Electronic Supplementary Material (ESI) for Chemical Communications

Directional Stack Exchange along Oriented Oligothiophene Stacks

Jetsuda Areephong, Edvinas Orentas, Naomi Sakai and Stefan Matile*

Department of Organic Chemistry, University of Geneva, Geneva, Switzerland

stefan.matile@unige.ch

Supporting Information

Table of Content

1. Material and Methods S2
2. Supporting Text S3
   2.1 Synthesis S3
      2.1.1 Synthesis of the Initiator S3
      2.1.2 Synthesis of the Propagator S7
      2.1.3 Synthesis of the Stack Exchangers S10
   2.2 Electrochemistry S12
   2.3 Self-Organizing Surface-Initiated Polymerization S12
   2.4 Stack Exchange S14
   2.5 Photocurrent Measurements S15
3. Supporting Schemes and Figures S16
4. Supporting Table S22
5. Supporting References S23

1. Materials and Methods

As in ref. S1, Supporting Information. Briefly, reagents for synthesis were purchased from Fluka and Acros, amino acid derivatives from Novabiochem and Bachem. Indium tin oxide (ITO) coated glass substrates were obtained from either Merck KGaA (Darmstadt, Germany) or Präzisions Glas & Optik GmbH (Iserlohn, Germany). Reactions were performed under N_2 or Ar atmosphere when specified. Unless stated otherwise, column chromatography was carried out on silica gel 60 (Fluka, 40-63 μm) and analytical (TLC) were performed on silica gel 60 (Fluka, 0.2 mm). $[\alpha]_D$ values were recorded at 20 °C on a Jasco P-1030 Polarimeter. Melting points (m.p.) were measured on a heating table from Reichert (Austria). UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 °C) and are reported as maximal absorption wavelength λ in nm (extinction coefficient ε in $mM^{-1}cm^{-1}$). Circular dichroism spectra were obtained using JASCO J-815 spectropolarimeter and are reported as extremum wavelength λ in nm ($\Delta\varepsilon$ in $M^{-1}cm^{-1}$). IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate, unless stated) and are reported as wavenumber υ in cm^{-1} with band intensities indicated as a s (strong), m (medium), w (weak). ^1H and ^{13}C spectra were recorded (as indicated) either on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and are reported as chemical shifts (δ) in ppm relative to TMS ($\delta = 0$). Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t), and quartet (q) with coupling constant (J) given in Hz, or multiplet (m). Broad peaks are marked as br. Proton signals with low deuterium exchange rates (half life ≥ 5 min) are marked "exchangeable". ^1H and ^{13}C resonances were assigned with the aid of additional information from 1D and 2D NMR spectra (H,H-COSY, DEPT 135, HSQC and HMBC). Multiplicity of ^{13}C signals are assigned with the aid of DEPT 135, and reported as s (*C*), d (*CH*), t (CH_2) and q (CH_3). ESI-MS were performed on an ESI API 150EX with 2 mM ammonium acetate in methanol as a solvent and are reported as m/z (%). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Sciex QSTAR Pulsar, MALDI-TOF on a Axima CFR+ (Shimadzu). 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 as measured using a radiant power energy meter (Newport model 70260).

Abbreviations. Boc = *t*-butoxycarbonyl, Cbz = benzyloxycarbonyl, CV = cyclic voltammetry, Cys = L-cysteine, DCM = dichloromethane, DCTB = 2-[(2*E*)-3-(4-*t*-butylphenyl)-2-methylprop-2-enylidene]malonitrile, DHB = 2,5-dihydroxybenzoic acid, DMF = *N*,*N*-dimethylformamide, DTT = DL-dithiothreitol, EDCI = *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide, Fc = Ferrocene, Fmoc = fluorenylmethyloxycarbonyl, HABA = 2-(4-hydroxyphenylazo)benzoic acid, HATU = 2-(1H-7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate methanaminium, HOBt = 1-hydroxybenzotriazole, *IPCE* = incident photon-to-current conversion efficiency, ITO = indium tin oxide, Lys = L-lysine, NDI = 1,4,5,8-naphthalenediimide, PDA = 3,4,9,10-perylenetetracarboxylicdianhydride, PDI = 3,4,9,10-perylenetetracarboxylicdiimide, RT = room temperature, SCE = saturated calomel electrode, SOSIP = self-organizing surface-initiated polymerization, TBTU = *O*-(benzotriazol-1-yl)-*N*,*N*,*N*',*N*"-tetramethyluronium tetrafluoroborate, TEA = triethylamine, TEOA = triethanolamine, TFA = trifluoroacetic acid, TMS = trimethylsilyl.

2. Supporting Text

2.1. Synthesis

2.1.1. Synthesis of the Initiator

The synthesis was performed as presented in Scheme S1 (see page S16).

Compound 25. This compound was prepared following the procedures in ref. S2.

Compound 26. To a solution of **25** (1.0 g, 4.8 mmol) in DMF (10 ml) were added TBTU (1.83 g, 4.8 mmol) and TEA (1.34 ml, 9.6 mmol). The mixture was stirred for

15 min at RT. The solution was then added to a mixture of H-Lys(Boc)-OH (1.42 g, 9.6 mmol) in dioxane/H_2O/THF 1:1:1 (15 ml) and 2.0 M Na_2CO_3 (5 ml). The mixture was stirred for 2 h, diluted with DCM and washed successively with 1.0 M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude compound was subjected to the next step without purification. To a solution of crude compound in DMF (10 ml) were added benzyl carbazate (1.6 g, 9.6 mmol), TBTU (1.83 g, 4.8 mmol), and TEA (1.34 ml, 9.6 mmol). The mixture was stirred for 2 h, diluted with DCM and washed with 1.0 M HCl, sat. $NaHCO_3$ aq. and brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 98:2, R_f = 0.5 with DCM/MeOH 95:5) gave the pure product **26** (0.8 g, 2 steps 28%) as a colorless powder. M.p.: 116-117 ^oC; $[\alpha]_D$ 10.5 (*c* 1.0, DCM); IR (neat): 3223 (w), 2968 (w), 1681 (s), 1615 (m), 1553 (m), 1519 (m), 1417 (m), 1216 (s), 1161 (m), 1022 (m), 821 (m), 730 (m), 693 (m); ^1H NMR (400 MHz, $CDCl_3$): 7.42-7.32 (m, 6H), 6.97 (d, ^3J (H,H) = 4.0 Hz, 1H), 5.11 (s, 2H), 4.60-4.58 (m, 1H), 3.13-3.03 (m, 2H), 1.88-1.73 (m, 4H), 1.52-1.46 (m, 2H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$/CD_3OD 1:1): 172.1 (s), 161.5 (s), 156.7 (s), 156.6 (s), 139.5 (s), 135.6 (s), 130.8 (d), 129.0 (d), 128.3 (d), 128.1 (d), 127.8 (d), 118.6 (s), 79.2 (s), 67.4 (t), 51.7 (d), 39.7 (t), 31.4 (t), 28.9 (t), 28.1 (q), 22.4 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 585 (80, $[M+H]^+$), 485 (100, $[M-Boc+H]^+$); HRMS (ESI, +ve) calcd for $C_{24}H_{31}BrN_4O_6S$: 583.1213, found: 583.1220.

Compound 15. This compound was prepared following the procedures in ref. S3.

Compound 21. A three-necked round bottom flask was charged with **26** (1.37 g, 1.9 mmol) and **15** (0.67 g, 0.9 mmol). The mixture was dissolved in distilled DMF (20 ml) and the solution was deaerated under vacuum and backfilled with argon three times prior to the addition of $Pd(PPh_3)_4$ (100 mg, 0.09 mmol). The reaction mixture was stirred at 80 ^oC for 24 h, diluted with EtOAc and washed with sat. aq. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 95:5, R_f = 0.35) gave the pure product **21** (0.63 g, 60%) as a yellow solid. M.p.: 115-117 ^oC; IR (neat): 3226 (w), 1681 (s), 1508 (m), 1450 (s), 1231 (m), 1163 (m), 1039 (m), 737 (w), 695 (m); CD ($CHCl_3$): 430 (+0.1); ^1H NMR (400 MHz, $CDCl_3$/CD_3OD 1:1): 7.54-7.51 (m, 2H),

7.46-7.41 (m, 2H, exchangeable), 7.37-7.26 (m, 10H), 7.15-7.05 (m, 6H), 5.12 (s, 4H), 4.57-4.48 (m, 2H), 3.05-2.93 (m, 4H), 1.97-1.71 (m, 4H), 1.55-1.45 (m, 8H), 1.38 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ 1:1): 173.0 (s), 162.8 (s), 157.3 (s), 157.2 (s), 142.6 (s), 137.3 (s), 136.6 (s), 136.2 (s), 135.9 (s), 130.2 (d), 128.8 (d), 128.6 (d), 126.1 (d), 125.2 (d), 124.4 (d), 79.6 (s), 67.9 (t), 52.4 (d), 40.2 (t), 31.9 (t), 29.5 (t), 28.6 (q), 23.1 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 1071 (80, $[M\text{-Boc}+H]^+$); MS (MALDI-TOF, DHB): 1193.40 $[M+Na]^+$.

