Stereoselective Self-Sorting on Surfaces: Transcription of Chiral Information

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Abstract

Templated self-sorting on surfaces has been introduced recently as a new approach to construct multicomponent architectures directly on solid oxide surfaces. In this process, two-dimensional information placed on the surface is transcribed into three-dimensional architectures with up to 97% intrinsic templation efficiency. Previously, we have shown that isosteric partners of different color do neither self-sort nor respond to templation during self-organizing surface-initiated copolymerization (co-SOSIP). To evaluate the importance of chirality in this process, co-SOSIP with mixtures of pseudo-enantiomers of isosteric partners is explored. The composition of the obtained SOSIP architectures is independent of the composition of the initiator mixtures on the surface. This absence of templation from the surface rules out the occurrence of uniform self-sorting of pseudo-enantiomeric isosters, a process similar to chiral resolution in conglomerates. Alternate self-sorting, the complementary process comparable with racemic crystallization, is indistinguishable from random mixing in structural studies. However, different […]

Reference


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Stereoselective Self-Sorting on Surfaces: Transcription of Chiral Information

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ABSTRACT Template self-sorting on surfaces has been introduced recently as new approach to construct multicomponent architectures directly on solid oxide surfaces. In this process, 2D information placed on the surface is transcribed into 3D architectures with up to 97% intrinsic templation efficiency. Previously, we have shown that isosteric partners of different color do neither self-sort nor respond to templation during self-organizing surface-initiated co-polymerization (co-SOSIP). To evaluate the importance of chirality in this process, co-SOSIP with mixtures of pseudo-enantiomers of isosteric partners is explored. The composition of the obtained SOSIP architectures is independent of the composition of the initiator mixtures on the surface. This absence of templation from the surface rules out the occurrence of uniform self-sorting of pseudo-enantiomeric isosters, a process similar chiral resolution in conglomerates. Alternate self-sorting, the complementary process comparable to racemic crystallization, is indistinguishable from random mixing in structural studies. However, different photocurrent generation by pseudo-racemic compared to pseudo-homo-chiral photosystems support, on the functional level, that alternate self-sorting occurs with pseudo-enantiomeric partners. These results support that chirality is important for the transcription of 2D information into 3D architectures, and suggest that alternate self-sorting dominates over uniform self-sorting as racemic crystallization dominates over chiral resolution.

RUNNING HEAD Chiral Self-Sorting on Surfaces

KEYWORDS self-sorting; templation; racemic crystallization; conglomerates; enantiomers; isosters

INTRODUCTION

The significance of chirality in functional supramolecular systems is a topic of constant interest. Examples exist for systems that require enantiopure building blocks to form and function, whereas chirality seems less important in many other cases. Functional relevance of chirality usually originates from supramolecular architectures that form stereoselectively. This stereoselectivity often originates from enantioselective self-sorting during dimerization processes. Homodimerization of enantiomers has been referred to as uniform self-sorting, whereas the alternate or social self-sorting processes include the heterodimerization of pairs of enantiomers. Interestingly, the term narcissistic self-sorting has been used for both processes, the former because identical partners are preferred over different partners, the latter because of the attraction to the mirror image. In supramolecular polymers, homodimerization of enantiomers by uniform self-sorting can be the origin of the amplification of chirality. In the single crystal, homodimerization is the beginning of chiral resolution in conglomerates, whereas heterodimerization leads to racemic crystals.

Recent progress with enantioselective self-sorting of π-stacked dimers revealed a clear preference for heterodimerization. This trend reflects the dominance of racemic crystals, only 5-10% of all racemates crystallize as conglomerates, including Pasteur’s tartaric acid. Indeed, a fruitful strategy to obtain the crystal structure of a protein is to synthesize the enantiomeric protein and crystallize the pair of enantiomers as racemic crystals.

