

# Self-Organizing Surface-Initiated Polymerization: Facile Access to Complex Functional Systems

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## Supporting Information

**ABSTRACT:** Facile access to complex systems is crucial to generate the functional materials of the future. Herein, we report self-organizing surface-initiated polymerization (SOSIP) as a user-friendly method to create ordered as well as oriented functional systems on transparent oxide surfaces. In SOSIP, self-organization of monomers and ring-opening disulfide exchange polymerization are combined to ensure the controlled growth of the polymer from the surface. This approach provides rapid access to thick films with smooth, reactivatable surfaces and long-range order with few defects and high precision, including panchromatic photosystems with oriented four-component redox gradients. The activity of SOSIP architectures is clearly better than that of disordered controls.

The construction of supramolecular functional multicompo-I nent architectures on solid surfaces that are both oriented and ordered is a key challenge in current materials sciences and beyond.<sup>1-19</sup> Essential processes and motifs such as lateral self-sorting and oriented antiparallel gradients are intrinsically inaccessible by solution processing and related current methods.<sup>19</sup> We have recently introduced zipper assembly of double-gradient supramolecular n/p-heterojunction (SHJ) photosystems as a powerful yet less practical solution.<sup>17</sup> "Polymer brushes" have been around for a while as promising high-speed, low-cost alternatives.<sup>14–16</sup> However, they seem to stop growing well as soon as more interesting chemistry concerning organization or function is addressed. Implementing lessons from nature, we here report self-organizing surface-initiated polymerization (SOSIP) as a general method to create ordered and oriented functional systems on transparent oxide surfaces.

We thought that reversible surface-initiated polymerization of functional monomers equipped with functional subunits embedded within self-organizing subunits would afford highly ordered and oriented architectures. To test the hypothesis, initiator 1 and propagators 2–6 were designed and synthesized (Figure 1A, also see Supporting Information). As functional subunits, naphthalenediimides (NDIs) were selected. Their  $\pi$ -stacks can be used to transport electrons efficiently, and their color and redox properties can be changed without global structural changes.<sup>20</sup> As self-organizing subunits in 1 and 2, lysine-derived diamides were envisioned to organize SOSIP architectures with networks of hydrogen bonds<sup>17–19,21,22</sup> around the equally organizing NDI  $\pi$ -stacks.<sup>22–24</sup>

For ring-opening surface-initiated polymerization, several candidates were screened. Reversible disulfide exchange turned out to be best. This reaction is well known from protein folding and has been used to tackle other challenges in chemistry and biology, such as lipid bilayer polymerization, dynamic molecular recognition, and mechanical bonding.<sup>23–29</sup> More classical methods such as ATRP<sup>14</sup> and ROMP.<sup>15</sup> as well as bio-inspired alternatives such as ring-opening thioester<sup>30</sup> or hydrazone exchange,<sup>31</sup> were more problematic in our hands. To realize SOSIP with ringopening disulfide-exchange polymerization, protected cysteine and asparagusic acid, a strained cyclic disulfide,<sup>27,28</sup> were added next to the self-organizing subunits in initiator 1 and propagators such as 2. To bind to indium tin oxide (ITO) surfaces in a welldefined orientation, initiator 1 was equipped with two diphosphonate "feet".<sup>32</sup> From here, SOSIP was designed to occur as follows: Reduction of the disulfides in 7 with (S,S)-dithiothreitol (DTT) liberates reactive thiolates on the surface of 8. Recognition of propagators such as 2 on the surface of 8 by the topologically matching self-organizing and functional subunits is expected<sup>21-24</sup> to position the terminal disulfides of **2** on top of two thiolates on the surface of 8. This self-organization was thus conceived to facilitate intramolecular ring-opening disulfide exchange at both termini of 2 to freeze the desired surface architecture in a covalent macrocycle.<sup>23</sup> At the same time, active thiolates are reproduced on the surface of intermediate 9 to react with the next propagator 2, to continue with reversible disulfide exchange to ultimately yield the desired ladderphane<sup>23,33</sup> polymer brush architecture 10.

Microcontact printing ( $\mu$ CP) was used to prove the occurrence of SOSIP.<sup>34</sup> An ITO surface was patterned with initiator 1 (Figure 2A), activated with DTT, and incubated with 2 and *i*Pr<sub>2</sub>NEt as a base catalyst under optimized conditions (see below). AFM images demonstrated that polymerization occurred exclusively on activated surfaces (Figure 2B).

