Antiparallel three-component gradients in double-channel surface architectures

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Supplementary Information

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1. Materials and Methods

As in ref. S1. Briefly, reagents for synthesis were purchased from Fluka, Acros and Apollo Scientific, amino acid derivatives from Bachem. Indium tin-oxide (ITO) coated glass substrates were obtained from Präzisions Glas & Optik GmbH (Iserlohn, Germany). Unless stated otherwise, column chromatography was carried out on silica gel 60 (Fluka, 40-63 μm). Analytical (TLC) and preparative thin layer chromatography (PTLC) were performed on silica gel 60 (Fluka, 0.2 mm) and silica gel GF (Analtech, 1 mm), respectively. $[\alpha]_D$ values were recorded on a Jasco P-1030 Polarimeter, melting points (Mp) on a heating table from Reichert (Austria) or Melting Point M-565 (BUCHI). UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 ºC) and are reported as maximal absorption wavelength λ in nm (extinction coefficient ε in $mM^{-1}cm^{-1}$). Circular dichroism (CD) spectra were obtained using JASCO J-815 spectropolarimeter and are reported as extremum wavelength λ in nm ($\Delta\varepsilon$ in $M^{-1}cm^{-1}$). Fluorescence measurements were performed with a FluoroMax-4 spectrofluorometer (Horiba Scientific) equipped with a stirrer and a temperature controller. Fluorescence spectra were corrected using instrument-supplied correction factors and are reported as the maximum emission wavelength λ in nm. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate, unless stated) and are reported as wavenumbers ν in cm^{-1} with band intensities indicated as 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 (δ = 0). Spin multiplicities are reported as a singlet (s), doublet (d), triplet (t) and quartet (q) with coupling constants (*J*) given in Hz, or multiplet (m). Broad peaks are marked as br. ^1H and ^{13}C resonances were assigned with the aid of additional information from 1D & 2D NMR spectra (H,H-COSY,

DEPT 135, HSQC and HMBC). Multiplicities of ^{13}C signals were reported as s (*C*), d (*CH*), t (CH_2) and q (CH_3). Multiplicity due to ^{13}C-^{31}P coupling is reported as ^{P}d, ^{P}t or ^{P}m. ESI-MS measurements were performed on a ESI API 150EX and are reported as *m*/*z* (%). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Sciex QSTAR Pulsar mass spectrometer, MALDI-TOF on a Axima CFR^{+} (Shimadzu) or Bruker autoflex. 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 was measured using a radiant power energy meter (Newport model 70260).

Abbreviations. Alloc: Allyloxycarbonyl; Bn: Benzyl; Boc: *tert*-Butoxycarbonyl; Bu_3SnCl: Tributyltin chloride; CV: Cyclic voltammetry; Cys: Cysteine; DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene; DCM: Dichloromethane; DCTB: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile; DHB: 2,5-Dihydroxybenzoic acid; DIPEA: *N*,*N*-Diisopropyl-ethylamine; DMAP: 4-(Dimethylamino)pyridine; DMF: *N*,*N*-Dimethylformamide; DPE: Diisopropylether; DPV: Differential pulse voltammetry; DTT: DL-Dithiothreitol; EDC: 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride; ESI-MS: Electrospray ionization-mass spectrometry; Fc: Ferrocene; Fmoc: 9-Fluorenylmethyl carbonyl; Fmoc-Cys(S-*t*-Bu)-OH: N^{α}-Fmoc-*S*-*tert*-butylmercapto-L-cysteine; Fmoc-Lys(Alloc)-OH: N^{α}-Fmoc-N^{ε}-allyloxycarbonyl L-lysine; HABA: 2-(4-Hydroxyphenylazo)benzoic acid; HATU: (dimethylamino)-*N*,*N*-dimethyl(3*H*-[1,2,3]triazolo[4,5-*b*]pyridin-3-yloxy) methaniminium hexafluorophosphate; HOBt: 1-Hydroxybenzotriazole; ITO: Indium tin oxide; LDA: lithium diisopropylamine; Lys: Lysine; MALDI-TOF: Matrix assisted laser desorption ionization-time of

flight; Mp: Melting point; NDI: 1,4,5,8-Naphthalenediimide; PE: Petroleum ether; rt: Room temperature; SOSIP: Self-organizing surface-initiated polymerization; TEA: Triethylamine; TFA: Trifluoroacetic acid; TLC: Thin layer chromatography; TMS: Tetramethylsilyl; TMSBr: Bromotrimethylsilane; TSE: Templated stack exchange; UV-Vis: Ultraviolet-visible.