Self-sorting at interfaces is a particularly challenging topic because it includes directionality. Uniform self-sorting in both axial and lateral directions produces larger microdomains of the separated partners. This process is of functional relevance in biomembranes, the microdomains are often referred to as “rafts”. A more demanding, directional self-sorting process is expected as ideal in artificial photosystems. Namely, axial self-sorting into uniform π-stacks is essential to assure high charge mobility, whereas alternate self-sorting of these charge-transporting channels is required for efficient charge separation. Despite this high importance in different fields, the development of the topic has been slow because of an inherent, somewhat overwhelming complexity. To contribute manageable approaches to tackle this challenge, we have recently introduced self-organizing surface-initiated polymerization (SOSIP).

For SOSIP, initiators such as (S)-R and propagators such as (S)-R are needed (Figure 1). They both contain an aromatic core, here core-substituted naphthalenediimides (NDIs), to pile up into charge-transporting π-stacks. These π-stacks are embedded in the self-organizing hydrogen-bonded networks of the peptide domains. At the termini, initiator (S)-R carries diphosphonate “feet” to bind covalently to indium tin oxide (ITO) surfaces. On the surface, the adjacent thiols are deprotected with...
Fig. 1. (A) Structure of initiators and propagators used for enantioselective self-sorting during co-SOSIP, i.e., i) deposition on ITO surfaces, ii) thiol deprotection with DTT and iii) self-organizing thiolate/disulfide exchange polymerization at an invariable $x^R$. (B) With uniformly red templates ($x^T = 1.0$), uniform self-sorting is detectable as $x^R_{PS} = 1.0$ for $PS^{1.0R}$, whereas alternate self-sorting in $PS^{1.0A}$ is with $x^R_{PS} = 0.5$ indistinguishable from random $PS^{1.0R}$. (C) At $x^T = 0.5$, uniform $PS^{0.5R}$, alternate $PS^{0.5A}$ and random $PS^{0.5R}$ have identical $x^R_{PS} = 0.5$ and are thus indistinguishable by absorption spectroscopy despite clearly different structures.
dithiothreitol (DTT), and the thiol nucleophiles are activated with base. Molecular recognition of propagators (S)-R by π-stacking and hydrogen bonding with the initiators on the surface is expected to place the strained disulfide of asparagusic acid directly on top of the thiolates. Ring-opening thiolate/disulfide exchange\textsuperscript{39,40} covalently binds the propagator to the initiator and at the same time reproduces thiolic acid on the surface for continuing SOSIP.

SOSIP turned out to provide general access to ordered and oriented surface architectures that generate much more photocurrent than their disordercontrolled controls. Experimental evidence for compatibility with other stacks (perylenediimides, oligothiophenes),\textsuperscript{41} expandable and exchangeable surroundings including additional stacks,\textsuperscript{31} oriented multicomponent gradients,\textsuperscript{30} antiparallel double-gradient systems\textsuperscript{31} and well as self-repair\textsuperscript{26} and reactivation\textsuperscript{30} exists. Self-sorting on surfaces was explored with Co-SOSIP.\textsuperscript{26,27} To template self-sorting from the surface, the red colored initiator (S)-R\textsuperscript{1} was deposited together with another initiator, for example the yellow (S)-Y\textsuperscript{1} (Figure 1).\textsuperscript{27}

The two partners are deposited at different mole fractions, ranging from pure (S)-R\textsuperscript{1} to pure (S)-Y\textsuperscript{1} (Figure 1). On these templates, co-SOSIP was performed at the necessarily constant SOSIP concentrations of (S)-R and (S)-Y. Without templation, the composition of the resulting photosystem was equal that of the propagators in solution. With perfect templation of uniform self-sorting, the final composition would be equal that of the initiators on the surface.

