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Directional stack exchange along oriented oligothiophene stacks†

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Directional growth of π-basic oligothiophene stacks on solid substrates is achieved by self-organizing, surface-initiated disulfide exchange polymerization. Successful addition of co-axial π-acidic stacks by templated hydrazone exchange provides general access to multicomponent architectures of unique complexity.

Biological functional systems operate with supramolecular architectures of highest sophistication. One of the longstanding questions with organic functional materials concerns what we would get if similar standards of molecular precision and complexity could be applied.[1,2] Contributions from this group to tackle this challenge have focused on the development of strategies for directional growth of multicomponent architectures directly on solid surfaces.[3] This directionality is difficult to achieve otherwise but unavoidable for photosystems that operate, like their biological counterparts, with oriented redox gradients.[3,4]

The emerging method of interest is self-organizing surface-initiated polymerization (SOSIP).[3] This approach was conceived to provide facile access to oriented multicomponent architectures: experimental evidence for templated self-sorting, self-repair, surface reactivation and templated stack exchange (TSE) exists.[3] However, SOSIP beyond the most favorable π-acidic naphthalenediimide (NDI) stacks is nearly unexplored.[3] In the following, we demonstrate the compatibility of SOSIP-TSE with the less favorable π-basic oligothiophenes. Oligothiophenes are some of the most ubiquitous components of molecular electronics, photonics and optoelectronics, including organic photovoltaics and sensors.[1,2,5] However, no other method is available that would provide access to similarly sophisticated architectures,[4] that is, directional growth of oligothiophene stacks and directional, NDI-templated stack exchange along the obtained oligothiophene stacks.

SOSIP with oligothiophenes was envisioned with initiator **1** and propagator **2** (Fig. 1). Their central quaterthiophene is embedded in a peptide-like hydrogen-bonded network to account, together with π–π stacking, for the self-organization of the system. Initiator **1** contains additional NDIs to template for post-SOSIP stack exchange (templation has been shown to be essential for successful stack exchange).[3c] Four terminal diphosphonates are available to bind to the ITO surface, and protected thiolates to initiate the polymerization after deprotection.[3] Propagator **2** contains benzaldehyde hydrazones to template the site for stack exchange and strained disulfides for ring-opening disulfide exchange polymerization.[6]

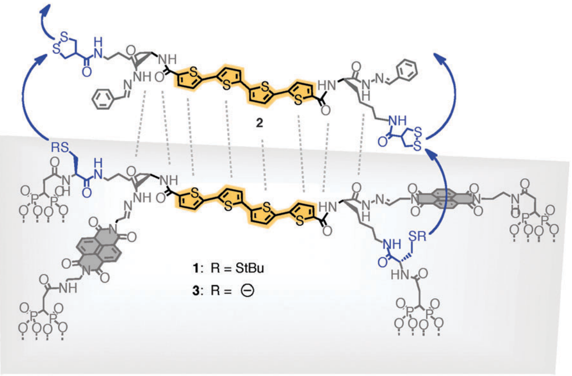

Fig. 1 Initiator **1** and propagator **2** for SOSIP-TSE with oligothiophenes on indium tin oxide (ITO). The grey background stands for an ITO surface, dashed grey lines from diphosphonates for covalent anchoring on this surface, dashed grey lines between **1** and **2** for self-organizing interactions, and blue arrows for polymerization after deprotection and deprotonation of the thiols on the surface.

The synthesis of initiator **1** and propagator **2** is outlined in Scheme 1, detailed procedures can be found in the ESI.† To prepare for SOSIP, ITO electrodes were dipped into a solution of **1** in DMSO (1 mM, 48 h). The coated surfaces were annealed for 1 h at 120 °C. Oligothiophene and NDI absorbance, surface coverage estimated from cyclic voltammetry and inhibition of ferricyanide reduction were consistent with the presence of a compact monolayer on ITO (Fig. S2 and S3, ESI†). To deprotect the thiols directly on the surface, the electrodes were incubated in aqueous DTT (20 mM, 1 h).