2. Synthesis

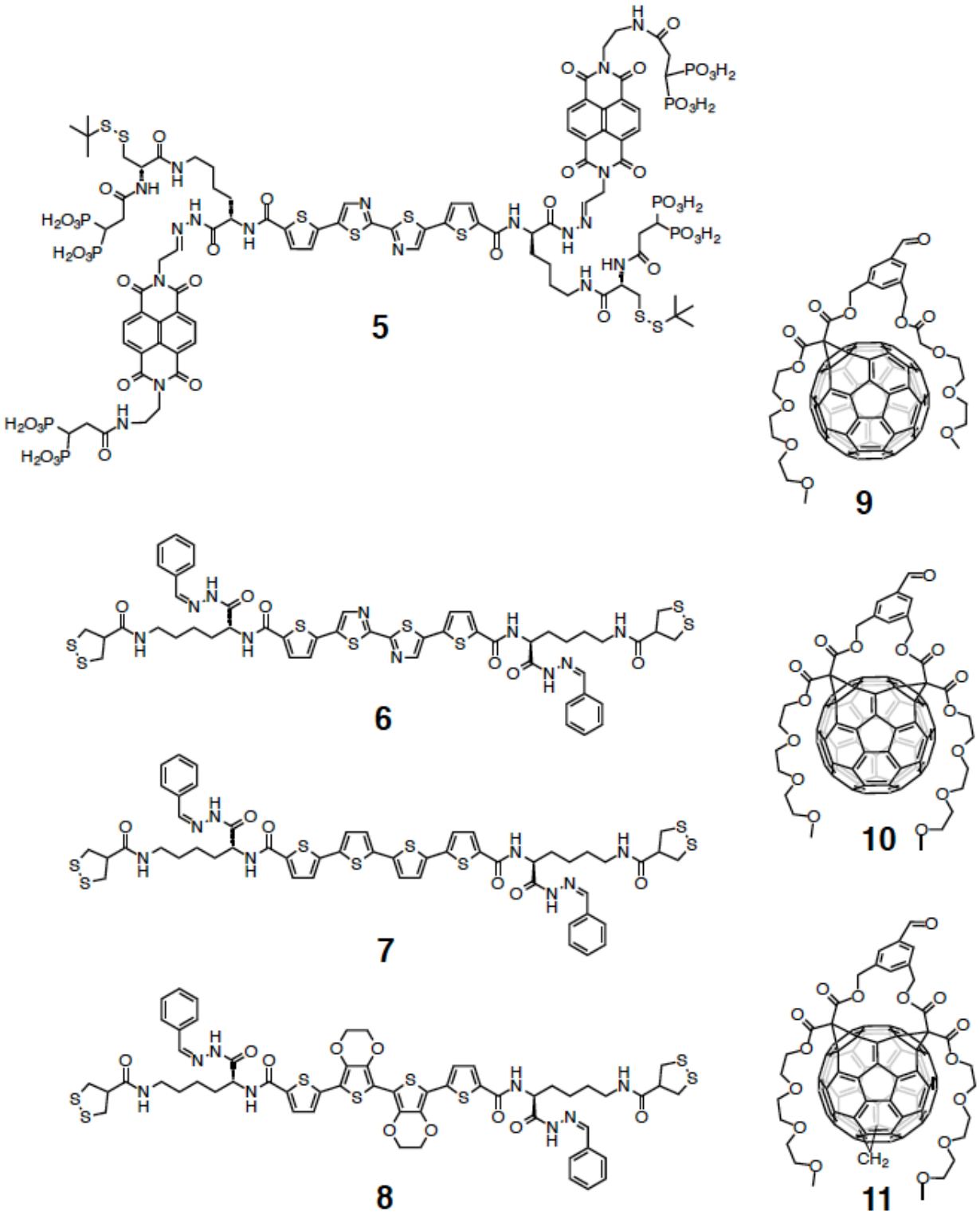
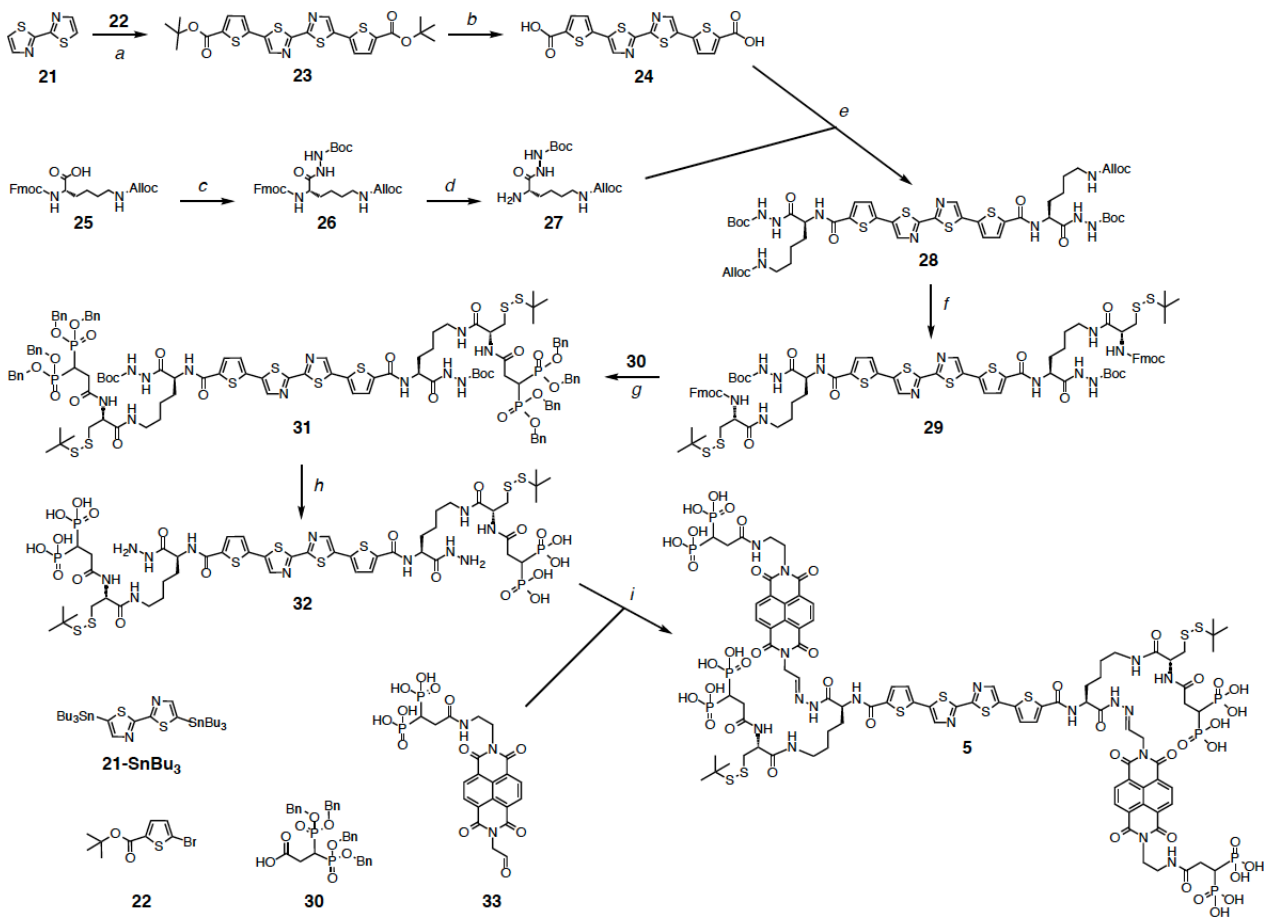


Figure S1. Full structure of all components (**5-11**) for SOSIP and TSE.