To describe partial templation quantitatively, a nonempirical theory was developed.\textsuperscript{27} A transcription plot is produced to compare the composition of the 2D templates on the surface with the composition of the obtained 3D architecture. The slope of the transcription plot gives \( \eta_{\text{eff}} \), the effective templation efficiency. The intrinsic templation efficiency \( \eta_{\text{int}} \) can be obtained from the dependence of \( \eta_{\text{int}} \) on the thickness of the architecture. This value characterizes the templation efficiency per layer and is thickness independent. With the isosteric initiators (S)-R\textsuperscript{1} and (S)-Y\textsuperscript{1} as templates and (S)-R and (S)-Y as propagators, templated self-sorting was not observed. However, already minor structural changes caused the appearance of quite significant self-sorting. For instance, templated self-sorting of (S)-R\textsuperscript{1} (S)-R or (S)-Y\textsuperscript{1} (S)-Y against NDEs without substituents in the core occurred with intrinsic sorting efficiencies up to \( \eta_{\text{int}} = 97\% \). Appreciating the occurrence of templated self-sorting with partners of nearly identical structure, we wondered if the inversion of absolute configuration in one of the two differently colored isomers (S)-R and (S)-Y would be sufficient to turn on templated self-sorting. We report that uniform self-sorting of the isotropic pseudo-enantiomers (S)-R and (S)-Y, corresponding to homodimerization in solution and chiral resolution in conglomerates, did not occur. The complementary alternate self-sorting of (S)-R and (S)-Y, corresponding to heterodimerization in solution and racemic crystals in the solid,\textsuperscript{42} was not detectable on the structural level. Support for the transcription of chiral information was however obtained on the functional level, although any observable impact of alternate self-sorting of (S)-R and (S)-Y is necessarily weak.

MATERIALS AND METHODS

General. All chemicals were used as received from Fluka, Aldrich, Sigma or other commercial suppliers. Materials and methods were as described previously.\textsuperscript{27} UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer and are reported as maximal absorption wavelength \( \lambda \) in nm (extinction coefficient \( \varepsilon \) in mM\textsuperscript{-1}cm\textsuperscript{-1}). Circular dichroism (CD) spectra were obtained using JASCO J-815 spectropolarimeter and are reported as maximal absorption wavelength \( \lambda \) in nm (maximal \( \Delta \varepsilon \) in M\textsuperscript{-1}cm\textsuperscript{-1}).

Electrochemical measurements were performed on an Electrochemical Analyzer with Picocamp booster and Faraday cage (CH Instruments 660C). Photocurrents were recorded using a 150 W Xe lamp with Oriel 1/8 m monochromator and an Electrochemical Analyzer (CH Instruments 660C). The irradiation power was determined using a radiant power energy meter (Newport model 70260).

Synthesis. The synthesis of (S)-R\textsuperscript{1}, (S)-R, (S)-Y\textsuperscript{1} and (S)-Y has been reported. (R)-Y\textsuperscript{1} and (R)-Y were prepared following the procedures reported for (S)-Y\textsuperscript{1} and (S)-Y (Scheme 1).\textsuperscript{27} All spectroscopic and analytical data were analogous to the one reported for the stereoisomers. The CD spectra of (S)-Y and (R)-Y are shown in Figure 2.

![Scheme 1. Synthesis of (R)-Y\textsuperscript{1} and (R)-Y](image_url)

Initiation. ITO electrodes, cleaned as described (RCA solution), were immersed in solutions of (S)-R\textsuperscript{1} and (R)-Y\textsuperscript{1} in MeOH at constant total concentration (c.0.7 mM) and varied \( \lambda \). After 10 hours, full surface coverage was confirmed by cyclic voltammetry of potassium ferricyanide (2 mM) in 1 M KNO\textsubscript{3} with the ITO electrode as working, a Pt wire as counter and Ag/AgCl as reference electrode. After rinsing with MeOH and sonication for 30 min in MeOH, the electrodes were heated for 1 h at 120 °C. The electrodes were activated with DTT (20 mM in 10 mM aq NH\textsubscript{4}HCO\textsubscript{3}) for 1 h at rt, washed with water and MeOH and dried under N\textsubscript{2}. 

