Lateral Self-Sorting on Surfaces: A Practical Approach to Double-Channel Photosystems

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S *Supporting Information*

ABSTRACT: We report that self-sorting during self-organizing surface-initiated copolymerization (co-SOSIP) provides facile access to oriented multicomponent architectures. Alternate lateral and uniform axial self-sorting into formal supramolecular n/p-heterojunction photosystems is found to generate up to 40 times more photocurrent. More or less topological matching gives rise to alternate axial self-sorting into inactive charge-transfer complexes or uniform lateral sorting into the less active macrodomains, respectively. Experimental support for self-repair during co-SOSIP is reported. Initiators on the surface are shown to serve as templates for the self-sorting into multichannel architectures of freely variable composition.

User-friendly access to oriented and ordered 3D architectures on surfaces will be essential to build the materials of the future, including organic optoelectronic devices such as solar cells.[1−3] Today, this is one of the key challenges in supramolecular chemistry. Available approaches such as layer-by-layer assembly give poor organization on the molecular level and little control over the lateral dimension.[2] Solution processing methods are intrinsically incompatible with directionality,[3,4] and surface-initiated polymerization seems to stop working as soon as the involved chemistry becomes more ambitious with regard to structure or function.[5]

Zipper assembly has been introduced to successfully build supramolecular n/p-heterojunctions with oriented double-channel gradients.[6] However, zipper assembly will never be of practical use because the synthetic organic chemistry involved is much too demanding. Recently we have introduced self-organizing surface-initiated polymerization (SOSIP) to do the impossible and provide user-friendly, low-cost, high-speed access to oriented and ordered multicomponent photosystems on solid surfaces.[7] However, to use SOSIP for the directional construction of multicomponent architectures, control over self-sorting will be needed. Here we report methods for lateral and axial, uniform and alternate self-sorting on surfaces (a process that is maybe best imagined as 3D Tetris on the molecular level with remote control). The introduced approach is shown to yield double-channel photosystems with more than 40 times increased activity.

In principle, the directional assembly of π-stacks of p- and n-type aromatics can occur either randomly or with uniform or alternate axial and lateral self-sorting.[4,8−10] Uniform or "narcissistic"[8a,d] axial self-sorting of π-stacks produces electron (e⁻ or n) and hole (h⁺ or p)-transporting pathways on the molecular level

(Figure 1D).[1,3] Their usefulness will be determined by lateral self-sorting. Uniform lateral self-sorting will produce photosystems **A** (ps**A**) with large domains that have interfaces that are too small to work together and give high activity (Figure 1A). This situation can correspond to phase segregation. Alternate lateral self-sorting at preserved uniform axial self-sorting will afford the coaxial n- and p-channels of supramolecular n/p-heterojunction (SHJ) ps**B** (Figure 1B). With maximal photoinduced charge separation at a molecular-level n/p-contact area and high charge mobility in the coaxial n- and p-channels, SHJs have been proposed to combine the advantages of current organic solar cells while bypassing their shortcomings.[1,3]

Alternate axial self-sorting, also referred to as social self-sorting,[8a,e] is supported by aromatic donor−acceptor interactions (or "charge-transfer complexes", Figure 1C,E).[3,4,9] This process is undesirable. It leads to ps**C** that is inactive because charge translocation along alternate donor−acceptor stacks is very poor.

To elaborate on self-sorting by co-SOSIP, we synthesized initiators and propagators **1**−**11** (Figure 1). Detailed procedures and analytical and spectroscopic data can be found in the Supporting Information.[11] They are all composed of functionalizing, self-organizing, and polymerizing subunits.[7] In the functional subunits, naphthalenediimides (NDIs)[12] of different colors and redox levels are envisioned to self-organize into n- and p-transporting π-stacks. Ordered π-stacking is supported by hydrogen-bonded networks and variable alkyl tails in the self-organizing subunits of propagators **1**−**9**.[4,9] Initiators **10** and **11** are equipped with two diphosphonate feet for a well-defined deposition on indium tin oxide (ITO) and activated with (S,S)-dithiothreitol (DTT). Molecular recognition of propagators **1**−**9** by activated initiators on the surface is thought to prepare for base-catalyzed ring-opening disulfide exchange[10] polymerization. The growth of oriented ladderphane[13] brushes by SOSIP has been characterized in detail on both structural and functional levels.[7]

