 66.8 (s, C₁₆-DAA), 66.7 (s, x 2, C₁₁-DAA), 66.5 (t, C-Pnz), 55.4 (d, C₆-Glu), 43.8 (t,
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C$_{27}$-DAA, 41.5 (t, C$_{2}$-en), 40.8 (t, C$_{3}$-en), 40.2 (t, C$_{37}$-DAA), 37.8 (t, C$_{4}$-DAA), 34.0 (t, C$_{5}$-Glu), 33.4 (t, C$_{22}$-DAA), 31.1 (t, C$_{17}$-DAA), 31.0 (t, C$_{29}$-DAA), 30.9 (t, C$_{18}$-DAA), 30.8 (t, C$_{19}$-DAA), 30.7 (t, C$_{21}$-DAA), 30.6 (t, C$_{2}$-DAA), 30.5 (t x 2, C$_{3}$ & C$_{16}$-DAA), 30.4 (t, C$_{7}$-DAA), 30.3 (t, C$_{15}$-DAA), 30.2 (t, C$_{6}$-DAA), 29.9 (t, C$_{12}$-DAA), 29.8 (t, C$_{7}$-DAA), 29.3 (q x 3, CH$_{3}$-Bu), 27.1 (t, C$_{2}$-DAA), 25.0 (t, C$_{8}$-Glu), 24.1 (t, C$_{23}$-DAA), 20.6 (t, C$_{8}$-DAA), 20.5 (t, C$_{13}$-DAA), 16.8 (q, C$_{2}$-Ethoxy), 15.5 (q, C$_{24}$-DAA); MS (ESI, +ve): 1156 (30, [M + Na]$^+$), 1151 (90, [M + NH$_3$]$^+$), 1133 (100, [M + H]$^+$), 1116 (25, [M – NH$_3$]$^+$), 1077 (40, [M – tBu]$^+$), 1060 (60, [M – Obu]$^+$);

H-en-[O(ethoxy), N(2-amino)-10,12-pentacosadimamde]-NDI-Glu(tert Bu)-NH$_2$123.

A compound 122 (60 mg, 0.05 mmol) was dissolved in acidic DMF (0.1 mmol acetic acid) (5 mL). To this SnCl$_2$ (100 mg, 0.5 mmol) and phenol (0.2 mg, 2.1 μmol) were added. The resulting reaction mixture was stirred at 50 °C and monitored by TLC. After 1 h when the consumption of the reactant compound 122 was observed then the solvent was removed under vacuum at rt and the crude product was purified by column chromatography (CH$_2$Cl$_2$/MeOH 100:5, R$_f$ = 0.4 with CH$_2$Cl$_2$/MeOH/TEA 100:10:0.5) compound 123 (37 mg, 74 %) as a red solid.
Mp: 95-96 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)/TEA 9:1, 25 °C, N/N = regioisomeric equivalents): 9.80 - 9.79/9.61 - 9.60 (m, N(en)\(\text{H}\)), 8.16/8.14 (s, 1H, C(Nap)\(\text{H}\)), 7.11 - 6.90 (br s, 1H, N(amide)\(\text{H}\)), 6.71 (br s, 1H, N(amide)\(\text{H}\)), 6.29-6.24 (br s, 1H, N(amide)\(\text{H}\)), 5.75 - 5.69 (m, 1H, C\(_\alpha\)(Glu)\(\text{H}\)), 4.42 - 4.33 (m 2H, C\(_1\)(Ethoxy)\(\text{H}\)), 4.10 - 4.07 (m, Hz, 2H, C\(_\alpha\)(en)\(\text{H}\)), 3.77 - 3.59 (m, 4H, C\(_{a1}\)(DAA)\(\text{H}\)), 2.98 - 2.92 (m, 2H, C\(_{a1}\)(en)\(\text{H}\)), 2.75-2.68 (m, 1H, C\(_\beta\)(Glu)\(\text{H}\)), 2.46 - 2.30 (m, 3H, C\(_\gamma\)(Glu)\(\text{H}\)), 2.38 - 2.00 (m, several m, 2H, C\(_\beta\)(en)\(\text{H}\)), 2.28 - 2.25 (m, 6H, C\(_5\), C\(_8\), C\(_{13}\)(DAA)\(\text{H}\)), 1.58-1.55 (m, 5H, C\(_2\)(Ethoxy)\(\text{H}\)), C\(_2\)(DAA)\(\text{H}\)), 1.48-1.42 (m, 4H, C\(_7\) & C\(_{14}\)(DAA)\(\text{H}\)), 1.37 - 1.29 (several m, 34H, C\(_{t}\)Bu)\(\text{H}\)), C\(_3\), C\(_4\), C\(_5\), C\(_6\), C\(_{15}\), C\(_{16}\), C\(_{17}\), C\(_{18}\), C\(_{20}\), C\(_{21}\), C\(_{22}\) & C\(_{23}\)(DAA)\(\text{H}\)), 0.93 (t, \(^3\)J(H,H) = 6.6 Hz, 3H, C\(_{24}\)(DAA)\(\text{H}\)). MS (ESI, +ve): 980 (20, [M + Na]+), 954 (100, [M + H]+), 936 (100, [M - NH\(_2\)]+).
To a solution of 83 (1.5 mg, 0.86 µmol), 123 (32 mg, 34.4 µmol), HATU (5 mg, 13 µmol), DTBP (15 µL, 103 µmol) and TEA (12 µL, 82 µmol) in distilled and degassed DMF (1 mL) was stirred at rt for 16 h. DMF was removed under high vacuum. A preliminary purification by column chromatography (DCM/MeOH 9:1) followed by PTLC (DCM/MeOH 9:1, Rf = 0.5) yielded 124 (3 mg, 33%) as a red solid.