3
Propagation. Solutions of (S)-R and (R)-Y (35 mM each in CHCl₃/MeOH/1-octanol 10:1:1 with i-Pr₂NEt (100 mM) were deaerated with Ar. ITO electrodes with activated initiators at varied xₚS were immersed in these solutions at room temperature for the time needed to obtain thickness N. The product was sonicated in CHCl₃/MeOH 1:1 and dried under N₂. The absorbance of the electrodes was recorded to determine xₚR. The thickness N was calculated by dividing the absorbance at the absorption maximum by the corresponding absorbance of the monolayer template.

Photocurrent measurements. The photosystems on ITO were used as a working electrode, a Pt wire as counter electrode and Ag/AgCl as reference electrode in an aqueous TEOA (50 mM) and Na₂SO₄ (100 mM). Irradiation with monochromatic light was at the absorption maximum of R (538 nm) and Y (470 nm), and changes in current were measured at 0 V. The measured current density JₛC was converted into incident photon-to-current conversion efficiency (IPCE) with equation (1)

\[
\text{IPCE}_{\lambda} = \frac{1240}{\lambda} \times \frac{\lambda}{\text{J}_{\text{SC}}} / \frac{1}{P_{\text{in}}}
\]  

The obtained IPCE was normalized against the transmission T at the maximum of interest using equation (2)

\[
Y_{\text{AB}} = \frac{\text{IPCE}_{\lambda}}{(1 - T)}
\]  

The obtained activity Y₆ was further normalized against the activity Y₆ generated by the respective single component photosystem

\[
Y_{\text{A}} = \text{IPCE}_{\lambda} / (1 - T)
\]

To give the fractional activity Y

\[
Y = Y_{\text{AB}} / Y_{\text{A}}
\]

From these values, the differential fractional activity ΔY was obtained with equation (5)

\[
\Delta Y = Y [(S)-R-(R)-Y] - Y [(S)-R-(S)-Y]
\]

The unit in ΔY corresponds to the photocurrent generation of the respective single-component photosystem. The values for Y [(S)-R-(S)-Y] were taken from reference 27.

RESULTS AND DISCUSSION

Design

The influence of chirality on templated self-sorting during SOSIP was explored with the previously reported red (S)-R² and (S)-R together with the newly synthesized yellow (R)-Y¹ and (R)-Y. Previous studies have shown that the isosteric (S)-R and (S)-Y do not self-sort. Self-sorting with the pseudo-enantiomeric isosters (S)-R and (R)-Y could thus originate only from differences in chirality.

The absolute configuration of the remote cysteines in initiators (R)-Y¹ and (S)-Y¹ was kept constant for practical reasons. Initiators (R)-Y¹ and (S)-Y¹ are thus pseudo-diastereomeric isosters. The retained remote chiral center of the initiators was expected to have little influence on the stereoselectivity of the recognition of either (S)-R or (R)-Y by initiators (S)-R² or (R)-Y¹. Propagators (S)-R or (R)-Y are pseudo-enantiomeric isosters. Their recognition on the chiral surface, however, occurs naturally with partners that contain acyclic thiols rather than cyclic disulfides at both termini. However, these different termini were again expected to have little influence on the stereoselectivity of the recognition of the pseudo-enantiomeric cores at the chiral surface.

To understand the possible outcomes with enantioselective self-sorting during co-SOSIP, we considered the following. The composition of mixed monolayer templates composed of (S)-R² and (R)-Y¹ is freely variable from purely yellow templates at mole fraction xₚR = 0.0 to purely red templates at xₚR = 1.0 (Figure 1). In clear contrast, the composition of (S)-R and (R)-Y is invariable at xₚY = 0.50, because the concentration of the two propagators required for SOSIP is identical and unchangeable. With red templates only at xₚR = 1.0, co-SOSIP without templated self-sorting would give the photosystem PS¹RR with xₚPS = 0.50 and a random distribution of the red and yellow propagators (Figure 1B). With perfect templation of uniform self-sorting, the red surface would attract red propagators only and produce an all-red homochiral photosystem PS¹RR with xₚPS = 1.00. Templation of uniform self-sorting would correspond to homodimers in solution and conglomerates in the solid (see Introduction). The alternative templation of alternate self-sorting corresponding to heterodimers in solution and pseudo-racemic crystals in the solid would give the pseudo-racemic photosystem PS¹RA. Although xₚPS = 0.50 in PS¹RA would be as with PS¹RR, the distribution of the red and yellow propagators wouldn’t be random but arranged in alternate layers. Whereas uniform PS¹RR with xₚPS = 1.00 would be easily detectably by absorption spectroscopy, alternate PS¹RA and random PS¹OR would afford the same xₚPS = 0.50 as long as co-SOSIP is fixed at xₚY = 0.50, and their differences in structure would pass unnoticed.