Compound 27. A solution of **21** (100 mg, 0.08 mmol) and thioanisole (19 mg, 0.16 mmol) in DCM (2 ml) and TFA (2 ml) was stirred for 1 h at room temperature. The reaction mixture was concentrated *in vacuo*, and the residue was washed with diethyl ether (solid-liquid extraction). To the residue was added DMF (3 ml) and the pH of the mixture was adjusted to about 8 using TEA. To this mixture was added a solution of Boc-Cys(S-*t*-Bu)-OH (100 mg, 0.32 mmol), EDCI (80 mg, 0.48 mmol), HOBt-H_2O (46 mg, 0.32 mmol) and 2,4,6-collidine (67 μl, 0.48 mmol) in DMF (3 ml). The mixture was stirred for 90 min, then diluted with DCM, washed successively with 1.0 M HCl, brine, sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 97:3, R_f = 0.4 with DCM/MeOH 95:5) gave pure **27** (73 mg, 55%) as a yellow solid. M.p.: 122-123 ^{o}C; IR (neat): 3273 (w), 2928 (w), 1655 (s), 1524 (s), 1451 (m), 1364 (m), 1219 (m), 1161 (m), 1044 (m), 790 (m), 737 (m); CD ($CHCl_3$): 450 (+0.05); ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ 1:1): 7.65-7.62 (m, 2H), 7.59-7.50 (m, 2H, exchangeable), 7.34-7.24 (m, 10H), 7.16-7.04 (m, 6H), 5.15 (s, 4H), 4.55-4.48 (m, 2H), 4.31-4.26 (m, 2H), 3.24-3.12 (m, 4H), 3.02-2.89 (m, 4H), 1.91-1.73 (m, 4H), 1.56-1.43 (m, 8H), 1.42 (s, 18H), 1.28 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ 1:1): 172.9 (s), 171.5 (s), 162.7 (s), 157.2 (s), 156.2 (s), 142.5 (s), 137.3 (s), 136.6 (s), 136.1 (s), 135.9 (s), 130.2 (d), 128.7 (d), 128.5 (d), 128.2 (d), 126.1 (d), 125.1 (d), 124.4 (d), 80.6 (s), 67.9 (t), 54.5 (d), 52.4 (d), 49.6 (s), 43.2 (t), 39.2 (t), 31.7 (t), 29.9 (q), 28.9 (t), 28.8 (t), 28.4 (q), 22.9 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 1555 (20, $[M+H]^+$), 1453 (100, $[M\text{-Boc}+H]^+$), 1353 (80, $[M\text{-2Boc}+H]^+$); MS (MALDI-TOF, DHB): 1573.08 $[M+Na]^+$.

Compound 22. This compound was prepared following the procedures in ref. S4.

Compound 23. A solution of **27** (50 mg, 0.03 mmol) and thioanisole (10 μl, 0.09 mmol) in DCM (1 ml) and TFA (1 ml) was stirred for 1 h at room temperature. The mixture was concentrated *in vacuo*, and the residue was washed with diethyl ether (solid-liquid extraction). The residue was diluted with DMF (1 ml) and the pH of the solution was adjusted to about 8 by addition TEA. To the mixture was added a solution of **22** (76 mg, 0.12 mmol), EDCI (30 mg, 0.18 mmol), and TEA (26 μl, 0.18 mmol) in DMF (1 ml) and DCM (1 ml). The mixture was stirred for 90 min, diluted with DCM, washed successively with 1.0 M HCl, brine, sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 95:5, R_f = 0.5 with DCM/MeOH 9:1) gave pure **23** (50 mg, 62%) as a yellow solid. M.p.: 91-92 °C; IR (neat): 3287 (w), 1738 (m), 1637 (s), 1522 (s), 1453 (m), 1216 (s), 991 (m), 821 (m), 732 (m), 694 (m); CD ($CHCl_3$): 397 (-0.09); ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 1:1): 7.62-7.57 (m, 2H), 7.47-7.42 (m, 2H, exchangeable), 7.34-7.17 (m, 50H), 7.15-7.05 (m, 6H), 5.12-4.81 (m, 20H), 4.68-4.50 (m, 4H), 3.52-3.35 (m, 2H), 3.28-3.01 (m, 6H), 2.97-2.72 (m, 6H), 1.94-1.68 (m, 4H), 1.57-1.38 (m, 8H), 1.26 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD 1:1): 172.7 (s), 171.0 (s), 170.6 (s), 162.6 (s), 157.2 (s), 142.5 (s), 137.3 (s), 136.8 (s), 135.9 (s), 136.0 (s), 135.9 (s), 130.2 (d), 128.9 (d), 128.8 (d), 128.6 (d), 128.5 (d), 128.4 (d), 128.3 (d), 128.2 (d), 126.2 (d), 125.2 (d), 124.5 (d), 69.1 (t), 69.0 (t), 68.9 (t), 68.8 (t), 67.9 (t), 53.8 (d), 52.5 (d), 49.5 (s), 42.1 (t), 39.3 (t), 34.3 (d), 31.9 (t), 30.0 (q), 28.6 (t), 22.9 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 2507 (10, $[M+H]^+$), 1254 (100, $[M+2H]^{2+}$); MS (MALDI-TOF, HABA): 2530.55 $[M+Na]^+$.

Compound 28. To a solution of **23** (30 mg, 12 μmol) in TFA 1 ml were added thioanisole (70 μl, 56 μmol) and TMSBr (80 μl, 56 μmol) at 0 °C. The mixture was stirred for 24 h at room temperature and was concentrated *in vacuo*. The residue was successively washed with diethyl ether and then with DCM/MeOH 1:1 (solid-liquid extraction) to give **28** (12 mg, 66%). UV/vis (DMSO): 416 (40); ^{1}H NMR (400 MHz, DMSO-d_6): 8.04-7.96 (m, 2H), 7.54-7.37 (m, 6H), 4.48-4.33 (m, 2H), 4.31-4.25 (m, 2H), 3.44-3.35 (m, 2H), 3.10-2.88 (m, 6H), 2.72-2.54 (m, 6H), 1.83-1.67 (m, 4H), 1.48-1.33 (m, 8H), 1.28 (s, 18H); MS (ESI, MeOH/TFA 99:1): 858 (100, $[M-2H+TFA]^{2-}$).

Compound 24. This compound was prepared following previously reported procedures in ref. S1. UV/vis (DMSO): 367 (18.0), 380 (24.0).

Compound 1. A solution of **28** (15 mg, 10 μmol) and **24** (12 mg, 22 μmol) in DMSO (0.95 ml) and TFA (0.1 ml) was stirred for 24 h. Such *in-situ* hydrazone formation has been used extensively for the preparation of otherwise difficult to access complex products such as **1** with extreme physical properties that exclude standard purification and characterization.[S1,S5] Following optimized procedures, the octa-anionic, poorly soluble, dynamic oligothiophene-diNDI conjugate **1** could thus be used without further purifications.

2.1.2. Synthesis of the Propagator

The synthesis was performed as presented in Scheme S2 (see page S17).

Compound 14. This compound was prepared following the procedures in ref. S6.

Compound 16. A three-necked round bottom flask was charged with **14** (0.59 g, 2.2 mmol) and **15** (0.7 g, 0.9 mmol). The reagents were dissolved in distilled DMF (10 ml), and the solution was deaerated under vacuum and backfilled with argon three times prior to the addition of the $Pd(PPh_3)_4$ (0.14 g, 0.09 mmol). The reaction mixture was stirred for 12 h at 80 ºC. The reaction was quenched with methanol and the orange precipitate was filtered and washed with diethyl ether (100 ml) to give the orange powder **16** (0.33 g, 70%). M.p.: > 220 ºC; IR (neat): 1680 (m), 1450 (m), 1300 (s), 1150 (m), 1080 (m), 790 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 7.61 (d, ^3J (H,H) = 3.9 Hz, 2H), 7.19 (d, ^3J (H,H) = 3.9 Hz, 2H), 7.11 (d, ^3J (H,H) = 3.9 Hz, 4H), 1.59 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.4 (s), 142.9 (s), 137.1 (s), 135.9 (s), 134.1 (s), 133.7 (d), 125.9 (d), 125.0 (d), 82.1 (s), 28.4 (q); MS (ESI, $CHCl_3$/MeOH 1:1): 530 (20, $[M+H]^+$), 474 (100, $[M-t\text{-}Bu+H]^+$); HRMS (ESI, +ve) calcd for $C_{26}H_{26}O_4S_4$: 530.0709, found: 530.0704.