For successful SOSIP, careful optimization of solvent, base and, most importantly, propagator concentration is essential. Below c_{SOSIP}, SOSIP does not occur. Above c_{SOSIP}, polymerization occurs also without an initiator. For SOSIP on monolayer **3**, a solution of propagator **2** at c_{SOSIP} = 4–6 mM in chloroform–methanol 3 : 1 with 100 mM Hünig base was best (Fig. S4, ESI†). The growth of photosystem **4** on ITO was followed by absorption spectroscopy (Fig. 2, dashed; Fig. S4, ESI†). The thickness of the obtained films could be estimated from the absorbance of the oligothiophenes.

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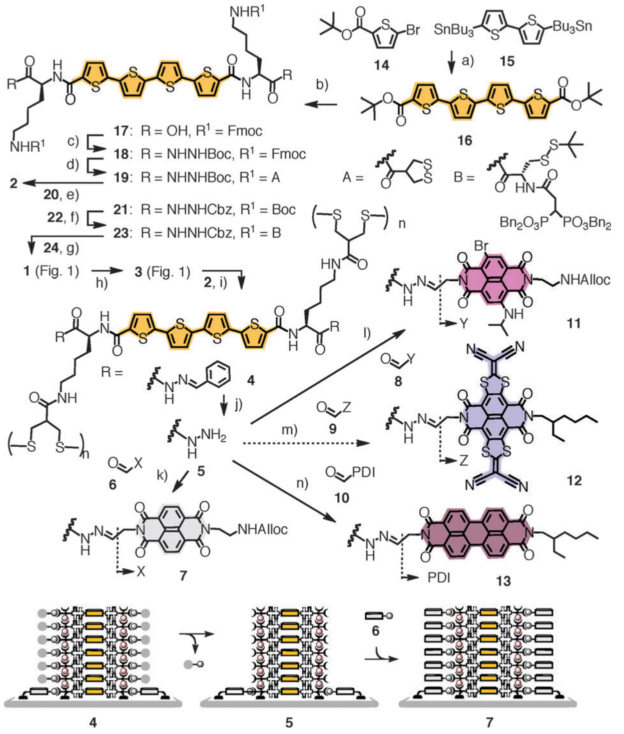

Scheme 1 Synthesis of initiator and propagator, SOSIP with oligothiophenes and TSE with NDIs and PDIs. (a) $Pd(PPh_3)_4$, DMF, 80 °C, 12 h, 70%; (b) 1. TFA, CH_2Cl_2, RT, 2 h; 2. HATU, TEA, DMF, RT, 5 min; 3. H-Lys(Fmoc)-OH, Na_2CO_3, dioxane–THF–H_2O, 55%; (c) NH_2NHBoc, HATU, TEA, DMF, RT, 2 h, 63%; (d) 1. piperidine, DMF, RT, 1 h; 2. **20**, TEA, DMF, RT, 30 min, 45% (2 steps); (e) TFA, thioanisole, benzaldehyde, RT, 90% (2 steps); (f) 1. TFA, CH_2Cl_2, RT, 1 h; 2. Boc-Cys(S-*t*-Bu)-OH, HOBt, EDCI, 2,4,6-collidine, DMF, 90 min, 55% (2 steps); 3. TFA, thioanisole, CH_2Cl_2, RT, 1 h; 4. **22**, EDCI, TEA, DMF–CH_2Cl_2, RT, 90 min, 62% (2 steps); (g) 1. TFA, TMSBr, thioanisole, CH_2Cl_2, 0 °C to RT, 24 h, 66%; 2. **24**, TFA, DMSO, RT, 24 h; 3. ITO, DMSO, RT, 48 h; (h); DTT, RT, 1 h; (i) **2**, *i*-$PrNEt_2$, $CHCl_3$–MeOH 3:1, RT, 24 h; (j) NH_2OH, MeOH–H_2O 1 : 1, 24 h; (k) **6**, TFA, DMSO, RT, 6–12 h, 87%; (l) same with **8**, 89%; (m) same with **9**, 30%; (n) the same with **10**, 87%. For structures of **20**, **22** and **24**, see ESI.†