Alternate self-sorting remains intrinsically indistinguishable from random at all possible compositions of the template. The difficulties to detect templated self-sorting in the absorption spectra of the final photosystems are maximal at xₚR = 0.50, with
identical amounts of red and yellow templates on the surface. In this case, $\text{PS}^{5,5R}$, $\text{PS}^{5,5A}$ and $\text{PS}^{5,2U}$ would all give $x^R_T = 0.50$ despite their completely different architectures. However, we have found previously that differences that pass undetected on the structural level can be detectable on the functional level without problems.\textsuperscript{26} In the following, we will show that this is also the case, at least partially, with enantioselective self-sorting on surfaces.

**Structural Studies**

The synthesis of initiators $(S)$-$\text{R}^1$ and $(S)$-$\text{Y}^1$ and propagators $(S)$-$\text{R}$ and $(S)$-$\text{Y}$ has been reported previously.\textsuperscript{27} Initiator $(R)$-$\text{Y}^1$ and propagators $(R)$-$\text{Y}$ were prepared as reported for $(S)$-$\text{Y}^1$ and $(S)$-$\text{Y}$ (Scheme 1). The CD spectra of $(S)$-$\text{Y}$ and $(R)$-$\text{Y}$ were mirror images, confirming that the two propagators are enantiomers (Figure 2A).

Stereoselective self-sorting during co-SOSIP was explored experimentally following the previously reported procedures.\textsuperscript{27} To produce mixed monolayers, ITO electrodes were dipped into solutions of initiators $(S)$-$\text{R}^1$ and $(R)$-$\text{Y}^1$ at the variable mole fraction $x^R_T = c^R / (c^R + c^Y)$ at a constant total concentration of 0.7 mM in methanol (Figure 1i). After annealing and deprotection of the thiols with DTT, the composition $x^R_T$ of the obtained monolayer template on the surface was assumed to be identical with $x^R_T$ (Figure 1ii). On this template, co-SOSIP with $(S)$-$\text{R}$ and $(R)$-$\text{Y}$ has to occur at constant $x^R_T$. This value is given by their respective $c_{\text{SOSIP}}$, that is the concentration where SOSIP occurs without competing polymerization in solution. Below $c_{\text{SOSIP}}$, polymerization does not occur, above $c_{\text{SOSIP}}$, polymerization occurs everywhere. For the pseudo-enantiomeric isosters, $(S)$-$\text{R}$ and $(R)$-$\text{Y}$ was roughly identical at $c_{\text{SOSIP}} = 35$ mM in CHCl$_3$/MeOH/1-octanol 10:1:1, with 100 mM $\text{Pr}_3\text{NET}$ to activate the thiols on the surface. This results in an invariable $x^R_T = 0.50$. Mixtures of $(S)$-$\text{R}$ and $(R)$-$\text{Y}$ appeared to be less soluble than mixtures of $(S)$-$\text{R}$ and $(S)$-$\text{Y}$. Although kept as qualitative observation only, this difference could support a preference for heterodimerization and pseudo-racemic crystallization of pseudo-enantiomeric isosters $(S)$-$\text{R}$ and $(R)$-$\text{Y}$.