Compound 17. The orange solid **16** (0.5 g, 0.94 mmol) was dissolved in DCM (3 ml) and TFA (3 ml). The reaction mixture was stirred at room temperature for 2 h. The

mixture was concentrated *in vacuo*, washed with diethyl ether (solid-liquid extraction), diluted with 1.0 M HCl (1 ml), and concentrated *in vacuo*. The residue was dissolved in DMF (5 ml) and then to it were added HATU (0.788 g, 2.06 mmol) and TEA (0.39 ml, 2.82 mmol). The mixture was stirred for 5 min. The solution was then added to a mixture of H-Lys(Fmoc)-OH (1.38 g, 3.76 mmol) in dioxane/H_2O/THF 1:1:1 (30 ml) and 2.0 M Na_2CO_3 (10 ml). The mixture was stirred for 2 h, diluted with DCM and washed successively with 1.0 M HCl and brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH/acetic acid 9:1:0.1, R_f = 0.3) gave compound **17** (0.55 g, 55%) as a yellow solid. M.p.: 198-200 ^oC; IR (neat): 2947 (w), 1694 (m), 1632 (m), 1524 (s), 1448 (m), 1251 (m), 842 (m), 791 (m), 737 (m); CD (DMSO): 409 (+0.27); ^1H NMR (400 MHz, $CDCl_3/CD_3OD$ 1:1): 7.70 (d, ^3J (H,H) = 7.4 Hz, 4H), 7.59-7.52 (m, 6H), 7.33 (dd, ^3J (H,H) = 7.4, ^3J (H,H) = 7.4 Hz, 4H), 7.29-7.24 (m, 4H), 7.12-6.93 (m, 6H), 4.61 (m, 2H), 4.29 (d, ^3J (H,H) = 6.9 Hz, 4H), 4.14 (t, ^3J (H,H) = 6.9 Hz, 2H), 3.14 (t, ^3J (H,H) = 6.2 Hz, 4H), 2.01-1.71 (m, 4H), 1.59-1.34 (m, 8H); ^{13}C NMR (125 MHz, DMSO-d_6): 173.5 (s), 160.8 (s), 156.0 (s), 143.9 (s), 140.7 (s), 140.0 (s), 138.1 (s), 135.6 (s), 135.0 (s), 129.6 (d), 127.5 (d), 127.0 (d), 126.4 (d), 125.8 (d), 125.1 (d), 124.8 (d), 120.1 (d), 65.1 (t), 52.6 (d), 46.7 (d), 39.9 (t), 30.4 (t), 28.9 (t), 23.1 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 1118 (50, $[M+H]^+$); MS (MALDI-TOF, DCTB): 1118.50 $[M+H]^+$.

Compound 18. To a solution of **17** (0.5 g, 0.44 mmol) in DMF (10 ml) were added HATU (0.42 g, 1.1 mmol), *t*-butyl carbazate (0.23 g, 1.76 mmol) and TEA (0.18 ml, 1.1 mmol). The reaction mixture was stirred for 2 h, diluted with DCM and washed successively with 1.0 M HCl and brine. The organic layer was concentrated in *vacuo*. Flash column chromatography of the residue (DCM/MeOH 97:3, R_f = 0.4 with DCM/MeOH 9:1) gave pure **18** (0.41 g, 63%) as a yellow solid. M.p.: 120-121 ^oC; IR (neat): 3287 (w), 2934 (w), 1690 (s), 1625 (m), 1553 (m), 1450 (m), 1367 (w), 1250 (m), 1154 (m), 1042 (w), 840 (m), 738 (m); CD ($CHCl_3$): 489 (-0.52), 397 (+0.54); ^1H NMR (400 MHz, $CDCl_3/CD_3OD$ 1:1): 7.72 (d, ^3J (H,H) = 7.5 Hz, 4H), 7.58-7.53 (m, 6H), 7.35 (dd, ^3J (H,H) = 7.5 Hz, ^3J (H,H) = 7.5 Hz, 4H), 7.26 (m, 4H), 7.06 (d, ^3J (H,H) = 3.7 Hz, 2H) 7.01-6.95 (m, 4H), 4.54 (m, 2H), 4.31 (d, ^3J (H,H) = 6.9 Hz, 4H), 4.16 (t, ^3J (H,H) = 6.9 Hz, 2H), 3.16 (t, ^3J (H,H) = 6.2 Hz, 4H), 1.96-1.82 (m, 4H), 1.54 (m, 8H), 1.44 (s, 18H); ^{13}C NMR (125 MHz, DMSO-d_6): 173.0 (s), 162.9 (s),

157.9 (s), 157.8 (s), 156.5 (s), 156.4 (s), 144.3 (s), 142.6 (s), 141.6 (s), 137.3 (s), 136.5 (s), 135.8 (s), 130.3 (d), 128.0 (d), 127.4 (d), 126.1 (d), 125.4 (d), 125.3 (d), 125.1 (d), 124.4 (d), 120.2 (d), 81.9 (s), 67.0 (t), 52.5 (d), 47.6 (d), 40.5 (t), 31.8 (t), 29.5 (t), 28.3 (q), 23.0 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 1369 (40, $[M+Na]^+$), 1148 (50, $[M-2Boc+H]^+$), 1115 (100, $[M-2Boc-NH_2NH_2+H]^+$); MS (MALDI-TOF, DCTB): 1345.40 $[M+H]^+$.

Compound 20. This compound was prepared following the procedures in ref. S7.

Compound 19. To a solution of **18** (250 mg, 0.18 mmol) in 20% piperidine in DMF solution (5 ml) was stirred at room temperature for 1 h. The mixture was concentrated *in vacuo*, and the residue was washed with diethyl ether (solid-liquid extraction). The residue was diluted with DMF (2 ml) and the pH of the solution was adjusted to about 8 by addition of TEA. To the mixture was added **20** (180 mg, 0.7 mmol). The mixture was stirred for 30 min, then diluted with DCM and washed successively with sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 95:5, R_f = 0.5 with DCM/MeOH 9:1) gave product **19** (92 mg, 45%). M.p.: 140-142 ^oC; IR (neat): 3284 (w), 2950 (w), 1614 (m), 1524 (s), 1448 (m), 1251 (m), 791 (m), 742 (m); CD ($CHCl_3$): 405 (-0.05); ^1H NMR (400 MHz, $CDCl_3$/CD_3OD 1:1): 7.51 (d, ^3J (H,H) = 3.5 Hz, 2H), 7.03 (d, ^3J (H,H) = 3.5 Hz, 2H) 7.00-6.95 (m, 4H), 4.50 (t, ^3J (H,H) = 6.3 Hz, 2H), 3.28-3.02 (m, 14H), 1.90-1.70 (m, 4H), 1.49 (m, 8H), 1.39 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD 1:1): 172.9 (s), 162.8 (s), 156.6 (s), 142.7 (s), 137.4 (s), 136.4 (s), 135.8 (s), 130.3 (d), 126.2 (d), 125.2 (d), 124.5 (d), 81.9 (s), 52.6 (d), 52.3 (d), 42.8 (t), 39.5 (t), 36.9 (t), 31.9 (t), 28.7 (t), 28.4 (q), 23.0 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 1167 (40, $[M+H]^+$), 967 (100, $[M-2-Boc+H]^+$); MS (MALDI-TOF, DCTB): 1167.8 $[M+H]^+$.

Compound 2. A solution of **19** (80 mg, 68 mmol) and thioanisole (140 mg, 1.12 mmol) in TFA (2 ml) and DCM (2 ml) was stirred for 2 h at room temperature. To the mixture was added benzaldehyde (0.6 ml, 6 mmol). After 30 min of stirring, the mixture was diluted with DCM, washed with sat. aq. $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was washed with diethyl ether (solid-

liquid extraction) to give compound **2** (70 mg, 90%) as a yellow solid. M.p.: 158-160 ^{o}C; IR (neat): 3285 (w), 2929 (w), 1619 (s), 1524 (s), 1448 (m), 1202 (m), 1134 (m), 790 (m), 742 (m); CD ($CHCl_3$): 406 (-0.04), 288 (+0.06); ^{1}H NMR (400 MHz, DMSO-d_6): 8.32-8.25 (m, 2H), 8.02-7.98 (m, 2H), 7.71-7.68 (m, 4H), 7.51-7.38 (m, 12H), 5.34-5.26 (m, exchangeable, 2H), 4.51-4.45 (m, 2H), 3.34-3.29 (m, 4H), 3.18-3.02 (m, 10H), 1.75-1.83 (m, 4H), 1.55-1.33 (m, 8H); MS (ESI, $CHCl_3$/MeOH 1:1): 1143 (40, $[M+H]^+$), 1055 (100, $[M\text{-benzaldehyde}+H]^+$).