2.1. Synthesis of Initiator 5



Scheme S1. a) 1. LDA, Bu_3SnCl, THF, -78 °C – rt, 2 h; 2. **22**, $Pd(PPh_3)_4$, DMF, 80 °C, 18 h, 87% (2 steps); b) TFA, DCM, rt, 3 h, 97%; c) **25**, *tert*-Butyl carbazate, HATU, DIPEA, DMF, rt, 20 min, 98%; d) Piperidine, DMF, rt, 30 min, 98%; e) **24**, HATU, DIPEA, **27**, DMF, rt, 30 min, 86%; f) 1. $Pd(PPh_3)_2Cl_2$, $PhSiH_3$, AcOH, DCM/MeOH, rt, 30 min; 2. Fmoc-Cys(S-*t*-Bu)-OH, HATU, collidine, DMF, rt, 30 min, 80% (2 steps); g) 1. Piperidine, DMF, rt, 30 min; 2. **30**, HATU, collidine, DMF, rt, 30 min, 80% (2 steps); h) TMSBr, DCM, rt, 96%; i) **33**, TFA, DMSO, rt, 24 h, 99%.

Compound 21 was synthesized according to procedures reported in ref. S2.

Compound 22. To a solution of 5-bromo-2-thiophenecarboxylicacid (2.0 g, 9.6 mmol) in *tert*-Butyl alcohol (80 ml) at rt was added DMAP (1.2 g, 9.6 mmol). The mixture was stirred for 10 min at rt, then Di-*tert*-butyl dicarbonate (6.3 g, 29 mmol) in *tert*-Butyl alcohol (20 ml) was added. The mixture was stirred for 2 h at rt, then concentrated *in vacuo*. Flash chromatography (DCM, R_f = 0.9) gave product **22** (2.1 g, 82%) as a colorless liquid. The physical properties were identical with those reported in refs. S3 and S4.

Compound 23. To a solution of LDA (4.9 ml of 2 M in THF/heptane/ethylbenzene, 9.8 mmol) in THF (50 ml) at -78 °C under argon atmosphere was added a solution of **21** (660 mg, 3.9 mmol) in THF (10 ml) dropwise during 20 min. The mixture was stirred for 15 min at -78 °C, then Bu_3SnCl (2.7 ml, 9.8 mmol) was added dropwise, and stirring continued under argon atmosphere for 2 h at rt. Then the mixture was diluted with diethyl ether, washed successively with saturated Na_2CO_3 and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography with PE as an eluent (R_f = 0.7) gave pure **21-SnBu$_3$** (2.81 g, 97%) as a pale yellow oil. To a solution of **21-SnBu$_3$** (2.81 g, 3.8 mmol) and **22** (2.0 g, 7.6 mmol) in degassed DMF (100 ml) under argon atmosphere was added $Pd(PPh_3)_4$ (0.84 g, 0.38 mmol). The solution was stirred for 15 h at 80 °C under argon atmosphere. The mixture was concentrated *in vacuo* and purified by flash chromatography (DCM/DPE/PE/acetone 5:3:2:1, R_f = 0.6) to give pure **23** (1.80 g, 90%) as a yellow fibrous solid. Mp: > 340 °C; IR (neat): 2975 (w), 1688 (s), 1541 (w), 1495 (w), 1442 (s), 1391 (m), 1367 (m), 1297 (s), 1160 (s), 1098 (s), 1032 (m), 927 (m), 884 (m), 845 (m), 817 (s), 750 (s), 750 (s), 724 (m), 613 (m); ^{1}H NMR (500 MHz, $CDCl_3$): 8.00 (s, 2H), 7.66 (d, ^3J (H,H) = 3.9 Hz, 2H), 7.22 (d, ^3J (H,H) = 3.9 Hz, 2H), 1.60 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): 160.9 (s), 160.0 (s), 140.8 (d), 138.2 (s), 135.8 (s), 134.2 (s), 133.5 (d), 126.4 (d), 82.4 (s), 28.2 (q); MS (ESI,

$CHCl_3$/MeOH 1:1): 533 (78, $[M+H]^+$), 477 (29, $[M-Bu+H]^+$), 421 (100, $[M-2Bu+H]^+$); HRMS (ESI, +ve) calcd for $C_{24}H_{25}N_2O_4S_4$: 533.0674, found: 533.0692.

Compound 24. To a solution of **23** (530 mg, 1.0 mmol) in DCM (90 ml) was added TFA (30 ml) at rt. The mixture was stirred for 3 h at rt. The mixture was centrifuged and the precipitate was washed with 100 ml of MeOH and then with 100 ml of DCM (solid-liquid extraction). The precipitate was dissolved in 20 ml of DMF/DIPEA 1:1 mixture, and precipitated by careful addition of HCl (4 M in MeOH). The precipitate was washed successively with MeOH and Et_2O (solid-liquid extraction) and dried *in vacuo*. The pure product **24** (480 mg, 97%) as 2×HCl salt was obtained as a yellow powder. Mp: > 330 °C; IR (neat): 3108 (w), 3071 (w), 2957 (w), 2815 (w), 2526 (w), 1676 (s), 1543 (m), 1501 (m), 1446 (s), 1390 (m), 1348 (m), 1300 (s), 1154 (m), 1114 (m), 1050 (m), 931 (m), 888 (m), 864 (m), 813 (s), 748 (s), 680 (w), 605 (m); ^{1}H NMR (500 MHz, DMSO-d_6): 8.42 (s, 2H), 7.73 (d, ^3J (H,H) = 3.9 Hz, 2H), 7.60 (d, ^3J (H,H) = 3.9 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6): 162.4 (s), 162.3 (s), 159.1 (s), 141.9 (d), 137.6 (s), 134.1 (d), 133.5 (s), 127.8 (d).