SOSIP was strongly dependent on the nature and concentration of propagators 2-6 and the base catalyst (Figures S5 and S6). The dependence on propagator concentration was characterized by  $c_{\text{SOSIP}}$ , the critical propagator concentration needed to achieve significant SOSIP. Above  $c_{\text{SOSIP}}$ , SOSIP showed a steep nonlinear increase with propagator concentration (Figure S5). This behavior, characteristic for polymerizations, hampered quantitative reproducibility, whereas the qualitative reproducibility of SOSIP was perfect. The onset of competing polymerization in solution occurred at higher concentration,  $c_{\text{SOL}}$ . Whereas absolute

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**Figure 1.** Design and model of SOSIP architectures with structures of initiator 1 and propagators 2-6. (A) Synthesis of 10 by (i) deposition of initiator 1 on ITO, (ii) activation with DTT, self-organizing recognition of propagator 2 and ring-opening disulfide exchange (iii), for continuing SOSIP (iv). For full chemical structures, see Figure S2. Polymerization mechanisms and polymer structures are shown only to explain design strategies. They can be considered as mostly speculative but are consistent with all reported experimental data. (B) General Amber Force Field (GAFF) models of 10 (NDIs, yellow; H-bond donors, red; H-bond acceptors, blue; polymer backbone, silver).

values for  $c_{\text{SOSIP}}$  and  $c_{\text{SOL}}$  varied from case to case, a significant SOSIP window  $c_{\text{SOSIP}} < c < c_{\text{SOL}}$  was reproducibly found for all bis-asparagusyl propagators. Very weak polymerization found with mono-asparagusyl propagator **6** supported the importance of surface-bound and preorganized dithiolates to template the polymerization (Figure SSD).<sup>35</sup>

SOSIP with propagator 2, performed in the window between  $c_{\text{SOSIP}} = 7 \text{ mM}$  and  $c_{\text{SOL}} = 11 \text{ mM}$ , exhibited saturation behavior with  $t_{50} = 6 \text{ h}$  and a maximal NDI absorption of ~0.15 at 470 nm (Figure S4). This inactive surface could be reactivated with DTT to continue with polymerization  $\geq 23$  times (Figures S7–S9). The resulting  $A_{470} \geq 0.9$  corresponds to a thickness of ~250 nm or, in an ideal SOSIP architecture, a stack of ~750 NDIs. Successful reactivation of smooth, ordered surfaces (Figure 2C,E) with DTT supported the expected vertical growth of the polymer from the surface and confirmed reversibility of the polymerization. The latter should be important for self-organization-driven self-repair<sup>23-29,36</sup> to minimize cross-linking and produce low-defect ladderphane<sup>23,33</sup> polymer brushes.

The polymeric precipitate obtained at  $c > c_{SOL}$  was insoluble in all common solvents. Only small oligomers could be detected by MALDI-MS (Figure S19). Polymers could adsorb randomly on initiator-free ITO surfaces when precipitating during their



**Figure 2.** Comparing SOSIP architectures **10** with disorganized controls **10**' obtained by polymerization in solution. Both were made with propagator **2**. (A) AFM height image after  $\mu$ CP of **1** on ITO; the printed areas are not visible at the AFM detection limits. (B)  $\mu$ CP becomes visible by AFM after treatment with DTT and then propagator **2** (z = 0 (black)-100 nm (white)). (C) AFM height images of **10**. (D) Same for **10**' (z = 0 (black)-50 nm (white)). (E) AFM phase-contrast image of **10** (corresponding to panel C). (F) Zoom-in of panel E. (G) Transient absorption at 550 nm of **10** (green) and **10**' (blue) after excitation at 400 nm with a 100-fs laser pulse. (H) Transmittance-normalized photocurrent generated by **10** (—) and **10**' (---).

synthesis at  $c > c_{SOL}$  in solution. Comparison of the obtained architectures **10'** with SOSIP architectures **10** was ideal to characterize the latter, using propagator **2** in both cases (Figure 2). According to AFM images, the surface of SOSIP architectures **10** (Figure 2C, roughness  $R_a = 5.1$  nm) was clearly smoother than that of solution-polymerized **10'** (Figure 2D,  $R_a = 87$  nm) and not much rougher than the bare ITO surfaces used. Phase-contrast images of SOSIP architectures **10** revealed long-range order with very few defects (Figure 2E) and exceptionally high resolution (Figure 2F).