2.1.3. Synthesis of the Stack Exchangers

Compounds **6** and **8** were prepared following the procedure in ref. S1. The synthesis of **9** and **10** was performed as presented in Scheme S3 (see page S17).

Compound 30. To a suspension of **29** (0.35 g, 0.89 mmol) in DMF (15 ml) were added 2-ethylhexylamine (1.14 g, 7.13 mmol), aminoacetaldehyde dimethylacetal (0.75 g, 7.13 mmol) and TEA (3.00 ml, 21.5 mmol). The mixture was stirred at 140 ^{o}C for 48 h. After cooling to room temperature, the mixture was poured into 1.0 M HCl (200 ml), the red precipitate was filtered and washed with water. The solid collected was sonicated in DCM/MeOH 10:1, centrifuged and then decanted. The procedure was repeated 4 times; the supernatants were combined, mixed with celite and evaporated to dryness. The solid was loaded onto the chromatography column and eluted with DCM/MeOH 20:1. The impure fractions containing the product were collected, mixed with celite and evaporated. The pure compound **30** was obtained as a red solid (55 mg, 10%) by flash chromatography applying the gradient elution from 1% to 8% acetone/DCM (R_f = 0.52 with DCM/acetone 50:1). M.p.: > 230 °C; IR (neat): 2913 (w), 1696 (s), 1657 (s), 1592 (s), 1345 (s), 1249 (s), 1074 (s), 809 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 8.74 (d, ^{3}J (H,H) = 8.0 Hz, 2H), 8.73 (d, ^{3}J (H,H) = 8.0 Hz, 2H), 8.66 (d, ^{3}J (H,H) = 8.0 Hz, 2H), 8.66 (d, ^{3}J (H,H) = 8.0 Hz, 2H), 4.99 (t, ^{3}J (H,H) = 5.8 Hz, 1H), 4.47 (d, ^{3}J (H,H) = 5.8 Hz 2H), 4.27-4.13 (m, 2H), 3.50 (s, 6H), 2.06-1.97 (m, 1H), 1.50-1.43 (m, 4H), 1.42-1.32 (m, 4H), 1.01 (t, ^{3}J (H,H) = 7.4 Hz, 3H), 0.95 (t, ^{3}J (H,H) = 6.7 Hz, 3H); MS (ESI, $CHCl_3$): 559 (100, $[M\text{-MeOH}+H]^+$).

Compound 10. A solution of **30** (20 mg, 0.034 mmol) in TFA (3 ml) was stirred for 1 h and then evaporated to dryness. The compound **10** was obtained in quantitative yield as a red solid and was used without further purification (R_f = 0.52 with DCM/acetone 50:1). M.p.: > 230 °C; IR (neat): 2928 (w), 1693 (s), 1652 (s), 1591 (s), 1436 (m), 1245 (m), 1175 (m), 1031 (w), 740 (w); ^{1}H NMR (300 MHz, $CDCl_3$): 9.80 (s, 1H), 8.75 (d, ^3J (H,H) = 8.1 Hz, 4H), 8.69 (d, ^3J (H,H) = 8.1 Hz, 4H), 5.13 (s, 2H), 4.24-4.11 (m, 2H), 2.05-1.93 (m, 1H), 1.48-1.26 (m, 8H), 0.98 (t, ^3J (H,H) = 7.3 Hz, 3H), 0.91 (t, ^3J (H,H) = 6.7 Hz, 3H); MS (ESI, $CHCl_3$): 545 (100, $[M+H]^+$).

Compound 31. This compound was prepared following the previous procedure in ref. S8.

Compound 32. To a solution of **31** (1.0 g, 1.71 mmol) in DMF (40 ml) at 50°C was added disodium dimercaptomaleonitrile (0.96 g, 5.16 mmol). The mixture was stirred at 50 °C overnight, cooled to room temperature and poured into 6.0 M HCl (100 ml) solution. The black crystalline precipitate formed was filtered, washed with 6.0 M HCl and subsequently with water until neutral, and then dried in the oven at 120°C for 3 h gave **32** (0.78 g, 84%). M.p.: > 230°C; IR (neat): 3317 (s), 2925 (w), 2212 (m), 1686 (s), 1640 (s), 1546 (s), 1493 (m), 1456 (s), 1321(m), 1271 (s), 1152 (s), 992 (s), 914 (m), 784 (w).

Compound 33. To a solution of **32** (0.06 g, 0.11 mmol) in DMF (15 ml) were added 2-ethylhexylamine (22.0 mg, 0.17 mmol), aminoacetaldehyde dimethylacetal (21.0 mg, 0.17 mmol) and TEA (0.19 g, 1.87 mmol). The mixture was stirred at 60 °C for 6 h. After cooling to room temperature, the mixture was poured into 1.0 M HCl (100 ml), the dark precipitate was filtered and washed with water. The solid collected was sonicated in DCM/MeOH 10:1, centrifuged and then decanted. The procedure was repeated 4 times. The supernatants were combined, mixed with celite and evaporated to dryness. The flash chromatography (DCM/acetone 98:2, R_f = 0.42 with DCM/acetone 50:1) afforded **33** as a dark pink solid (7.0 mg, 9%). M.p.: > 230°C; IR (neat): 2925 (w), 2212 (s), 1690 (m), 1638 (s), 1591 (s), 1460 (m), 1325 (m), 1300 (s), 1219 (s), 788 (w); ^{1}H NMR (400 MHz, $CDCl_3$): 4.95 (t, ^3J (H,H) = 5.5 Hz, 1H), 4.53 (d, ^3J (H,H) = 5.5 Hz, 2H), 4.35-4.22 (m, 2H), 2H), 3.48 (s, 6H), 2.07-1.98 (m, 1H),

1.51-1.33 (m, 8H), 1.02 (t, ^3J (H,H) = 7.4 Hz, 3H), 0.96 (t, ^3J (H,H) = 6.9 Hz, 3H); MS (ESI, $CHCl_3$): 711 (100, $[M\text{-}MeOH+H]^+$).

Compound 9. A solution of **33** (7.0 mg, 9.43 μmol) in TFA (2 ml) was stirred for 1 h and then evaporated to dryness. The compound **9** was obtained in quantitative yield as a pink solid and was used without further purification (R_f = 0.73 with DCM/acetone 50:1). M.p.: > 230°C; IR (neat): 2926 (w), 2213 (m), 1736 (w), 1686 (w), 1641 (s), 1534 (w), 1485 (s), 1454 (s), 1328 (s), 1304 (s), 1218 (s), 743 (m); ^{1}H NMR (300 MHz, $CDCl_3$): 9.83 (s, 1H), 5.29 (s 2H), 4.32-4.21 (m, 2H), 2.05-1.91 (m, 1H), 1.48-1.22 (m, 8H), 0.98 (t, ^3J (H,H) = 7.7 Hz, 3H), 0.93 (t, ^3J (H,H) = 6.9 Hz, 3H); MS (ESI, $CHCl_3$): 697 (48, $[M+H]^+$).