$^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD 1:1, 25 °C): 8.17 – 7.70 (m, 20H, C(Naph)H), 6.98 - 6.58 (m, 12H, C$_x$(penta phenyleneethynylene)H), 5.65 - 5.48 (m, 10H, C$_x$(Lys)H), 4.47 - 4.10 (several m, 60H, C(penta phenyleneethynylene)H$_2$ [20H], C$_x$(en)H$_2$ [20H], C$_x$(Ethoxy)H$_2$ [20H]), 3.67 - 1.70
3.46 (several m, 60H, C$_{a1}$ (DAA)$_2$ [20H], C$_{b2}$ (en)$_2$ [20H]), 2.64 - 2.54 (m, 10H, C$_{b}$ (Glu)$_2$), 2.27 - 2.14 (several m, 90H, C$_{b}$ (Glu)$_2$ [10H], C$_{a}$ (Glu)$_2$ [20H], C$_{a}$, C$_{b}$ & C$_{a1}$ (DAA)$_2$ [60H]), 1.58 - 1.41 (several m, 90H, C$_{2}$ (Ethoxy)$_2$ [30H], C$_{1}$, C$_{7}$ & C$_{a4}$ (DAA)$_2$ [60H]), 1.28 - 1.19 (several m, 280H, C(Bu)$_3$ [90H], C$_{4}$, C$_{5}$, C$_{6}$, C$_{15}$, C$_{16}$, C$_{17}$, C$_{18}$, C$_{19}$, C$_{20}$, C$_{21}$, C$_{22}$ & C$_{23}$ (DAA)$_2$ [350H]), 0.82 – 0.79 (m, 30H, C$_{24}$ (DAA)$_3$); MS (MALDI +ve linear, HABA): 10596 (100, [M + Na]$^+ $).

4.3 Preparation of Stock Solutions

4.3.1 Stock Solution of HH-NDI-OPE Initiator 54

A stock solution was prepared by dissolving 54 in DMSO, the concentration was confirmed by UV-visible spectroscopy at concentration $c = c_{\text{stock}}/10$ in MeOH. 100 µL of the stock solution was placed in an UV-cuvette, diluted to 1 mL with MeOH and UV absorption was measured. From the UV measurements, the concentration, $c$, was calculated using the Beer-Lambert Equation 4:

$$c = \frac{A}{\varepsilon l} \quad \text{Equation 4}$$

Where, $A = \text{absorbance}$, $\varepsilon = \text{molar extinction coefficient}$ ($\varepsilon_{\text{NDI}} = 64015 \text{ L mM}^{-1} \text{ cm}^{-1}$, at $\lambda_{\text{max}} = 381 \text{ nm in MeOH}$) and $l = \text{path length of UV-cuvette}$ ($l = 1 \text{ cm}$). From $c$, $c_{\text{stock}}$ was calculated as, $c_{\text{stock}} = c \times 10 = 30 \text{ mM}$. 