Compound 26. To a solution of Fmoc-Lys(Alloc)-OH (**25**, 900 mg, 2.0 mmol) in DMF (40 ml) at rt were added DIPEA (0.70 ml, 4.0 mmol) and HATU (760 mg, 2.0 mmol). The solution was stirred for 2 min at rt, then *tert*-Butyl carbazate (540 mg, 4.1 mmol) was added, and stirring maintained for 20 min at rt. The mixture was diluted with DCM, washed successively with HCl (1 M), saturated Na_2CO_3 and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by flash chromatography (DCM/MeOH 98:2, R_f = 0.55 with DCM/MeOH 95:5) to give **26** (1.1 g, 98%) as a colorless powder. Mp: 121-122 °C; $[\alpha]^{20}_D$ −18.9 (*c* 1.00, DCM); IR (neat): 3287 (m), 2937 (w), 1686 (s), 1634 (s), 1538 (s), 1462 (s), 1369 (w), 1264 (s), 1163 (s), 1088 (w), 990

(w), 937 (w), 859 (w), 738 (s), 648 (m); ^{1}H NMR (400 MHz, $CDCl_3$): 8.49 (s, 1H), 7.75 (d, ^{3}J (H,H) = 7.4 Hz, 2H), 7.57 (d, ^{3}J (H,H) = 7.7 Hz, 2H), 7.39 (t, ^{3}J (H,H) = 7.4 Hz, 2H), 7.29 (m, 2H), 6.82 – 6.72 (m, 1H), 5.98 – 5.67 (m, 2H), 5.26 (d, ^{3}J (H,H) = 20.4 Hz, 1H), 5.16 (d, ^{3}J (H,H) = 13.8 Hz, 1H), 4.75 – 4.08 (m, 4H), 3.17 (m, 2H), 1.93 – 1.62 (m, 2H), 1.62 – 1.48 (m, 2H), 1.43 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): 171.8 (s), 156.8 (s), 156.6 (s), 155.5 (s), 143.9 (s), 141.5 (s), 133.2 (t), 127.9 (d), 127.3 (d), 125.3 (d), 120.2 (d), 117.8 (t), 82.1 (q), 67.4 (t), 65.7 (t), 53.3 (d), 47.3 (d), 40.3 (t), 32.0 (t), 29.4 (t), 28.3 (q), 22.2 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 589 (38, $[M+Na]^+$), 584 (47, $[M+NH_4]^+$), 567 (50, $[M+H]^+$), 489 (19, [M-Boc+Na]$^+$), 467 (100, [M-Boc+H]$^+$).

Compound 27. To a solution of **26** (1.1 g, 1.9 mmol) in DMF (40 ml) was added piperidine (10 ml). The mixture was stirred for 30 min at rt and then concentrated *in vacuo*. The product was washed twice with hexane (100 ml) (solid-liquid extraction), and then dissolved in a small amount of chloroform. The product precipitated by the addition of hexane (50 ml), and was separated by centrifugation. The pure product **27** (640 mg, 98%) was obtained as a viscous colorless oil. IR (neat): 3276 (m), 2931 (m), 1689 (s), 1526 (m), 1367 (m), 1241 (s), 1160 (s), 1005 (s), 926 (m), 868 (m), 760 (m); ^{1}H NMR (500 MHz, DMSO-d_6): 7.12 (t, ^{3}J (H,H) = 6.1 Hz, 1H), 5.98 – 5.84 (m, 1H), 5.28 – 5.22 (m, 1H), 5.15 (d, ^{3}J (H,H) = 10.3 Hz, 1H), 4.43 (d, ^{3}J (H,H) = 5.4 Hz, 2H), 3.09 (t, ^{3}J (H,H) = 6.3 Hz, 1H), 2.94 (m, 2H), 1.57 – 1.33 (m, 15H); ^{13}C NMR (125 MHz, DMSO-d_6): 174.9 (s), 155.8 (s), 155.2 (s), 133.8 (d), 116.8 (t), 78.9 (s), 64.1 (t), 53.2 (d), 40.2 (t), 35.0 (t), 29.3 (t), 28.0 (q), 22.4 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 689 (66, $[2M+H]^+$), 367 (18, $[M+Na]^+$), 345 (100, $[M+H]^+$), 289 (65, [M-t-Bu+H]$^+$), 245 (70, [M-Boc+H]$^+$).

Compound 28. To a solution of **24** (275 mg, 0.56 mmol) in DMF (30 ml) and DIPEA (0.63 ml, 3.4 mmol) at rt was added HATU (425 mg, 1.1 mmol). The mixture was stirred for 2 min and the formed orange suspension was added to **27** (960 mg, 2.8 mmol). After 30 min of stirring at rt, reaction mixture was diluted with DCM, washed with saturated $NaHCO_3$ and dried over Na_2SO_4. The organic phase was concentrated *in vacuo* and purified by flash chromatography (DCM/MeOH 99:1 to 97:3 R_f = 0.5 with DCM/MeOH 9:1) to give pure product **28** (520 mg, 86%) as a yellow powder. Mp: 195-198 °C; CD (DCM/MeOH 1:1): 420 (–1.08), 334 (–0.17), 292 (–1.25); IR (neat): 3252 (m), 2933 (m), 1690 (s), 1617 (m), 1525 (s), 1368 (m), 1250 (s), 1155 (s), 1013 (m), 931 (m), 842 (s), 750 (m); ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD 1:1): 7.94 (s, 2H), 7.60 (d, ^3J (H,H) = 3.9 Hz, 2H), 7.16 (d, ^3J (H,H) = 3.9 Hz, 2H), 5.95 – 5.82 (m, 2H), 5.28 (d, ^3J (H,H) = 17.2 Hz, 2H), 5.18 (d, ^3J (H,H) = 10.3 Hz, 2H), 4.58 – 4.55 (m, 2H), 4.54 – 4.50 (m, 4H), 3.17 (m, 4H), 2.01 – 1.80 (m, 4H), 1.61 – 1.56 (m, 4H), 1.53 (m, 4H), 1.48 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD 1:1): 174.2 (s), 163.5 (s), 160.9 (s), 158.7 (s), 157.4 (s), 141.8 (d), 140.1 (s), 138.6 (s), 135.7 (s), 134.3 (s), 131.1 (d), 128.1 (d), 118.3 (t), 82.5 (s), 66.6 (d), 53.7 (d), 41.5 (t), 32.4 (t), 30.3 (t), 29.1 (q), 24.1 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 1073 (13, $[M+H]^+$), 885 (63, $[M-2Boc+Na]^+$), 873 (32, $[M-2Boc+H]^+$), 841 (95, $[M-2Boc-NHNH+H]^+$), 783 (16, $[M-2BocNHNH-CO+H]^+$); MS (MALDI-TOF, DCTB): 1111 (100, $[M+K]^+$), 1095 (88, $[M+Na]^+$).