2.2. Electrochemistry

The oxidation potential of oligothiophene **18** and the reduction potential of NDI **9** were determined using cyclic voltammetry (CV, scan rate 100 mV/s) vs Fc/Fc^+ in DCM (supporting electrolyte: 100 mM Bu_4NPF_6, working electrode: glassy carbon, counter electrode: Pt wire, reference electrode: SCE; Supporting Figure S1). HOMO and LUMO energies *vs* vacuum were calculated from the onset of oxidation and reduction wave using Supporting Equation (S1).[S9]

$$E_{HOMO/LUMO} = -5.1\ eV - E_{onset}\ vs\ (Fc/Fc^+) \qquad (S1)$$

The optical band gap E_g^{opt} was calculated from the onset of the lowest energy band using Supporting Equation (S2)

$$E_g^{opt} = 1240 / \lambda_{max}^{onset}\ (nm) \qquad (S2)$$

2.3. Self-Organizing Surface-Initiated Polymerization

Initiation. ITO electrodes were cut to give the area ~1 x 2 cm^2, cleaned in the RCA solution (H_2O/24% NH_4OH/30% H_2O_2 5:1:1, 60 °C, 15 min), rinsed with bidistilled water and ethanol, dried over argon and immersed in the solution of **1** (1 mM in

DMSO). The coated electrodes were tested for pin holes by measuring CV of potassium ferricyanide (0.5 mM $K_4Fe(CN)_6$, 0.1 M Na_2SO_4) using the covered ITO as a working electrode (Pt wire as a counter and Ag/AgCl as reference; Supporting Figure S2a).[S10]

Complete disappearance of the redox waves after 2 days of the immersion confirmed the good coverage of the electrode by the initiator. The obtained ITO electrodes were heated in an oven for 1 h at 120 ^oC to achieve better bonding between diphosphonates and ITO substrate. The CVs of the bound initiator were obtained using the ITO electrodes as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode in 0.1 M Bu_4NPF_6 in DCM (for oxidation potential) and in 0.2 M Na_2SO_4 in H_2O (for reduction potential) (Supporting Figure S2b). The observed linear dependence of the peak currents to the scan rate (Supporting Figure S3) confirmed the covalent binding of the redox active oligothiophene on the electrode surface. Surface coverage Γ was estimated from the charge Q (μC/cm^2) of the oxidation wave using Supporting Equation (S3).[S11]

$$Q = nFA\Gamma \qquad \text{(S3)}$$

in which n is the number of electrons, F the Faraday constant and A the area of the electrode. The obtained $\Gamma = 2 \times 10^{-11}$ mol·cm^{-2} is consistent with the nearly complete coverage of the surface by the initiator anchored with all phosphonate groups to the surface. These results from an established characterization procedure[S1] provided compelling experimental support that compound **1** forms monolayers on ITO.

The electrodes were activated by treatment with DTT (20 mM in 10 mM aq. NH_4HCO_3) for 1 h at room temperature.

Propagation: Concentration dependence of monomer 2. ITO electrodes with and without activated initiator were placed next to each other in deaerated solutions of propagator **2** at different concentrations (0.75-6.00 mM) in $CHCl_3$/MeOH 3:1, with *i*-Pr_2NEt (0.1 M) and shaken under argon atmosphere at room temperature. After 24 h, the electrodes were rinsed with $CHCl_3$/MeOH 1:1, DMF, and EtOH and dried under flow of N_2. Absorbance of the electrodes was recorded at 420 nm, corresponding to the absorption maximum of the yellow oligothiophene. Based on these results, the

SOSIP concentration of **2** under these conditions was determined to be 4-6 mM. Stack exchange experiments were performed with films obtained under these conditions (Supporting Figure S4). SOSIP of **2** in different solvent mixtures has been studied (e.g., $CHCl_3$/octanol 8:1, $CHCl_3$/*i*-PrOH 1:1, $CHCl_3$/MeOH 1:1 and $CHCl_3$/*i*-PrOH/TFE 5:1:0.2); none of them gave a good result.

The thickness of the obtained films could be estimated by dividing absorbance at the absorption maximum by corresponding absorbance of the monolayer and multiplying the resulting value by the typical face-to-face π-π stacking distance.[S12,S13]

2.4. Stack Exchange

Hydrazone-oxime exchange. An ITO electrode with benzaldehyde-hydrazone SOSIP **4** was placed in a solution of NH_2OH HCl (1 ml, 1 M, pH 3, MeOH/H_2O 1:1). Aliquots (20 μl each) of the solution were analyzed by HPLC (YMC ODS-A 4 x 50 mm, 10-40% CH_3CN/H_2O (with 0.1% TFA) over 5 min, 1 ml / min; Supporting Figure S5a). The area of the peak at R_t = 2.2 min was compared to that of the standard to calculate the concentration of released benzaldehyde oxime in the solution. The time course (Supporting Figure S5b) revealed the completion of hydrazone-oxime exchange in about 1 day.

Hydrazone formation. Coated ITO electrodes after NH_2OH treatment (**5**) were placed in solutions of aldehydes **6** (40 mM), **8** (50 mM), **9** (2 mM) or **10** (2 mM) in DMSO with TFA 4% v/v. Hydrazone formation was monitored by UV-vis measurements. In general, the reaction was left for 6-12 h to assure the completion of the hydrazone formation (Supporting Figure S6).

To estimate yields of stack exchange, the extinction coefficients of the individual chromophores in surface architectures were determined, if possible, by dissolving the entire photosystem with 20 mM mercaptoethanol, 0.1 M DIPEA in MeOH and correcting the changes for known extinction coefficients in solution or compared with literature values for stacks if available. The following values were used oligothiophene (as in **4**): ΔA420 nm, ε = 40.0 $mM^{-1}cm^{-1}$, u-NDI (as in **7**): ΔA367 nm, ε = 18.0 $mM^{-1}cm^{-1}$,[S14] r-NDI (as in **11**): ΔA540 nm, 15.0 $mM^{-1}cm^{-1}$,[S15] ce-

NDI (as in **12**): ΔA580 nm, 41.0 $mM^{-1}cm^{-1}$ and PDI (as in **13**): ΔA540 nm, 15.0 $mM^{-1}cm^{-1}$.[S16]

The yield of stack exchange was estimated from the ratio *R* of the absorption maxima of u-NDI (as in **7**), r-NDI (as in **11**), ce-NDI (as in **12**) and PDI (as in **13**) compared to oligothiophene (as in **4**). Quantitative yield $\chi = 100\%$ was assumed for a 2:1 ratio ($R = 2.0$).

The obtained values of $\chi \sim 90\%$ ($R = 1.74$) in photosystem **7**, **11**, and **13** indicated that the subunit exchange is almost quantitative. For photosystem **12**, $\chi \sim 30\%$ ($R = 0.6$) was obtained.

2.5. Photocurrent Measurement

Coated ITO electrodes 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 N_2 gas) aqueous solution of TEOA (50 mM) and Na_2SO_4 (0.1 M) and irradiated with a solar simulator (area of irradiation: $a \sim 0.5$ cm^2). Changes in current upon on-off switching of irradiations were measured at 0 V vs Ag/AgCl unless stated. The power of irradiation was 66 $mWcm^{-2}$ unless stated otherwise. Currents were normalized using transmittance (*T*) at 420 nm.

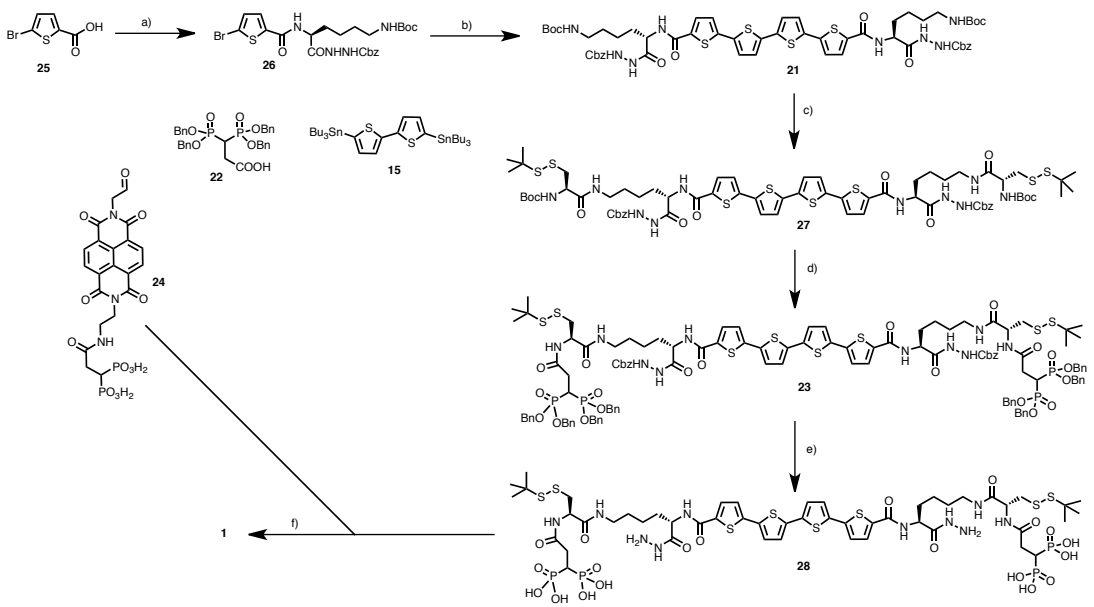
Action Spectra. Photocurrent densities ($J_{sc} = I_{sc}/a$) were measured using TEOA (50 mM) and Na_2SO_4 (0.1 M) at 0 V vs Ag/AgCl upon excitation by monochromatic light (150 W Xe lamp with Oriel 1/8 m monochromator). The obtained current densities were converted into incident photon-to-current conversion efficiencies (*IPCE*) by using equation (S4).[S17]