In ultrafast spectroscopy measurements, SOSIP architectures 10 and the disorganized control 10', both made with propagator 2, had identical properties except for the important background noise produced by the rough surface of 10' (Figures 2G, S12, and S18). This finding confirmed that both the long-range organization and the orientation with respect to the oxide surface account for the superior performance of SOSIP photosystem 10 compared to solution-polymerized 10', whereas their local structures are indistinguishable. Transient absorption spectra with SOSIP architectures (Figure S14) compared to those of photochemically generated  $\mathrm{NDI}^{-\bullet \ 18}$  and  $\mathrm{NDI}^{+\bullet}$  (Figure S15) demonstrated that the yellow NDIs in architectures 10 and 10' can function as both donors and acceptors to undergo symmetry-breaking photoinduced charge separation (PCS) (Figure S16).<sup>37</sup> Ultrafast nonradiative deactivation in fluorescence kinetics confirmed that PCS occurs with an average time constant of about 6 ps (Figure S12). The decay of the transient absorption of the charge-separated



Figure 3. Panchromatic photosystems with four-component redox gradients. (A) HOMO and LUMO energies of 1, 2, 4, and  $5^{20}$  with possible electron- and hole-transfer cascades. (B) SOSIP of 11 by deposition (i) and activation (ii) of 1 on ITO followed by incubation with propagators 2 (iii), 4 (iv), and 5 (v). (C) Transmission spectrum of 11. (D) Action spectra of multicolor photosystem 11 ( $\bullet$ ) compared to unicolor photosystem 10 ( $\bigcirc$ ) in transmittance-normalized IPCE (in %).

state was found to be biphasic, with lifetimes of 80 ps and >2 ns (Figures 2G and S18).

Photocurrent generation was determined with a wet setup analogue to dye-sensitized solar cells,<sup>38,39</sup> using SOSIP photosystems **10** as working electrode, a Pt wire counter electrode, a Ag/AgCl reference electrode, and TEOA as mobile electron carrier (Figure 2H, solid line).<sup>17–19</sup> Compared to disorganized photosystems **10'**, SOSIP photosytems produced about 5 times more photocurrent (Figure 2H, dashed line). Photocurrent generation by SOSIP **10** compared to control **10'** was also much faster, consistent with decreasing resistivity with increasing organization (Figure S10).

To build panchromatic SOSIP photosystems 11 with oriented four-component redox gradients, red and blue propagators 4 and 5 were designed and synthesized (Figure 3). Increasing bandgap with decreasing LUMO energies produces gradients for directional electron ( $e^-$ ) transport from blue toward red, yellow, and colorless NDIs (i.e.,  $5 \rightarrow 4 \rightarrow 2 \rightarrow 1$ ), whereas holes ( $h^+$ ) could move in the other direction (i.e.,  $1 \rightarrow 2 \rightarrow 4 \rightarrow 5$ , Figure 3A).

With SOSIP, the construction of multicomponent photosystems 11 was very straightforward. Deposition of initiator 1 was followed by activation with DTT and incubation with yellow, red, and blue propagators 2, 4, and 5 for 1 h each (Figure 3B). The absorption spectrum of the panchromatic photosystem 11 demonstrated that all chromophores are incorporated in roughly equal amounts (Figure 3C). The action spectrum of multicomponent SOSIP photosystem 11 compared to that of the uniform 10 revealed that already the presence of one redox gradient suffices to increase photocurrent generation by yellow NDIs significantly (Figure 3D,  $\bullet$  and  $\bigcirc$ ). Much poorer photocurrent generation by the red and particularly the blue NDIs in the same system indicated that these electron-rich stacks transport holes better than electrons.

Taken together, these results identify SOSIP as a user-friendly and attractive approach to oriented surface architecture with precise long-range organization. Now we are moving on to expand the approach with the introduction of more ambitious selforganizing units (i.e.,  $\mathbb{R}^3 \neq H$ , CH<sub>3</sub>, Figure 1) and  $\pi$ -stacks used in organic solar cells to ultimately build the oriented multicolored antiparallel redox gradient (OMARG) SHJ architectures<sup>19</sup> needed for long-distance PCS and high efficiencies.<sup>35,36</sup> Preliminary results confirm that double-channel SHJ architectures obtained by co-SOSIP and self-sorting of NDI propagators already suffice to obtain at least 40 times higher activity.<sup>40</sup>

# 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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