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4.3.2 Stock Solution of NBr-NDI-OPE Cationic Propagator 55

A stock solution was prepared by dissolving 55 in MeOH, the concentration was confirmed by UV-visible spectroscopy at concentration $c = c_{stock}/10$ in MeOH. Molar extinction coefficient of 10-NBr-NDI ($\varepsilon_{10-NBr-NDI} = 160000 \text{ LM}^{-1}\text{cm}^{-1}$, at $\lambda_{max} = 533 \text{ nm}$) in MeOH was used to calculate the concentration of $c$ and $c_{stock} = c x 10 = 84.1 \times 10^6 \text{ M}$ (Equation 4).

4.3.3 Stock Solution of NBr-NDI-OPE Anionic Propagator 56

A stock solution was prepared by dissolving 56 in MeOH, the concentration was confirmed by UV-visible spectroscopy at concentration $c = c_{stock}/10$ in MeOH. Molar extinction coefficient of 10-NBr-NDI ($\varepsilon_{10-NBr-NDI} = 160000 \text{ LM}^{-1}\text{cm}^{-1}$, at $\lambda_{max} = 540 \text{ nm}$) in MeOH was used to calculate the concentration of $c$ and $c_{stock} = c x 10 = 28.64 \times 10^6 \text{ M}$ (Equation 4).

4.3.4 Stock Solution of ON-NDI-OPE Cationic Propagator 90

A stock solution was prepared by dissolving 90 in MeOH, the concentration was confirmed by UV-visible spectroscopy at concentration $c = c_{stock}/10$ in MeOH. Molar extinction coefficient of 10-ON-NDI ($\varepsilon_{10-ON-NDI} = 177000 \text{ LM}^{-1}\text{cm}^{-1}$, at $\lambda_{max} = 552 \text{ nm}$) in MeOH was used to calculate the concentration of $c$ and $c_{stock} = c x 10 = 40 \times 10^6 \text{ mM}$ (Equation 4).

4.3.5 Stock Solution of ON-NDI-OPE Anionic Propagator 91

A stock solution was prepared by dissolving 91 in MeOH, the concentration was confirmed by UV-visible spectroscopy at concentration
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c = c_{stock}/10 in MeOH. Molar extinction coefficient of 10-ON-NDI ($\varepsilon_{10-ON-NDI} = 177000$ $\text{LM}^{-1}\text{cm}^{-1}$, at $\lambda_{\text{max}} = 562$ nm) in MeOH was used to calculate the concentration of $c$ and $c_{stock} = c \times 10 = 158 \times 10^6$ M (Equation 4).

4.4 Electrochemistry

Oxidation and reduction potentials of $NBr$-NDI and OPE rod were determined using cyclic voltammetry (CV) at room temperature in DCM, with 100 mM Bu4NPF6 as supporting electrolyte, a Pt disk working electrode, a Pt wire counter electrode, a Ag/AgCl reference electrode, the ferrocene/ferricenium couple (Fc/Fc$^+$) as internal standard, and a scan speed of 100 mV/s except for $NBr$-NDI (20 mV/s). Results are summarised in Table 2. HOMO and LUMO energies vs vacuum were calculated from the onset of oxidation and reduction waves using Equation 5.

$$E_{\text{HOMO/LUMO}} = -4.8 \text{ eV} - E_{\text{onset}} \text{ vs (Fc/Fc$^+$)}$$

Equation 5

The optical band gap $E_g^{\text{opt}}$ was calculated from the onset of the lowest energy band using Equation 6.

$$E_g^{\text{opt}} = 1240 / \lambda_{\text{max onset}} \text{ (nm)}$$

Equation 6

And compared to the band gaps obtained from CV ($E_g^{\text{CV}}$, Table 2).