$$IPCE = 1240 / \lambda\,(\text{nm}) \times J_{sc}/P_{in} \qquad \text{(S4)}$$

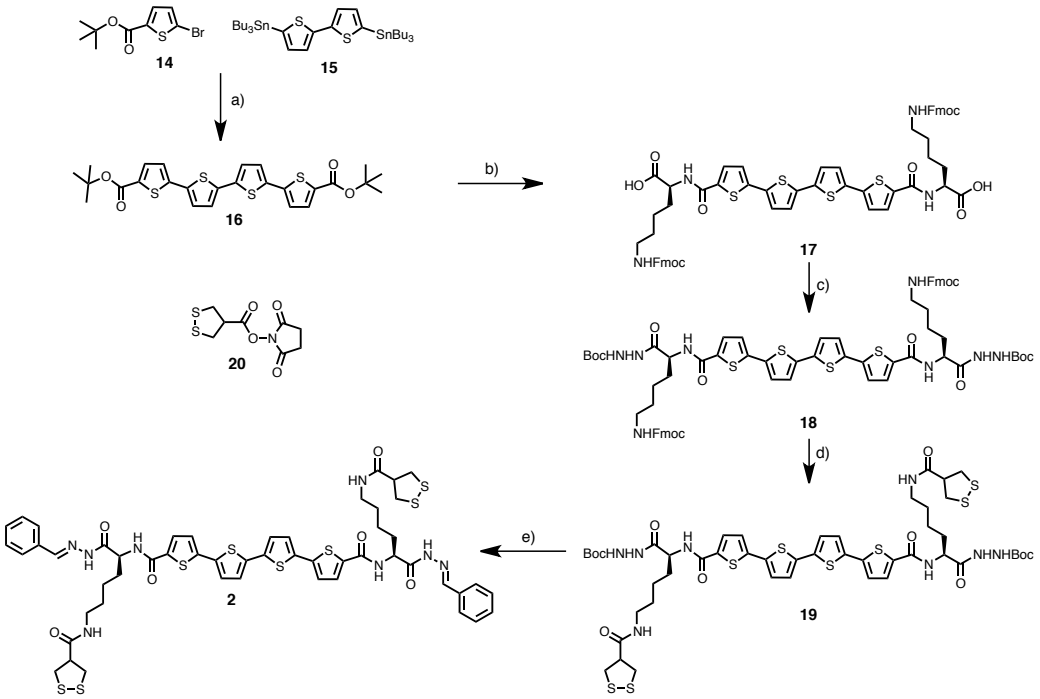
To facilitate the comparison, the obtained *IPCE* values were further normalized using the transmittance (*T*) of the film at 420 nm as in equation (S5).

$$Y = IPCE / (1-T_{420}) \qquad \text{(S5)}$$

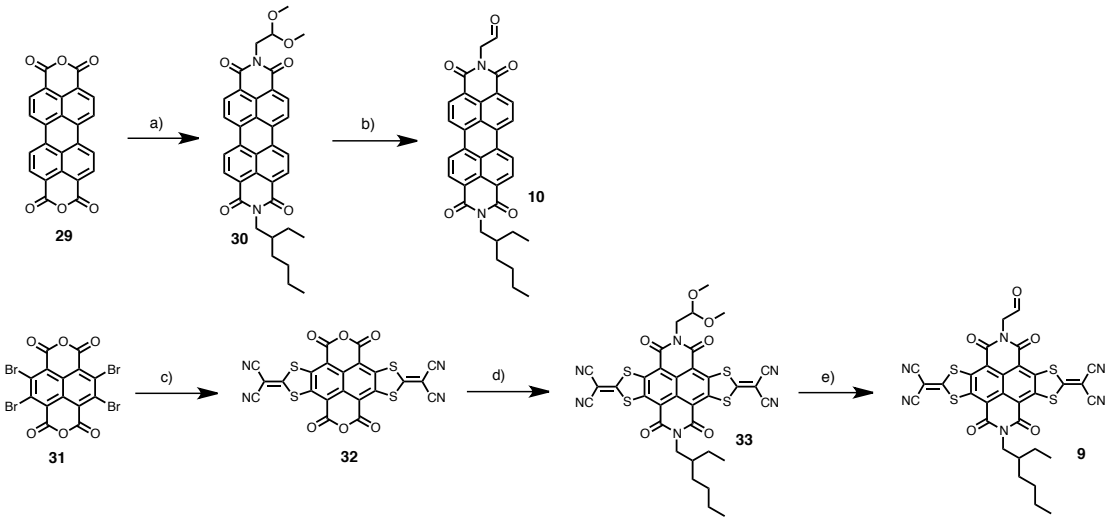
3. Supporting Schemes and Figures



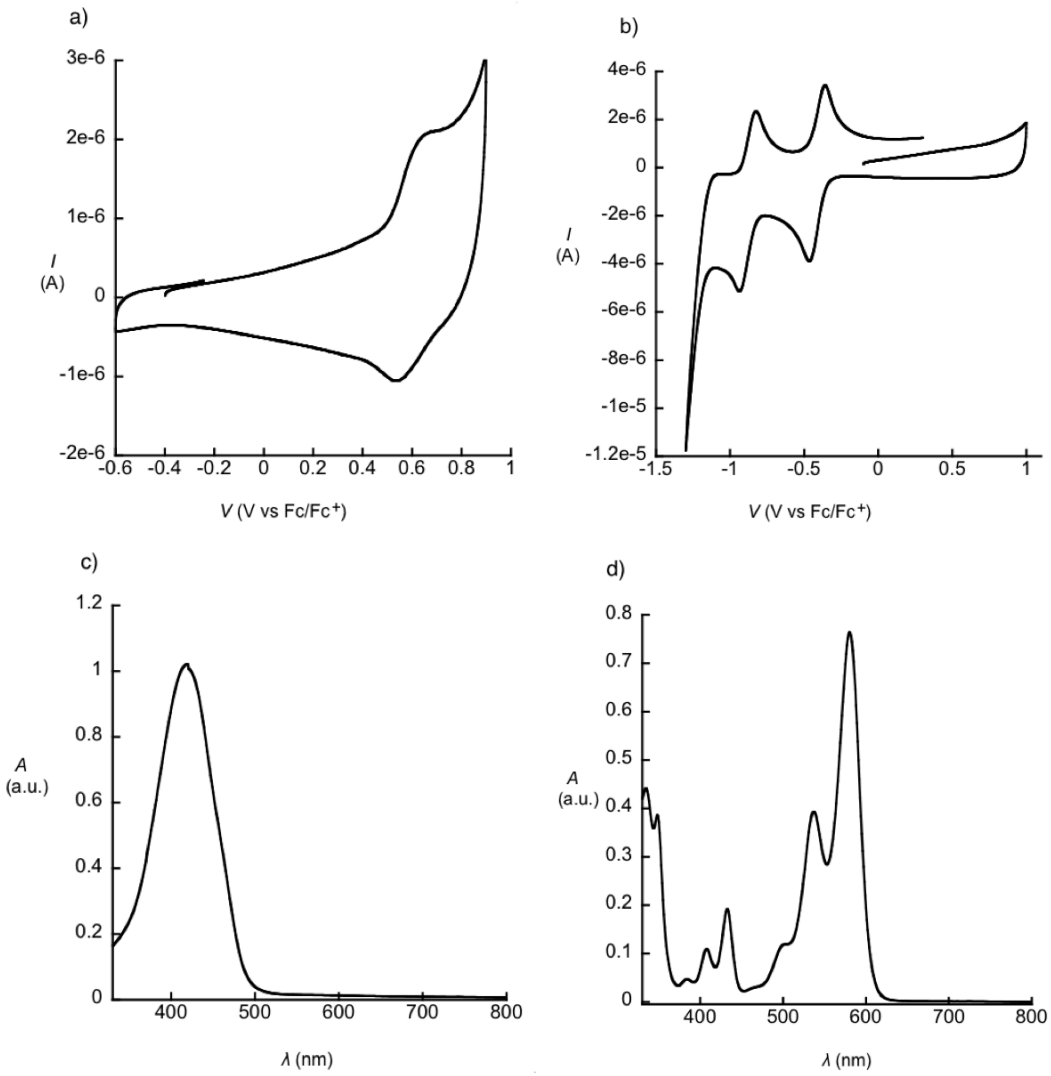
Supporting Scheme S1. a) 1. TBTU, TEA, DMF, H-Lys(Boc)-OH, dioxane/THF/ H_2O 1:1:1, RT, 2 h; 2. TBTU, TEA, DMF, NH_2NHCbz, RT, 2 h, 28% (2 steps); b) **15**, $Pd(PPh_3)_4$, DMF, 24 h, 80 ºC, 60%; c) 1. TFA, thioanisole, DCM; 2. Boc-Cys(S-*t*-Bu)-OH, HOBt, EDCI, DMF, 2,4,6-collidine, RT, 1.5 h, 55% (2 steps); d) 1. TFA, thioanisole, DCM, RT, 1 h; 2. **22**, EDCI, TEA, DMF, RT, 1.5 h, 62% (2 steps); e) TMSBr, thioanisole, TFA, DCM, 66%; f) **24**, TFA, DMSO, RT, 24 h, quant.