The composition of the obtained photosystems was determined from their absorption spectra (Figure 3). To correct for eventual changes of extinction coefficients in SOSIP surface architectures, selected photosystems were redissolved with excess mercaptoethanol. The changes found were negligible. The identified compositions $x^R_{\text{PS}}$ were plotted as a function of the compositions $x^R_T$ of the template (Figure 4). In the transcription plots for $(S)$-$\text{R}$ and $(R)$-$\text{Y}$, $x^R_{\text{PS}}$ was nearly independent of $x^R_T$. The very minor increase of $x^R_{\text{PS}}$ with increasing $x^R_T$ was independent of the number $N$ of layers of the photosystem and therefore unrelated to the templation of uniform self-sorting. As discussed in the introduction, the occurrence of uniform self-sorting would be detectable by a significant excess of $\text{R}$ in $\text{PS}^{14R}$ at $x^R_T = 1.0$ or significant excess of $\text{Y}$ in $\text{PS}^{14Y}$ at $x^Y_T = 0.0$, that is high effective templation efficiency $\eta_{\text{eff}}$ (Figure 1B). The obtained independence of $x^R_{\text{PS}}$ on $x^R_T$ demonstrated that uniform self-sorting of $(S)$-$\text{R}$ and $(R)$-$\text{Y}$ into pseudo-homochiral architectures $\text{PS}^{Y}$ does not occur. This result was consistent with preferential heterodimerization of related enantiomers in solution and in single crystals.\textsuperscript{6} However, spectroscopic studies fail to distinguish the more likely alternate self-sorting in $\text{PS}^{Y}$ from disorganization in $\text{PS}^{R}$. At the invariable $x^R_T = 0.5$, $x^R_{\text{PS}} = x^R_T$ holds for all possible $x^Y_T$. To differentiate between systems with identical composition but possibly different structure, e.g., the random $\text{PS}^{1,6R}$ against the layered $\text{PS}^{1,6A}$ or the random $\text{PS}^{0,5R}$ against the chessboard $\text{PS}^{0,5A}$ (Figure 1), functional studies were considered next.

**Functional Studies**

Photocurrent generation by the photosystems composed of $(S)$-$\text{R}$ and $(R)$-$\text{Y}$ were measured under the conditions used to characterize the photosystems composed of $(S)$-$\text{R}$ and $(S)$-$\text{Y}$. Namely, the photosystems were used as anodes, a Pt electrode
as cathode, Ag/AgCl as reference electrode and 50 mM triethanolamine (TEOA) as sacrificial carrier in 100 mM aqueous Na₂SO₄. The photosystems were irradiated with monochromatic light at the respective absorption maxima at 538 nm for R and 470 nm for Y. The measured photocurrents were normalized into fractional activities Y following reported procedures described in the experimental part. The reported activities Y for the pseudo-homochiral photosystems (S)-R/(S)-Y were subtracted from the obtained Y for pseudo-racemic photosystems (S)-R/(R)-Y, and the resulting differences ΔY were plotted as a function of xₚₜ.

The resulting functional transcription plots showed differences between pseudo-homochiral photosystems (S)-R/(S)-Y and pseudo-racemic photosystems (S)-R/(R)-Y (Figure 5A). The differences were in the range of ΔY ± 1, that is around the total activity of the respective single-component photosystems composed of R or Y only. Whereas the significance of individual data points could arguably be questioned, the observed global trend was significant and obviously reproducible. Namely, compared to pseudo-homochiral photosystems (S)-R/(S)-Y, the activity of pseudo-racemic photosystems (S)-R/(R)-Y was high near the central xₚₜ = 0.5 and low near the extremes xₚₜ = 0.0 and xₚₜ = 1.0 (Figure 5A). These differences implied that the structures of pseudo-homochiral photosystems (S)-R/(S)-Y and pseudo-racemic photosystems (S)-R/(R)-Y are indeed different. Previous results have suggested that the homochiral photosystems (S)-R/(S)-Y are not self-sorted.²⁷ With uniform self-sorting into PS₀⁴ safely excluded from negligible nₑₑ in spectroscopic studies, partial alternate self-sorting of pseudo-racemic photosystems (S)-R/(R)-Y into structures similar to PS₀³ was the only conceivable explanation of the observed changes in activity. Decreasing activity at xₚₜ = 1.0 thus implied partial alternate self-sorting into the layered photosystem PS₀³⁴ (Figure 1B). Reduced activity of this architecture would be compatible with reduced charge mobility perpendicular to the layers. The same explanation was applicable to rationalize the reduced activity of layered pseudo-racemic photosystems (S)-R/(R)-Y similar to PS₀³⁴ (Figures 1B and 5A). Increasing relative activity of pseudo-racemic photosystems (S)-R/(R)-Y near xₚₜ = 0.5 implied the existence of chessboard architectures similar to PS₀³⁴ (Figures 1C). Moreover, the observed trends suggested that charge mobility in chessboard PS₀³⁴ is better than in the layered PS₀³⁴ and PS₁⁴⁸, particularly in the yellow channel (Figure 5A, empty bars). This interpretation was again in agreement with theoretical expectations.