Activities were determined from the photocurrent generation in a wet setup analogue to dye-sensitized solar cells, using SOSIP photosystems as anodes, a Pt electrode as cathode, and triethanolamine (TEOA) as mobile hole acceptor in 100 mM aqueous Na_2SO_4.[7] The incident photon-to-current efficiency (IPCE) at 470 nm in the obtained action spectra was normalized against the transmission at 470 nm, the absorption maximum of the most relevant yellow NDIs **1**−**6** (Figure S3). For purely yellow ps**D** grown from initiator **10** and propagators **1**−**6**, the normalized activity at 470 nm was independent of the length of the alkyl tail in the self-organizing subunits (Figure 2, ×). This value was
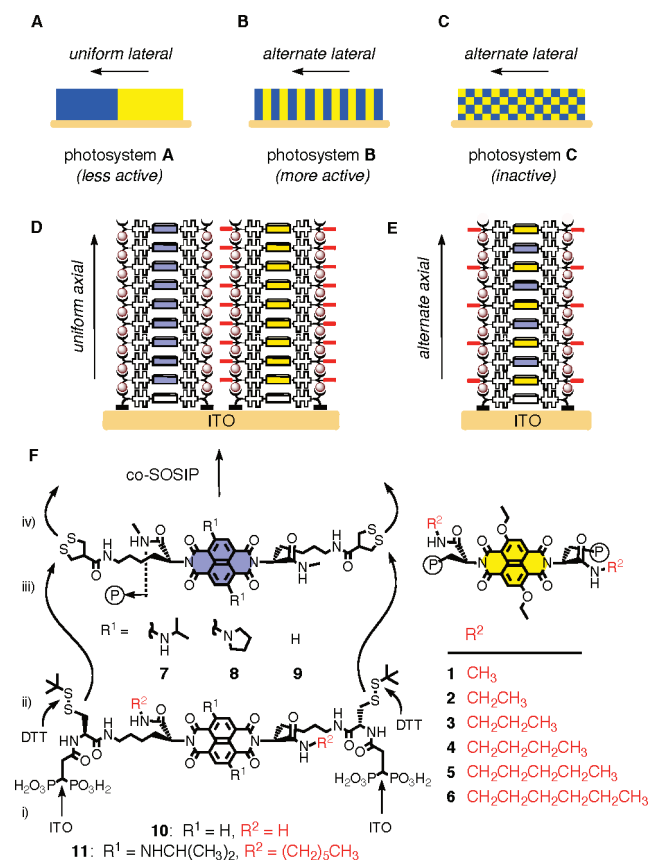
Figure 1. Lateral (A−C) and axial (D,E) self-sorting into less active macrodomains **A** (A), more active SHJs **B** (B), and inactive "charge-transfer complexes" **C** (C) by co-SOSIP of yellow propagators **1**−**6** with various partners (**7**−**9**) on initiators **10** or **11** (F). SOSIP is accomplished by (i) initiator deposition on ITO, (ii) activation with DTT, and (iii) ring-opening disulfide exchange with recognized propagators for (iv) continuing polymerization.
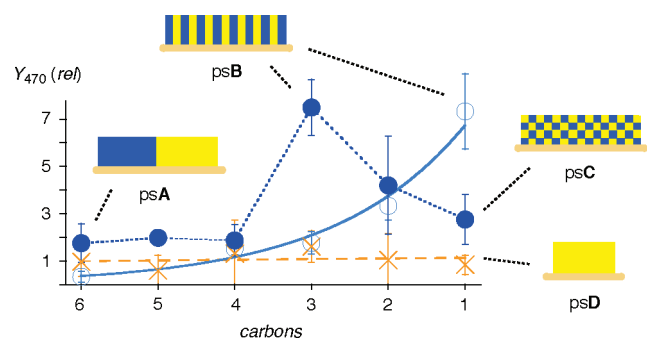

Figure 2. Activity Y_{470} as a function of the number of carbons in the alkyl tail of yellow propagators **1**−**6** after SOSIP alone (×) or together with blue propagators **7** (○) and **8** (●) on initiator **10** at their c_{SOSIP}. $Y_{470} = \{IPCE_{470}/(1 − T_{470})\}/\{IPCE_{470}/(1 − T_{470})\}_0$, i.e., the incident photon-to-current conversion efficiency IPCE normalized against the transmittance T at 470 nm and a reference value (0), here the average value obtained for single-component SOSIP with **1**−**6** (×).

taken as reference activity $Y_{470} = 1$ for further studies on self-sorting with co-SOSIP.