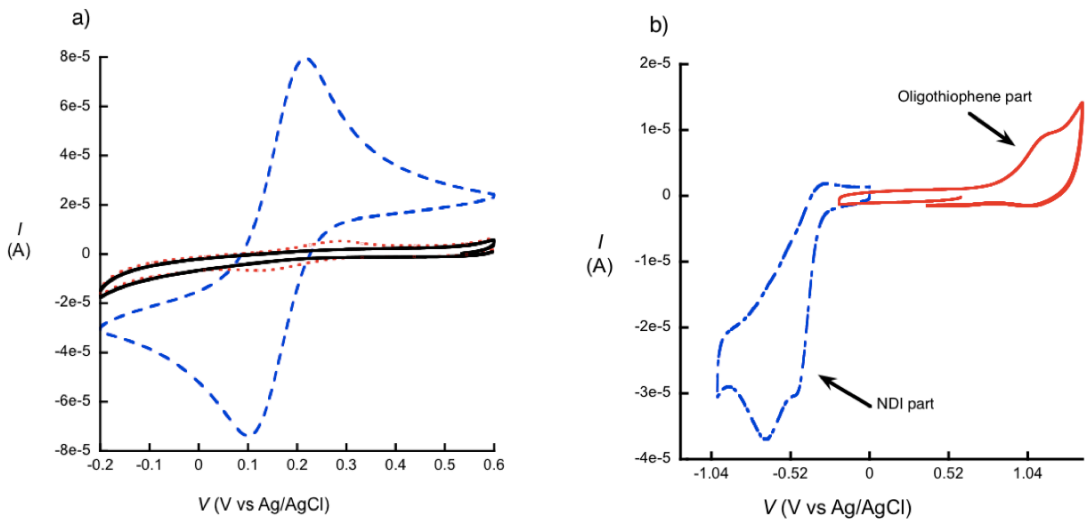
Supporting Scheme S2. a) 1. $Pd(PPh_3)_4$, DMF, RT, 70%; b) 1. TFA, RT, 2 h, quant, 2. HATU, DMF, TEA, RT, 5 min; 3. H-Lys(Fmoc)-OH, Na_2CO_3, dioxane/THF/H_2O 1:1:1, RT, 55%; c) HATU, DMF, TEA, NH_2NHBoc, 63%; d) 1. piperidine, DMF, RT, 1 h; 2. **20**, TEA, DMF, RT, 30 min, 45% (2 steps); e) TFA, thioanisole, benzaldehyde, RT, 90% (2 steps).



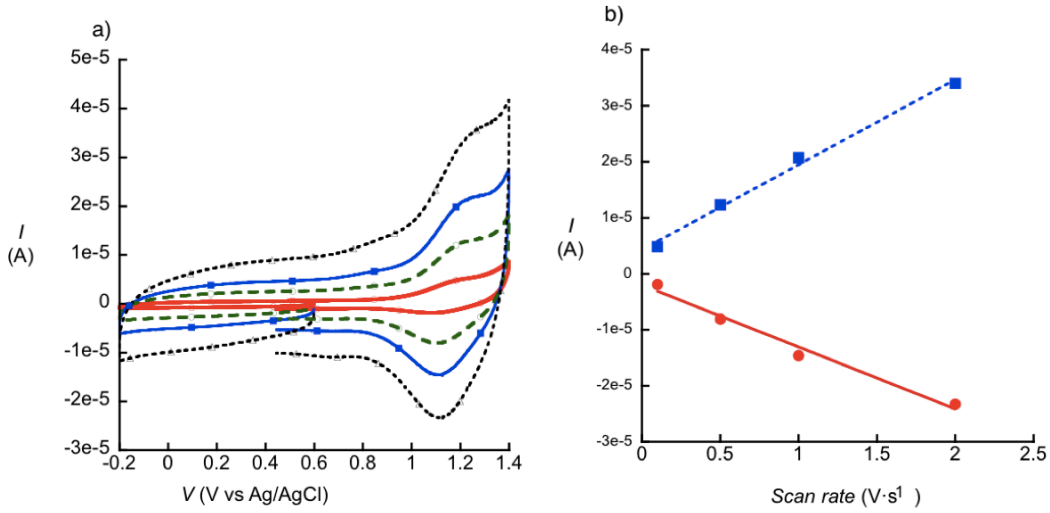
Supporting Scheme S3. a) 2-Ethylhexyl amine, aminoacetaldehyde dimethylacetal, TEA, DMF, 140 ºC, 10%; b) TFA, quant; c) disodium dimercaptomaleonitrile, DMF, 70 ºC, 84%; d) 2-ethylhexyl amine, aminoacetaldehyde dimethylacetal, TEA, DMF, 140 ºC, 9%; e) TFA, quant.



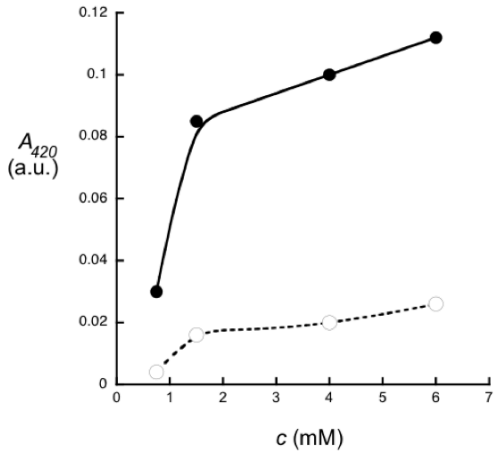
Supporting Figure S1. a) Cyclic voltammogram of oligothiophene **18**. b) Cyclic voltammogram of ce-NDI **9** in 0.1 M Bu_4NPF_6/DCM. c, d) UV-vis absorption of **18** and **9** in $CHCl_3$.



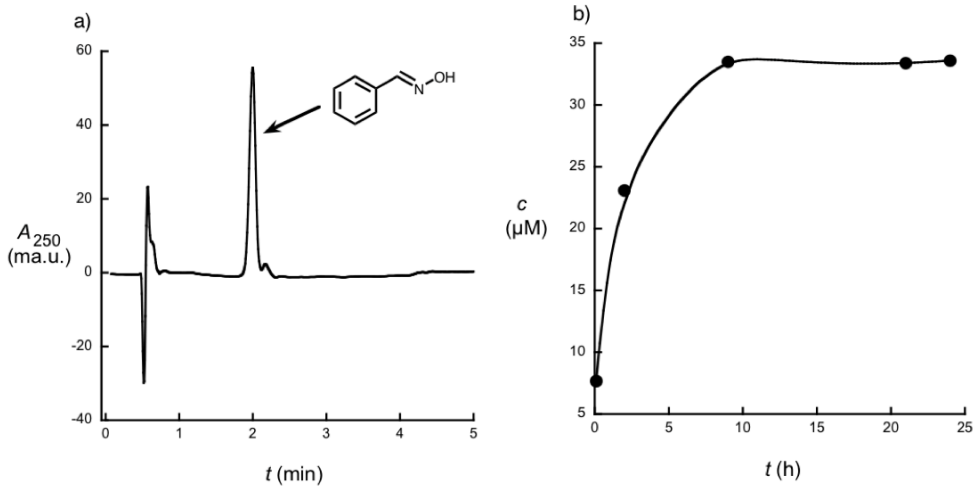
Supporting Figure S2. a) Cyclic voltammograms of aqueous ferriccyanide measured with an ITO electrode (---) before the deposition of initiator **1**, (—) after 24 h and (•••) 48 h in the solution of the initiator as working electrode. b) Cyclic voltammograms of the initiator coated ITO electrodes (red, measured in 0.1 M Bu_4NPF_6/DCM, blue, measured in 0.1 M Na_2SO_4).