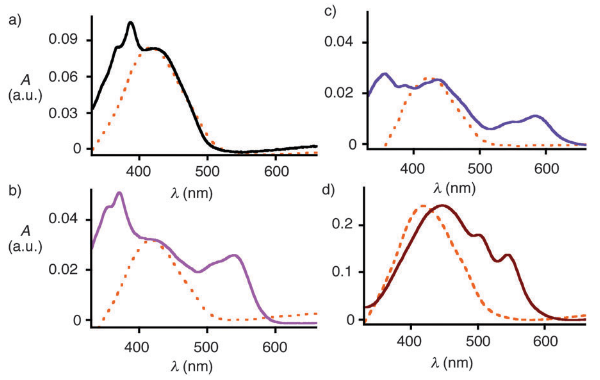

Fig. 2 Absorption spectra of SOSIP photosystems before (**4**, dashed) and after TSE for (a) **7**, (b) **11**, (c) **12** and (d) **13** (solid).

For stack exchange, the benzaldehydes in photosystem **4** were removed with 1.0 M hydroxylamine in H_2O–MeOH 1 : 1 (HPLC kinetics: Fig. S5, ESI†). The hydrazide-rich pores drilled into in photosystem **5** were filled immediately by dipping the electrode for 6 h into a solution of aldehyde **6** in DMSO. Nearly quantitative formation of NDI stacks in photosystem **7** was indicated by the intensity of their absorption below 400 nm, easily recognizable by the characteristic vibrational fine structure (Fig. 2a and Fig. S6, ESI†).[7]

The compatibility of oligothiophene architectures with post-SOSIP-TSE was explored with the core-substituted NDIs **8**, the core-expanded NDI **9** and the elongated perylenediimide (PDI)[8] homolog **10** (Scheme 1). The red NDI **8** with an amine and a bromine in the core showed highest activity in previous studies.[3] The core-expanded NDI **9** has appeared recently in the literature as exceptionally promising, air-stable n-semiconductor with broad absorption at low energy.[9] PDI **10**, finally, was of interest to probe for compatibility with elongated rather than broadened stacks. Of similar color, the frontier molecular orbitals (FMOs) of core-substituted NDI **8** and PDI **10** are above the original NDI **6**, whereas core-expanded NDI **9** is clearly below (Fig. 3a and Table S1, ESI†). The FMOs of all NDIs and PDIs are clearly below oligothiophenes, confirming that their stacks could serve as electron-transporting channels next to the hole-transporting quaterthiophene stacks.[4]

NDIs **6** and **8** were prepared as described,[3] the new, core-expanded NDI **9** and the longer PDI **10** were accessible in a few steps by adapting procedures from the literature (Scheme S3, ESI†).[8,9] Both had to be equipped with branched alkyl tails to increase their solubility (Scheme 1).

The absorption spectra of photosystems **11** and **12** suggested that the infiltration of the core-substituted aldehyde **8** into the porous, reactive photosystem **5** was nearly quantitative, whereas stack exchange with the core-expanded NDI **9** occurred with 30% yield only (Fig. 2b and c).[7] This failure originated presumably from the poor solubility of NDI **9**, providing access only to solutions that are too dilute for efficient stack exchange.

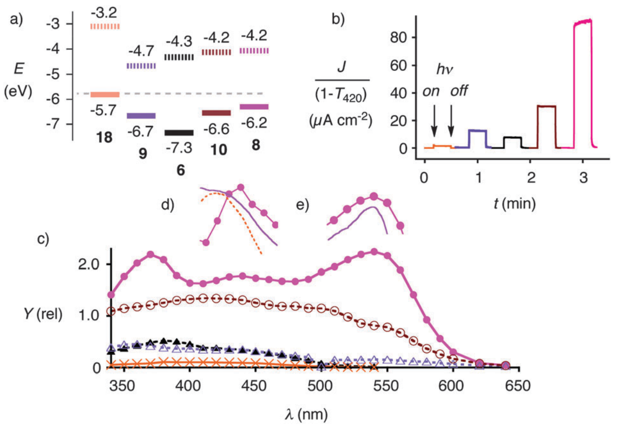

Fig. 3 (a) HOMO (bold) and LUMO (dashed) energy levels against vacuum of oligothiophenes (**18**), NDIs (**6**, **8**, **9**) and PDIs (**10**), from cyclic voltammetry with −5.1 eV for Fc/Fc^+, (Fig. S7, ESI†). (b) Photocurrent generated by photosystems **4**, **12**, **7**, **13** and **11** (left to right), irradiated with a solar simulator (66 mW cm^{-2}). (c) Action spectra of photosystems **4** (x), **12** (▲), **7** (△), **13** (○) and **11** (●), $Y = IPCE/(1 - T_{420})$, IPCE = incident photon-to-current efficiency, T_{420} = transmittance at 420 nm. (d) Comparison of oligothiophene maxima in action (●) and absorption spectra before (**4**, dashed) and after TSE (**11**, solid, Fig. 2b). (e) The same for NDI maxima.