4.5 Absorption Spectra

UV-visible spectra of compound HH-NDI-OPE initiator, $NBr$-NDI-OPE cationic propagator and ON-NDI-OPE cationic propagator
90 were measured on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 °C) using quartz cells with a path length of 1 cm and are reported as maximal absorption wavelength $\lambda$ in nm (extinction coefficient $e$ in nM$^{-1}$ cm$^{-1}$).

### 4.6 Supramolecular Assembly Formation and Photocurrent Generation of NBr-NDI-OPE

#### 4.6.1 Preparation of Gold Electrodes

Gold electrodes were prepared as reported previously$^{53,58}$. Gold-coated glass slides (22 x 22 mm$^2$) were purchased from Mivitec GmbH, Analytical µ-Systems (Germany). Before use, the plates were cut in half (~ 1 x 2 cm$^2$), and cleaned using ‘piranha’ solution ($\text{H}_2\text{SO}_4$/30% $\text{H}_2\text{O}_2$ 3/1; 35°C for 5 min).\textsuperscript{179} Caution: piranha solution reacts violently with organic compounds. It should be handled with extreme care. After the treatment with piranha solution, the plates were thoroughly rinsed with bidistilled water and EtOH, and used immediately.

#### 4.6.2 Zipper Assembly Initiation

Zipper assembly initiation was done as reported previously$^{53,58}$. The cleaned gold plates were immersed in the solution of the anionic initiator \textsuperscript{54} (0.3 mM) in a 1:0.4 mixture of DMF:water for 4 days. The obtained Au-\textsuperscript{54} electrodes were tested for defects using the standard procedure in which reduction-oxidation of $\text{K}_3\text{Fe(CN)}_6$ (2 mM in 1 M aqueous KNO$_3$) was measured by cyclic voltammetry using Au-\textsuperscript{54} as working electrode (Figure
The absence of redox wave confirmed the absence of large uncovered areas on the Au electrode.

### 4.6.3 Zipper Assembly Propagation

The initiated Au-54 electrodes were immersed in the solution of cationic propagator 55 (10 μM) in a 1:1 mixture of TFE and 0.5 mM sodium phosphate buffer, 1 M NaCl, pH 7. The plate was intermittently taken out of the solution, rinsed with bidistilled water and TFE, and the photocurrent was recorded (see below). As the photocurrent reached the saturation after about 24 h (Figure 40), the duration of depositions of 55 was set for 24 h each for the following layers. Obtained Au-54-55 electrodes were similarly treated with anionic propagator 56 to give Au-54-55-56 electrodes. The same sequences were repeated using alternately charged propagators (55 and 56) to build up the Au-54-(55-56)n zipper assembly.

### 4.6.4 Zipper Assembly Termination

Au-54-55 electrodes were immersed in the solution of terminator 54 (10 mM) in a 1:1 mixture of TFE and 0.5 mM sodium phosphate, 1 M NaCl buffer, pH 7, for one day. After successive rinsing with bidistilled water and TFE, the obtained terminated Au-54-55-54 electrodes were treated repeatedly with cationic propagator 55, and then with anionic propagator 56 as described in the above “propagation” section.
4.6.5 LBL Assembly Initiation

The cleaned gold plates were immersed in the solution of the lipoic acid 89 (10 mM) in a 1:1 mix of TFE and 0.5 mM sodium phosphate, 0.5 M NaCl buffer, pH 7, for 3 days. The obtained Au-89 electrodes were tested for defects using the procedure described above for “zipper assembly initiation”.

4.6.6 LBL Assembly Propagation

The Au-89 electrodes were treated with cationic propagator 55 and anionic propagator 56 as described in “zipper assembly propagation” to build up the Au-89-(55-56)n LBL assembly.

4.6.7 LBL Assembly Termination

Au-89-55 electrodes were treated with terminator 54, and then with 55 and 56 as described in “zipper assembly termination”.