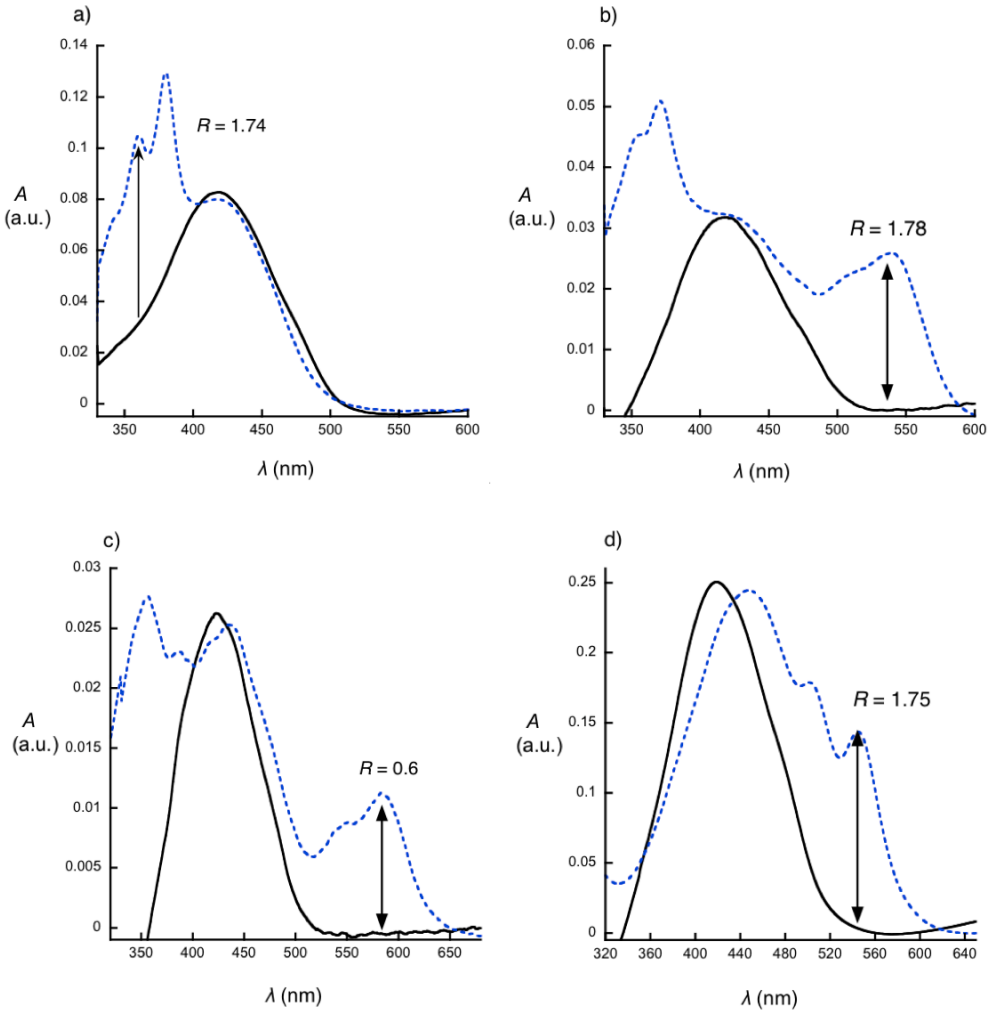
Supporting Figure S3. a) Cyclic voltammograms of the initiator coated ITO electrode, at different scan rates (0.1, 0.5, 1.0, and 2.0 $V \cdot s^{-1}$). b) Peak current of the oxidation and the reduction wave of oligothiophene moieties on initiator **1** as a function of scan rates.



Supporting Figure S4. Concentration dependence of SOSIP of monomer **2**, filled circles: ITO electrode coated with initiator **1**; open circles: ITO without the initiator after 24 h of incubation with varied propagator concentrations at constant concentration of *i*-Pr_2NEt (0.1 M) in $CHCl_3$/MeOH 3:1.



Supporting Figure S5. Kinetics of hydrazone-oxime exchange. a) Typical HPLC chromatogram. b) Time course of the change in concentration of benzaldehyde-oxime released in the solution.



Supporting Figure S6. UV-vis absorption spectra of the SOSIP films obtained by hydrazone-exchanges from photosystem **4** to a) **7**, b) **11**, c) **12** and d) **13**.

4. Supporting Table

Table S1. Summary of optoelectronic data[a]

Compound	λ_{max}/nm (ε/mM^{-1}cm^{-1})	$E_{1/2}$/V[b]	E_{HOMO}/eV[c]	E_{LUMO}/eV[c]	ΔE/eV[d]	Refs.
6	367 (18), 380 (24)	-0.81 -1.10	-7.30	-4.30	3.0	S14
8	536 (15)	-0.95	-6.20	-4.20	2.0	S14, S15
9	580 (41) 534 (20)	-0.41 -0.88	-6.68	-4.68	2.0	
10	540 (15)	-0.86	-6.60	-4.20	2.4	S16, S18
18	420 (40)	0.59	-5.69	-3.16	2.5	

[a]For original data, see Supporting Figure S1, [b]First oxidation and reduction potential in V against Fc/Fc^+, [c]LUMO and HOMO energies in eV against vacuum; from $E_{HOMO}/_{LUMO}$ = -5.1 eV(Fc) - $E_{red/ox}$, and [d]$\Delta E_{HOMO/LUMO}^{opt} = 1240/\lambda_{max}^{onset}$ (nm).

5. Supporting References

S1 N. Sakai and S. Matile, *J. Am. Soc. Chem.*, 2011, **133**, 18542-18545.

S2 E. Dalcanale and F. Montanari, *J. Org. Chem.*, 1986, **51**, 567-569.

S3 S. Kawano, N. Fujita and S. Shinkai, *Chem. Eur. J.*, 2005, **11**, 4735-4742.

S4 P. Page, M. Mckenzie and J. J. Gallagher, *J. Org. Chem.*, 2001, **66**, 3704-3708.

S5 (*a*) T. Takeuchi, J. Montenegro, A. Hennig and S. Matile, *Chem. Sci.*, 2011, **2**, 303-307; (*b*) J. Montenegro and S. Matile, *Chem. Asian J.*, 2011, **2**, 281-289; (*c*) J. Montenegro, E.-K. Bang, N. Sakai and S. Matile, *Chem. Eur. J.*, 2012, **18**, 10436-10443.

S6 S. W. Wright, D. L. Hageman, A. S. Wright and L. D. McClure, *Tetrahedron Lett.*, 1997, **38**, 7345-7348.

S7 (*a*) R. Singh and G. M. Whitesides, *J. Am. Chem. Soc.*, 1990, **112**, 1190-1197; (*b*) J. P. Danehy and V. Elia, *J. Org. Chem.*, 1972, **37**, 369-373; (*c*) L. Schotte and H. Ström, *Acta Chem. Scand.*, 1956, **10**, 687-688; (*d*) F. Unger and E. Liehl, GB 2 148 296 A, 1985.

S8 C. Röger and F. Würthner, *J. Org. Chem.*, 2007, **72**, 8070-8075.

S9 J. Míšek, A. Vargas Jentzsch, S. Sakurai, D. Emery, J. Mareda and S. Matile, *Angew. Chem. Int. Ed.*, 2010, **49**, 7680-7683.

S10 S. Paniagua, P. Hotchkiss, S. C. Jones, S. R. Marder, A. Mudalige, F. Marrikar, J. Pemberto and N. R. Armstrong, *J. Phys. Chem. C*, 2008, **112**, 7809-7817.

S11 D. Bonifazi, O. Engerc and F. Diederich, *Chem. Soc. Rev.*, 2007, **36**, 390-414.

S12 N. Sakai, M. Lista, O. Kel, S. Sakurai, D. Emery, J. Mareda, E. Vauthey and S. Matile, *J. Am. Chem. Soc.*, 2011, **133**, 15224-15227.

S13 E. Orentas, M. Lista, N.-T. Lin, N. Sakai and S. Matile, *Nat. Chem.*, 2012, **4**, 746-750.

S14 N. Sakai, J. Mareda, E. Vauthey and S. Matile, *Chem. Commun.*, 2010, **46**, 4225-4237.

S15 F. Würthner, S. Ahmed, C. Thalacker and T. Debaerdemaeker, *Chem. Eur. J.*, 2002, **8**, 4742-4750.

S16 Z. Chen, V. Stepanenko, V. Dehm, P. Prins, L. D. A. Siebbeles, J. Seibt, P.

Marquetand, V. Engel and F. Würthner, *Chem. Eur. J.*, 2007, **13**, 436-449.

S17 H. Yamada, H. Imahori, Y. Nishimura, I. Yamazaki, T. Ahn, S. Kim, D. Kim and S. Fukuzumi, *J. Am. Chem. Soc.*, 2003, **125**, 9129-9139.

S18 B. A. Jones, A. Facchetti, M. R. Wasielewski and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 15259-15278.