Compound 29. To a solution of **28** (360 mg, 0.33 mmol) in DCM/MeOH (1:1, 60 ml) were added $PhSiH_3$ (410 µl, 3.3 mmol), AcOH (200 µl, 3.3 mmol) and $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol). The mixture was stirred for 30 min at rt, and then DIPEA (1.7 ml, 9.9 mmol) was added. The mixture was concentrated *in vacuo*, and the residue was washed with diethyl ether (solid-liquid extraction) and dried *in vacuo*. The yellow solid residue was dissolved in DMF (25 ml) and the pH of the solution was adjusted to about 8 by addition of collidine. The resulting mixture was added to

a solution of Fmoc-Cys(S-*t*-Bu)-OH (710 mg, 1.65 mmol), collidine (1.1 ml, 8.25 mmol) and HATU (630 mg, 1.65 mmol) in DMF (10 ml). The combined mixture was stirred for 30 min at rt, then diluted with DCM, washed successively with HCl (1 M), brine, saturated $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 97:3 to 95:5, R_f = 0.55 with DCM/MeOH 9:1) gave pure **29** (460 mg, 80%) as a yellow solid. Mp: 145-146 °C; CD (DCM/MeOH 1:1): 422 (–1.53), 378 (+0.20), 294 (–0.66); IR (neat): 3251 (w), 2962 (w), 1842 (w) 1683 (s), 1620 (s), 1551 (s), 1447 (m), 1364 (m), 1237 (m), 1160 (m), 1043 (m), 933 (m), 739 (m); ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 1:1): 7.88 (s, 2H), 7.67 (d, ^3J (H,H) = 7.4 Hz, 4H), 7.59 (d, ^3J (H,H) = 3.9 Hz, 2H), 7.55 (d, ^3J (H,H) = 7.4 Hz, 4H), 7.29 (t, ^3J (H,H) = 7.4 Hz, 4H), 7.21 (t, ^3J (H,H) = 7.4 Hz, 4H), 7.11 (d, ^3J (H,H) = 3.9 Hz, 2H), 4.50-4.10 (m, 10H), 3.20-3.10 (m, 4H), 3.05-2.80 (m, 4H), 1.90-1.45 (m, 12H), 1.41 (s, 18H), 1.31 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$/CD_3OD 1:1): 172.1 (s), 163.0 (s), 160.5 (s), 157.6 (s), 157.6 (s), 156.9 (s), 144.7 (s), 142.1 (d), 141.4 (s), 139.7 (s), 138.1 (s), 135.1 (s), 130.5 (d), 128.4 (d), 127.8 (d), 127.8 (d), 127.7 (d), 125.9 (d), 120.6 (d), 81.8 (s), 67.8 (t), 55.6 (s), 53.2 (s), 49.6 (s), 47.9 (d), 43.2 (t), 39.8 (t), 32.0 (t), 30.1 (q), 29.3 (t), 28.5 (q), 23.7 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 1731 (40, $[M+H]^+$), 1631 (20, $[M\text{-}Boc+H]^+$), 1531 (80, $[M\text{-}2Boc+H]^+$), 1500 (100, $[M\text{-}2Boc\text{-}NHNH_2+H]^+$), 1468 (60, $[M\text{-}2BocNHNH_2+H]^+$); MS (MALDI-TOF, DHB): 1753 (100, $[M+Na]^+$).

Compound 30 was synthesized according to procedures reported in ref. S5.

Compound 31. To a solution of **29** (310 mg, 0.18 mmol) in DMF (20 ml) was added piperidine (20 ml). The mixture was stirred for 30 min at rt, concentrated *in vacuo*, and the residue was washed with diethyl ether (solid-liquid extraction). The yellow solid residue was dissolved in

DMF (25 ml) and the pH of the solution was adjusted to about 8 by addition of collidine then mixed with a solution of **30** (660 mg, 1.1 mmol) and collidine (590 µl, 4.5 mmol) and HATU (420 mg, 1.1 mmol) in DMF (10 ml) stirred for 2 min at rt. The combined mixture was stirred for 30 min at rt, then diluted with DCM, washed successively with 1 M HCl, brine, saturated $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 97:3 to 94:6, R_f = 0.6 with DCM/MeOH 9:1) afforded pure **31** (350 mg, 80%) as a yellow solid. Mp: 165-166 °C; CD (DCM): 468 (+3.49), 399 (-6.42), 304 (+1.05); IR (neat): 3262 (w), 3113 (w), 2952 (w), 1843 (s), 1682 (s), 1620 (s), 1541 (s), 1447 (m), 1237 (s), 1159 (m), 1042 (m), 951 (m), 842 (m), 740 (m); ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ 1:1): 8.08 (s, 2H), 7.77 (d, ^3J (H,H) = 3.9 Hz, 2H), 7.32 – 7.27 (m, 42H), 5.04 – 4.94 (m, 16H), 4.63 – 4.59 (m, 4H), 3.45 (tt, ^3J (H,H) = 5.5 Hz, ^2J (H,P) = 23.9 Hz, 2H), 3.22 – 3.15 (m, 6H), 2.93 – 2.87 (m, 2H), 2.71 (dt, ^3J (H,H) = 5.7 Hz, ^3J (H,P) = 16.9 Hz, 4H), 1.92 – 1.42 (m, 12H), 1.41 (s, 18H), 1.31 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ 1:1): 173.9 (s), 171.8 (s), 171.4 (d, ^{P}t, ^3J (C,P) = 7.3 Hz), 163.1 (s), 160.5 (s), 160.4 (s), 157.1 (s), 141.6 (d), 140.0 (s), 138.1 (s), 136.9 (s, ^{P}m), 135.3 (s), 130.7 (d), 129.4 (d), 129.1 (d), 129.0 (d), 128.9 (d), 128.8 (d), 127.8 (d), 81.7 (s), 69.5 (t, ^{P}dd, ^2J (C,P) = 18.7 Hz, ^4J (C,P) = 7.5 Hz), 54.6 (d), 53.4 (d), 49.6 (s), 42.6 (t), 40.0 (t), 33.4 (d, ^{P}t, ^1J (C,P) = 140 Hz), 32.1 (d, ^{P}t, ^2J (C,P) = 4.3 Hz), 32.0 (t), 30.1 (q), 29.3 (t), 28.5 (q), 23.9 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 2462 (20, $[M+Na]^+$), 2439 (40, $[M+H]^+$), 2339 (35, $[M-Boc+H]^+$), 2239 (30, $[M-2Boc+H]^+$), 1220 (50, $[M+2H]^{2+}$), 1120 (100, $[M-2Boc+2H]^{2+}$); MS (MALDI-TOF, HABA): 2462.48 (100, $[M+Na]^+$).