4.6.8 Photocurrent Measurements

The coated gold electrodes obtained by zipper or LBL assemblies of NBr-NDI-OPE were used as a working electrode with a Pt wire as a counter electrode and Ag/AgCl as a reference electrode. The electrodes were immersed in a deaerated (by bubbling N2 gas) aqueous solution of TEOA (50 mM) and Na2SO4 (0.1 M) and irradiated with a 150 W solar simulator (Oriel, area of irradiation ~0.7 cm2). Changes in current upon on-off switching of irradiations (20 seconds each) were measured at +0.4 V vs Ag/AgCl unless stated. The
irradiation power (65 mW cm$^{-2}$) was measured using Oriel 70260 radiant power/energy meter.

4.6.9 $J$-$V$ Measurements

Short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$) of zipper and LBL assemblies were determined by $I$-$V$ measurements of Au-54-(55-56)$_6$-55 and Au-89-(55-56)$_6$-55, having theoretically nearly the same numbers of NDI chromophores. Experimental conditions are as described in the above “photocurrent measurements”. Results are summarized in Table 3. Fill factors ($FF$) were calculated from the maximum power ($P_m$), $I_{sc}$ and $V_{oc}$ using Equation 1.$^{180}$

$$ FF = \frac{P_m}{I_{sc} V_{oc}} $$

Equation 1

The efficiencies $\eta$ were calculated using Equation 2,$^\text{175}$

$$ \eta = \frac{P_m}{a P_in} $$

Equation 2

in which $a$ is the irradiated area of the electrode in the electrolyte solution (cm$^2$), $P_in$ is the input power (W cm$^{-2}$). Short circuit currents and efficiencies are best appreciated after consideration of plasmon resonance quenching on gold by factors up to 280.$^{175}$

4.6.10 Action Spectra Measurements

Photocurrent densities ($J_{sc} = I_{sc} / a$) were measured at 0V vs Ag/AgCl upon excitation by monochromatic light (150 W Xe lamp with
Oriel 1/8 m monochromator). Obtained current densities were converted into incident photon to current conversion efficiencies (IPCEs) by using the Equation 3.¹⁸⁰

\[
\text{IPCE} = \frac{1240}{\lambda (\text{nm})} \times \frac{J_{sc}}{P_{in}}
\]

Equation 3

IPCEs are best appreciated after consideration of plasmon resonance quenching on gold by factors up to 280¹⁸¹ and confirmed access to thicker zippers.

4.6.11 Quartz Crystal Microbalance (QCM) Measurements of \(NBr\)-NDI-OPE

The quartz crystal microbalance (QCM) measurements were conducted using a Q-sense E4 device with flow cells. The temperature was kept constant at 23.3 °C throughout the experiments. A monolayer of an initiator 54, or 89 was formed ex-situ on a gold coated AT-cut crystal \((f_0 = 5\text{MHz})\) as described in OPE zipper-, or LBL initiation, respectively (section 4.6.). The crystal resonance frequencies and energy dissipation at overtones \(n = 3, 5, 7, 9\) were measured in a buffer solution (pH 7.0, 50 % aqueous TFE with 0.5 mM sodium phosphate and 1 M NaCl). Initiator coated crystals were immersed (~2 days / layer) in the solution of appropriate “propagators” as described in the section 4.6.3 to deposit multilayers. Resonance frequencies were measured after the deposition of average three layers, and differences to the frequency of the initiator-coated crystal were recorded \((\Delta f)\). Using the Sauerbrey Equation 7,¹⁸² the change in the total mass of the crystal \((\Delta m; \text{ng cm}^{-2})\) was calculated from \(\Delta f\).

\[
\Delta m = -\left(17.7 / n\right) \Delta f
\]

Equation 7
Note, the layers are deposited on the both sides of the quartz crystals because of the ex-situ depositions.

Small difference in $\Delta f/n$ found between overtones 3 and 9 is indicative of relative rigidity of the layers.