Photosystems made exclusively with propagator **7** were essentially inactive, not only at 470 nm but also at the absorption
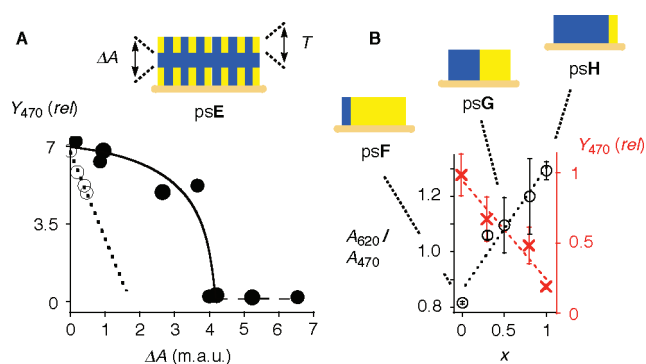

Figure 3. (A) Activity Y_{470} as a function of the absorption ΔA of a blue layer from SOSIP with **7** only inserted after co-SOSIP with **1** and **7** at 25 °C and before co-SOSIP with **1** and **7** at 25 (●) and 40 °C (○). (B) Fractional absorption and activity Y as a function of the mole fraction $x = [\textbf{11}]/([\textbf{11}] + [\textbf{10}])$ deposited on ITO before co-SOSIP with **1** and **7** at their c_{SOSIP}.

maximum of blue NDIs, 620 nm. However, co-SOSIP of the yellow propagator **1** in the presence of the inactive blue propagator **7** caused a more than 7-fold increase in activity (Figure 2, ○). Co-SOSIP of the yellow propagator **6** together with **7** caused a complementary decrease in activity (Figure 2, ○). These trends suggested that increasing structural similarity induces the contraction of less active macrodomains in ps**A** toward more active SHJ-type ps**B**. The macrodomains in ps**A** were directly visible under microscope (Figure S4).

The highest activity indicative for SHJ-like ps**B** was found for co-SOSIP of propagators **1** and **7** with identical self-organizing subunits. This implied that the structural differences between blue and yellow NDIs alone were sufficient to avoid alternate axial self-sorting into inactive ps**C**. To increase the similarity between the two partners, blue propagator **8** without hydrogen-bond donors in the NDI core was synthesized.[12] Co-SOSIP of **8** with yellow propagators **1**−**6** gave maximal activity with yellow propagators **3** with intermediate propyl chains, whereas activities with highly similar and highly different self-organizing subunits were low (Figure 2, ●). This suggested that at least partial alternate axial self-sorting into "charge-transfer complex" ps**C** occurs with blue and yellow NDIs **8** and **1**. This unfavorable sorting could be suppressed by the addition of either hydrogen-bond donors as in **7** (with **1**, Figure 2, ○) or increasingly different hydrophobic subunits as in **3** (with **8**, Figure 2, ●) to give uniform axial and alternate lateral self-sorting into ps**B** for highest activity. Incomplete inactivation of yellow propagators with longer tails **4**−**6** by the blue partner **8** suggested that increasing similarity in the NDI core hinders complete transition toward uniform lateral self-sorting into ps**A**.

To probe for eventual self-repair, co-SOSIP with propagators **1** and **7** was briefly interrupted by dipping into solutions with the blue inhibitor **7** only and then restarted at either 25 or 40 °C (Figure 3A). The thickness of the blue barrier placed on top of the alternate lateral ps**B** was measured by the additional blue absorption ΔA in ps**E**. Post-barrier co-SOSIP experiments at 40 °C resulted in a roughly linear decrease in activity with increasing barrier thickness (Figure 3A, ○), whereas post-barrier co-SOSIP at 25 °C was clearly nonlinear (Figure 3A, ●). In the absence of thiol nucleophiles and base catalysts, co-SOSIP architectures are stable, also at 40 °C.
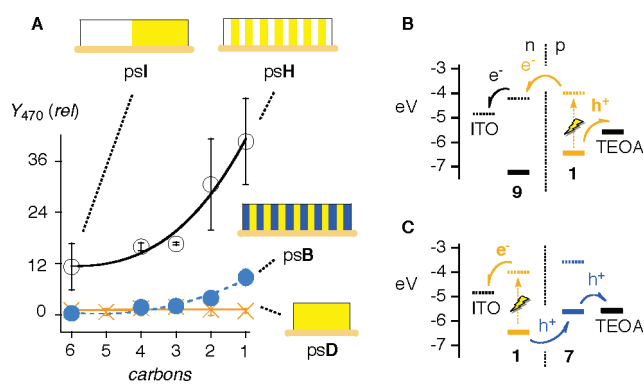
Figure 4. (A) Activity Y_{470} as a function of the number of carbons in the alkyl tail of yellow propagators **1**−**6** after SOSIP alone ($\times$) or together with propagators **7** ($\bullet$) and **9** ($\bigcirc$) at their c_{SOSIP}. (B) Energy diagram for photocurrent generation with **1** and **9** ($\bigcirc$). (C) Same for **1** and **7** ($\bullet$), with HOMO (—) and LUMO (---) energy levels given in eV against vacuum.