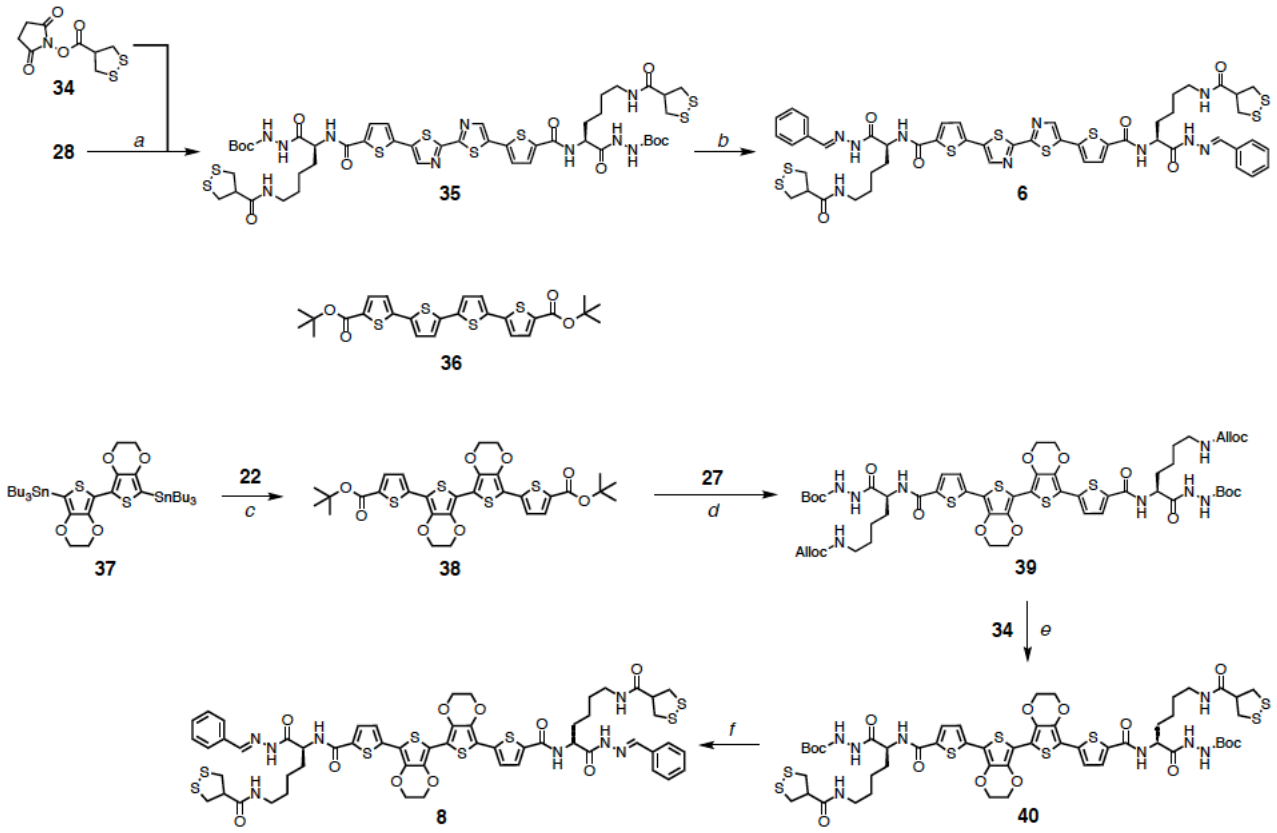
Compound 32. To a solution of **31** (100 mg, 41 µmol) in DCM (5.0 ml) was added TMSBr (110 µl, 820 µmol) at rt. The mixture was stirred for 2 h at rt and concentrated *in vacuo*. The residue was dissolved in MeOH and the mixture was stirred for 2 h at rt and concentrated *in vacuo*.

The residue was washed with diethyl ether (solid-liquid extraction) and dried *in vacuo* to afford **32** (60 mg, 96%) as a yellow solid. Mp: 165-166 °C; IR (neat): 2913 (w), 1832 (m), 1661 (s), 1451 (m), 1344 (s), 1241 (s), 1074 (m), 928 (m); ^{1}H NMR (400 MHz, DMSO-d_6): 8.29 (s, 2H), 7.98 (d, ^{3}J (H,H) = 3.9 Hz, 2H), 7.54 (d, ^{3}J (H,H) = 3.9 Hz, 2H), 4.49 – 4.39 (m, 4H), 3.20 – 2.84 (m, 8H), 2.82 – 2.54 (m, 6H), 1.70 – 1.30 (m, 12H), 1.25 (s, 18H); ^{13}C NMR (125 MHz, DMSO-d_6): 171.7 (s), 171.0 (s, ^{P}t, ^{3}J (C,P) = 7.5 Hz), 169.9 (s), 161.4 (s), 159.5 (s), 159.4 (s), 159.1 (s), 141.8 (d), 139.8 (s), 136.6 (s), 134.2 (s), 130.6 (d), 128.0 (d), 53.1 (d), 52.5 (d), 47.9 (s), 42.2 (t), 38.8 (t), 34.9 (d, ^{P}t, ^{1}J (C,P) = 122 Hz), 32.0 (t), 30.9 (t), 29.8 (q), 28.8 (t), 23.3 (t); MS (MALDI-TOF, sinapic acid): 1517 (100, $[M-H]^-$).