4.7 Supramolecular Assembly Formation and Photocurrent Generation of the ON-NDI-OPE

4.7.1 Preparation of Gold Electrodes

Gold electrodes were prepared as described in section 4.6.1 and reported previously.$^{53,58}$

4.7.2 Zipper Assembly Initiation

Zipper assembly initiation was done as described in section 4.6.2 and reported previously.$^{53,58}$

4.7.3 Zipper Assembly Propagation

The initiated Au-54 electrodes were immersed in the solution of cationic propagator 90 (10 $\mu$M) in a 1:1 mixture of TFE and 0.5 mM sodium phosphate buffer, 1 M NaCl, pH 7. The plate was intermittently taken out of the solution, rinsed with bidistilled water and TFE, and the photocurrent was recorded (see below). As the photocurrent reached the saturation after about 48 h, the duration of depositions of 90 was set for 48 h each for the following layers. Obtained Au-54-90 electrodes were similarly treated with anionic
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propagator 91 to give Au-54-90-91 electrodes. The same sequences were repeated using alternately charged propagators (90 and 91) to build up the Au-54-(90-91)n zipper assembly.

4.7.4 LBL Assembly Initiation

LBL assembly initiation was done as described in section 4.6.5 having lipoic acid 89 as an initiator.

4.7.5 LBL Assembly Propagation

The Au-89 electrodes were treated with cationic propagator 90 and anionic propagator 91 as described in zipper assembly propagation Section 4.8.3. to built up the Au-89-(90-91)n LBL assembly.

4.7.6 Photocurrent Measurements

The coated gold electrodes obtained by zipper or LBL assembly of ON-NDI-OPE were used as a working electrode for measurement of photocurrent as described in section 4.6.8.

4.7.7 J-V Measurements

Short circuit current ($I_{sc}$), open circuit voltage ($V_{oc}$), Fill factors ($FF$) and efficiencies ($\eta$) of zipper and LBL assemblies were determined by $I-V$ measurements of Au-54-(90-91)n-90 and Au-89-(90-91)n-90 as described in section 4.6.9., having theoretically nearly the same numbers of NDI chromophores.
4.7.8 Action Spectra Measurements

Action spectra measurement and IPCE calculation of ON-NDI-OPE assembly were done as described in section 4.6.10.

4.8 Supramolecular Oriented Multicolored Antiparallel Redox Gradients Zipper Assembly Formation and Photocurrent Generation

4.8.1 Formal OMARG-SHJs Zipper Assembly Formation

Zipper assembly initiation and deposition of first nine layers of cationic propagator 35 and anionic propagator 36 was done as described in the literature. The obtained zipper assembly Au-34-(35-36)₉-35 was treated with anionic propagator 56 and cationic propagator 55 as described in the Section 4.6.3 to build up the formal OMARG-SHJs zipper assembly Au-34-(35-36)₉-35-(56-55)₉.

4.8.2 Reversed OMARG-SHJs Zipper Assembly Formation

Zipper assembly initiation and deposition of first nine layers of cationic propagator 35 and anionic propagator 56 was done as described in the Section 4.6.2 and 4.6.3. The obtained zipper assembly Au-54-(55-56)₉-55 was treated with anionic propagator 36 and cationic propagator 35 as described in the literature to build up the reversed OMARG-SHJs zipper assembly Au-54-(55-56)₉-55-(36-35)₉.
4.8.2 Photocurrent Measurements

The photocurrent measurement of the formal OMARG-SHJs zipper assembly \( \text{Au-34-(35-36)_{n}-35-(56-55)_{n}} \) and reversed OMARG-SHJs zipper assembly \( \text{Au-54-(55-56)_{n}-55-(36-35)_{n}} \) was done as described in section 4.6.8.

4.8.3 \( J-V \) Measurements

The photovoltaic properties of the formal OMARG-SHJs zipper assembly \( \text{Au-34-(35-36)_{n}-35-(56-55)_{n}} \) was determined by I-V measurements as described in section 4.6.9.

4.8.4 Action Spectra Measurements

The action spectra of the formal OMARG-SHJs zipper assembly \( \text{Au-34-(35-36)_{n}-35-(56-55)_{n}} \) and the reversed OMARG-SHJs zipper assembly \( \text{Au-54-(55-56)_{n}-55-(36-35)_{n}} \) was measured as described in section 4.6.10.
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