The consistent trends found for the differences in activity between pseudo-homochiral photosystems (S)-R/(S)-Y and pseudo-racemic photosystems (S)-R/(R)-Y were small yet quite remarkable considering the similarity of the involved isosters. Both isosters are capable of disproportionating photoinduced charge separation and ambipolar charge transport.²⁶-³¹ Considering their HOMO and LUMO energy levels, electron (e⁻) transfer from R to Y and hole (h⁺) transfer from Y to R appears favorable (Figure 5B). Y should preferably transport electrons (n) and R transport holes (p), but their preference shouldn’t be very pronounced. Electrons could thus be trapped in a yellow layer of PS₀³⁴, but the barrier to move across the red barrier would not be very high (Figure 1B). The same holds for hole trapping in red layers of PS₁⁴⁸. Detectable differences thus suggest that the structures of quasi-homochiral and quasi-racemic photosystems of identical composition differ significantly, i.e., support the occurrence of significant alternate self-sorting into quasi-racemic photosystems (S)-R/(R)-Y with more active chessboard architectures around xₚₜ = 0.5 and less active layered architectures around xₚₜ = 0.0 and xₚₜ = 1.0.

**Fig. 5.** (A) Changes in activity ΔY comparing photocurrents generated by pseudo-racemic photosystems (S)-R/(R)-Y compared to pseudo-homochiral photosystems (S)-R/(S)-Y as a function of the mole fraction xₚₜ of (S)-R/(R)-Y² and (S)-R/(S)-Y²³ templates, respectively. Normalized ICPEs are compared at the maximal absorption of Y (470 nm, empty bars) and R (538 nm, filled bars). (B) HOMO and LUMO energies of Y and R with possible electron- and hole transfer to ITO and TEOA (compared to -5.1 eV for the Fc/Fc⁺ couple).

In summary, functional evidence is reported to support the occurrence of pseudo-enantioselective transcription of 2D information into 3D architectures. Transcription plots from spectroscopic studies show that the composition xₚₜ of the 3D architectures is independent on the composition xₚₜ of the 2D template. This independence shows that pseudo-enantiomeric isosters do not self-sort in a uniform manner, a process that corresponds to homodimerization in solution and chiral resolution in single crystals. Functional studies provide transcription plots with bell-shaped differences in activity between pseudo-homochiral and pseudo-racemic photosystems. This trend is consistent with alternate enantioselective self-sorting on surfaces. The likely occurrence of significant alternate self-sorting of pseudo-enantiomeric isosters on surface templates is consistent with the previously reported “narcissistic” heterodimerization of enantiomeric NDIs in solution and the
formation of racemic crystals in the solid. The differences in activity found for alternate self-sorting of pseudo-enantiomeric isosters were naturally small. To observe homodimerization in solution and chiral resolution in the solid will be essential. This will be difficult, the literature on racemic or pseudo-racemic components should be avoided, and c) homochiral components are best.

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LITERATURE CITED