Compounds 33 was synthesized according to procedures reported in ref. S1.

Compound 5. A solution of **32** (15 mg, 10 μmol) and **33** (12 mg, 22 μmol) in DMSO (1.0 ml) and TFA (100 μl) was stirred for 24 h at rt. The mixture was diluted by diethyl ether, centrifuged and the supernatant was discarded. The residue was washed three times with diethyl ether (solid-liquid extraction) and dried *in vacuo* to afford **5** (26 mg, 99%) as a yellow solid. MS (MALDI-TOF, sinapic acid): 2615 (100, $[M-H]^-$).

2.2. Synthesis of Propagator 6



Scheme S2. a) 1. **28**, $Pd(PPh_3)_2Cl_2$, $PhSiH_3$, AcOH, DCM/MeOH, rt, 30 min; 2. **34**, DIPEA, DMF, rt, 30 min, 74% (2 steps); b) TFA, thioanisole, benzaldehyde, DCM, rt, 3 h, 85%; c) **22**, **37**, $Pd(PPh_3)_4$, THF, reflux, 48 h, 49%; d) 1. TFA, DCM, rt, 2 h; 2. **27**, HATU, DIPEA, DMF, rt, 30 min, 79% (2 steps); e) 1. $Pd(PPh_3)_2Cl_2$, $PhSiH_3$, *p*-nitrophenol, DCM/MeOH, rt, 30 min; 2. **34**, TEA, DMF, rt, 40 min, 69% (2 steps); f) TFA, thioanisole, benzaldehyde, DCM, rt, 2 h, 55%.

Compound 34. This compound was prepared following the literature procedures.[S6-S8]

Compound 35. To a solution of **28** (120 mg, 0.11 mmol) in DCM/MeOH (1:1, 20 ml) were added $PhSiH_3$ (135 µl, 1.10 mmol), AcOH (60 µl, 1.10 mmol) and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). The mixture was stirred for 30 min at rt and DIPEA was added (575 µl, 3.30 mmol). The

mixture was concentrated *in vacuo*, and the residue was washed with diethyl ether (solid-liquid extraction) and then dried *in vacuo*. The yellow solid residue was dissolved in DMF (10 ml) in a flask covered by aluminum foil, the pH of the solution was adjusted to about 8 by addition of DIPEA and mixed with **34** (110 mg, 0.44 mmol). The mixture was stirred for 30 min at rt, then concentrated *in vacuo*. The residue was purified by flash chromatography (DCM/MeOH 98:2 to 93:7, R_f = 0.5 with DCM/MeOH 9:1) to afford pure product **35** (95 mg, 74%) as a yellow solid. Mp: >220 °C; CD (DCM/MeOH 1:1): 475 (0.18), 406 (–1.18), 342 (–0.21), 294 (–0.74); IR (neat): 3261 (w), 2928 (w), 1730 (w), 1646 (s), 1624 (s), 1551 (s), 1441 (m), 1388 (w), 1367 (m), 1346 (w), 1304 (m), 1243 (s), 1158 (s), 1046 (w), 1019 (w), 930 (w), 850 (w), 819 (w), 751 (w), 630 (m), 610 (m), 576 (m), 551 (m); ^{1}H NMR (500 MHz, DMSO-d_6): 9.78 (brs, 2H), 8.76 (brd, ^3J (H,H) = 8.1 Hz, 2H), 8.35 (s, 2H), 8.07 (brt, ^3J (H,H) = 5.6 Hz, 2H), 7.97 (d, ^3J (H,H) = 4.0 Hz, 2H), 7.58 (d, ^3J (H,H) = 3.8 Hz, 2H), 4.49 – 4.40 (m, 2H), 3.35 – 3.30 (m, 4H), 3.16 – 3.05 (m, 10H), 1.75 – 1.66 (m, 4H), 1.48 – 1.41 (m, 6H), 1.39 (s, 18H), 1.36 – 1.31 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): 171.2 (s), 170.1 (s), 160.4 (s), 158.8 (s), 155.1 (s), 141.4 (d), 140.2 (s), 135.7 (s), 133.8 (s), 129.7 (d), 127.7 (d), 79.1 (s), 64.9 (s), 51.6 (d), 51.5 (d), 41.9 (t), 38.6 (t), 31.5 (t), 28.5 (t), 28.1 (q), 22.9 (t); MS (ESI, $CHCl_3$/MeOH 1:1): 1169 (25, $[M+H]^+$), 969 (60, $[M\text{-}2Boc+H]^+$), 937 (100, $[M\text{-}2Boc\text{-}NHNH_2+H]^+$), 905 (80, $[M\text{-}2BocNHNH_2+H]^+$).

Compound 6. In a flask covered with aluminum foil, a solution of **35** (95 mg, 80 μmol) and thioanisole (4.0 ml) in TFA (610 μl, 8.0 mmol) and DCM (4.0 ml) was stirred for 2 h at rt. To the mixture was added benzaldehyde (4.1 ml, 40 mmol). The mixture was stirred for 1 h at rt, then concentrated *in vacuo*. The residue was purified by flash chromatography (DCM/MeOH 97:3 to 94:6, R_f = 0.6 with DCM/MeOH 9:1) to give pure product **6** (78 mg, 85%) as a yellow solid. Mp: 183-185 °C; CD (DCM/MeOH 1:1): 440 (+1.56), 378 (+0.10), 292 (+6.88); IR (neat): 3259 (w),