In contrast, TSE with PDI **10** occurred in 90% yield (Fig. 2d). The obtained photosystem **13** showed the characteristic, strongly hypochromic absorptions of PDI stacks at 501 and 545 nm (monomer: 528 nm).[3d,8] The blue shift to 501 nm is characteristic of face-to-face *H*-aggregates, the red shift to 545 nm of rotational displacement between neighboring PDIs in the helical stacks.

The photocurrents generated by photosystems **4**, **7** and **11–13** were measured under routine assay conditions.[3] In brief, the photosystems were used as a working electrode together with a Pt counter electrode, a Ag/AgCl reference electrode and triethanolamine (TEOA) as a mobile carrier.[10] Irradiated with a solar simulator, the oligothiophene photosystem **4** generated comparably[3] little photocurrent (Fig. 3b).[11] The addition of co-axial channels for electron transport improved the situation slightly with photosystem **7** and dramatically with photosystem **11**. Stacks with the newly introduced, core-expanded NDI **9** in photosystem **12** generated clearly less photocurrent. Incomplete TSE rather than intrinsic properties of the chromophore is likely to account for this poor performance, although exceptional activity of the core-expanded NDIs should be observable also in this less than perfect photosystem. Compared to the 64-fold increase achieved with core-substituted NDIs in photosystem **11**, the 21-fold increase obtained with PDI stacks in photosystem **13** was mildly disappointing.

The action spectrum of the most active photosystem **11** demonstrated that both the yellow oligothiophene and the red NDI stacks generate photocurrent (Fig. 3c, ●). Oligothiophenes generated maximal photocurrent around 440 nm, which is slightly red-shifted compared to the absorption maximum of the photosystem **11** around 420 nm (Fig. 3d). With NDIs, absorption and photocurrent maxima coincided at 540 nm (Fig. 3e). The red-shifted maximum for oligothiophenes in the action spectrum of photosystem **11** could thus indicate the presence of highly active stacks with planarized oligothiophenes.[5] Other possible contributions to the high activity of photosystem **11** include absorption of light up to 600 nm, efficient charge separation in co-axial donor–acceptor stacks,[3,4] slow charge recombination (high LUMO of NDI, heavy-atom effects) as well as high charge mobility in the co-axial hole- and electron-transporting pathways.[3,4]

In summary, these results demonstrate that SOSIP-TSE is a general (and so far unique) method to build sophisticated surface architectures in a directional manner. Introducing oligothiophenes, SOSIP with the least favorable π-basic stacks is shown, for the first time, to occur as reliably as with the most favorable π-acidic stacks. Templated by NDIs on the surface, post-SOSIP stack exchange along the oligothiophene stacks is compatible with NDI and PDI stacks as long as the solubility of the building blocks is sufficient. Ultimately, SOSIP-TSE is expected to provide general access to multichannel architectures with multiple gradients of freely variable composition. Oligothiophenes are particularly attractive to build oriented p-channels with multicomponent gradients because their HOMO energies are extensively variable with terminal and lateral substituents as well as with thiophene analogues in their backbone (*e.g.*, benzothiadiazoles). Efforts to live up to these high expectations are ongoing and will be reported in due course.

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10 Carriers other than TEOA gave similar results, including MDESA.[3d]

11 Comparisons of results obtained under non-optimized test conditions without any special precautions should be done with caution and on a relative scale; quantitative comparisons with dedicated device engineering are not meaningful in this context. Without alternative synthetic methods to produce comparably sophisticated architectures, meaningful negative controls were not available either (increasing activities compared to random deposition have been confirmed).