The nonlinear response to barriers could indicate that the blue barrier is removed by self-repair during post-barrier co-SOSIP at 25 °C. The transition to linear response for post-barrier co-SOSIP under at least partial thermal denaturation at 40 °C could demonstrate that molecular recognition and self-organization are needed for self-repair to occur. Identical trends have been observed with error correction for gene repair.[14] Moreover, lessons from protein folding as well as surface reactivation experiments with SOSIP[7] demonstrate that the reversibility[10] of disulfide exchange polymerization is compatible with self-repair. However, it will be difficult to fully confirm the validity of this interpretation. Possibly, the blue stacks simply go on growing selectively in the absence of yellow propagators and collapse into the void over the terminated yellow stacks only once they are long enough.

During self-sorting by co-SOSIP, the propagator concentrations have to be kept constant at the critical SOSIP concentration, c_{SOSIP}. Below c_{SOSIP}, polymerization does not occur; above c_{SOSIP}, polymerization occurs also in solution (Figures S1 and S2).[7] To vary the composition of self-sorted SOSIP architectures in a controlled manner, surface templation was explored. Namely, the blue initiator **11** and the original initiator **10** were deposited on the surface at various mole fractions x (Figure S5). Their different alkyl tails were selected to hopefully template for uniform lateral self-sorting into the straightforward, non-cooperative macro-domain photosystems ps**F**−**H**. The absorption of blue NDI in ps**F**−**H** obtained by co-SOSIP with blue and yellow propagators **7** and **1** at their respective c_{SOSIP} increased with increasing mole fractions of blue initiators **11** (Figure 3B, $\bigcirc$). The activity of photosystems correspondingly decreased with the increase of the inactive blue macrodomains (Figure 3B, $\times$). Clearly, blue initiators **11** templated SOSIP of blue propagators **7**, whereas the original initiators **10** templated SOSIP of yellow propagators **1**. These results confirmed the fundamental importance of initiators for SOSIP and identified surface templation as an attractive method to grow multicomponent architectures on solid surfaces.

In SHJ photosystem **B**, yellow NDI stacks act as n-channels, and blue NDI stacks act as p-channels (Figure 4C). Propagator **9** was prepared to explore SHJ photosystem **H**, where yellow NDI stacks act as p-channels next to n-transporting stacks formed by colorless NDIs without substituents in the core (Figure 4B). Co-SOSIP of the new propagator **9** with the yellow probes **1**−**6**

gave exponentially increasing activity with decreasing structural differences (Figure 4A, $\bigcirc$). This trend was exactly the same as with the blue propagator **7**, indicating that the transition from uniform toward alternate lateral self-sorting into SHJ photosystems with increasing structural similarity can be generalized (Figure 4A, $\bullet$). SHJ photosystem **H** was 40 times more active than single-component ps**D** (Figure 4A, $\bigcirc$ vs $\times$). Moreover, ps**H** was clearly more active than ps**B**, suggesting that yellow NDIs transport holes better than electrons (Figure 4A, $\bullet$ vs $\bigcirc$, and Figure 4B,C).

In summary, these results identify self-sorting during co-SOSIP as a promising, surprisingly reliable, and general strategy to build complex surface architectures with very little effort in a rational manner. Current studies focus on multichannel systems with multicomponent gradients of the highest possible sophistication and the application to n- and p-stacks of confirmed relevance in practice.

■ ASSOCIATED CONTENT

ⓢ **Supporting Information.** Details on experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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