2930 (w), 1842 (s), 1621 (s), 1589 (s), 1547 (s), 1407 (m), 1240 (m), 1196 (m), 898 (m), 783 (m); ^{1}H NMR (400 MHz, DMSO-d_6): 11.68 (s, 1H), 11.45 (s, 1H), 8.88 (brd, ^{3}J (H,H) = 7.7 Hz, 1H), 8.75 (brd, ^{3}J (H,H) = 8.1 Hz, 1H), 8.38 (d, 1H), 8.37 (d, 1H), 8.26 (brt, ^{3}J (H,H) = 5.7 Hz, 2H), 8.05 – 8.00 (m, 3H), 7.71 – 7.68 (m, 4H), 7.62 – 7.60 (m, 2H), 7.49 – 7.41 (m, 6H), 5.35 – 5.31 (m, 1H), 4.53 – 4.46 (m, 1H), 3.37 – 3.29 (m, 4H), 3.16 – 3.08 (m, 10H), 1.90 – 1.72 (m, 4H), 1.60 – 1.40 (m, 8H); ^{13}C NMR (125 MHz, DMSO-d_6): 173.1 (s), 170.1 (s), 168.2 (s), 160.7 (s), 158.8 (s), 147.1 (d), 143.4 (d), 141.5 (d), 141.4 (s), 140.2 (s), 140.0 (s), 135.8 (s), 135.7 (s), 134.2 (s), 134.1 (s), 133.8 (s), 133.7 (s), 130.0 (d), 129.8 (d), 129.6 (d), 128.9 (d), 128.8 (d), 127.7 (d), 127.0 (d), 126.7 (d), 52.6 (d), 51.5 (d), 49.9 (d), 42.0 (t), 41.9 (t), 38.5 (t), 31.1 (t), 30.1 (t), 28.6 (t), 28.5 (t), 23.1 (t), 23.0 (d); MS (ESI, $CHCl_3$/MeOH 1:1): 1167 (25, $[M+Na]^+$), 1145 (60, $[M+H]^+$), 1025 (50, $[M\text{-BenzylimineNHNH}_2+H]^+$), 905 (100, $[M\text{-2xBenzylimineNHNH}_2+H]^+$).

2.3. Synthesis of Propagator 7

Compound 7 was synthesized from **36** according to procedures reported in ref. S9.

2.4. Synthesis of Propagator 8

Compound 37 was synthesized according to procedures reported in ref. S10.

Compound 38. A solution of **22** (1.2 g, 4.4 mmol) and **37** (0.50 g, 1.8 mmol) in dry THF (60 ml) was deaerated under vacuum and backfilled with argon three times prior to the addition of $Pd(PPh_3)_4$ (210 mg, 0.18 mmol). The reaction mixture was refluxed for 48 h, diluted with DCM and washed with 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/Hexane 2:1, R_f = 0.4)

resulted the pure product **38** (0.56 g, 49%). Mp: >220 °C; IR (neat): 1688 (s), 1433 (s), 1358 (m), 1326 (m), 1294 (s), 1167 (m), 1097 (s), 1069 (s), 931 (w), 851 (w), 791 (w), 746 (m); ^{1}H NMR (400 MHz, DMSO-d_6): 7.64 (d, ^{3}J (H,H) = 4.0 Hz, 2H), 7.25 (d, ^{3}J (H,H) = 4.0 Hz, 2H), 4.54 – 4.47 (m, 8H), 1.54 (s, 18H); ^{13}C NMR (100 MHz, DMSO-d_6): 161.1 (s), 140.6 (s), 139.5 (s), 138.2 (s), 134.2 (d), 131.9 (s), 123.2 (d), 109.2 (s), 108.4 (s), 81.9 (s), 65.8 (t), 65.7 (t), 28.3 (q); MS (ESI, MeOH/DCM 1:1): 647 (100, $[M+H]^+$), 591 (88, $[M-Bu+H]^+$), 535 (44, $[M-2Bu+H]^+$); HRMS (ESI, +ve) calcd for $C_{30}H_{30}O_8S_4$: 647.0896, found: 647.0919.

Compound 39. Compound **38** (0.55 g, 0.85 mmol) was dissolved in DCM (10 ml) and TFA (4.0 ml). The reaction mixture was stirred at rt for 2.5 h. The mixture was concentrated *in vacuo*, washed with diethyl ether (solid-liquid extraction), and dried *in vacuo*. The residue was dissolved in DMF (10 ml) and then were added HATU (0.65 g, 1.7 mmol) and DIPEA (0.85 ml, 5.1 mmol). After 5 min of stirring, a solution of **27** in DMF (4.0 ml) was added to the reaction mixture. The mixture was stirred for 40 min, and the solvent was removed *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 96:4, R_f = 0.15) gave compound **39** (0.79 g, 79 %) as an orange solid. Mp: 157-158 °C; CD (DCM/MeOH 1:1): 456 (–0.43), 362 (+0.18), 312 (–0.10); IR (neat): 3211 (w), 1690 (m), 1612 (s), 1554 (s), 1515 (m), 1478 (s), 1446 (s), 1427 (m), 1365 (m), 1344 (w), 1320 (m), 1242 (s), 1163 (m), 1081 (s), 936 (w), 843 (s), 611 (m), 592 (w), 557 (s); ^{1}H NMR (400 MHz, DMSO-d_6): 9.76 (s, 2H), 8.77 (s, 2H), 8.50 (d, ^{3}J (H,H) = 8.4 Hz, 2H), 7.89 (d, ^{3}J (H,H) = 4.0 Hz, 2H), 7.25 (d, ^{3}J (H,H) = 4.0 Hz, 2H), 7.18 (br t, ^{3}J (H,H) = 8.0 Hz, 2H), 5.94 – 5.85 (m, 2H), 5.29 – 5.23 (m, 2H), 5.17 – 5.13 (m, 2H), 4.49 (br s, 8H), 4.46 – 4.40 (m, 6H), 2.97 (m, 4H), 1.75-1.69 (m, 4H), 1.43 – 1.31 (m, 26H); ^{13}C NMR (100 MHz, DMSO-d_6): 172.0 (s), 161.4 (s), 156.3 (s), 155.6 (s), 138.9 (s), 138.6 (s), 138.0 (s), 137.3 (s), 134.3 (d), 129.7 (d), 123.2 (d), 117.3 (t), 109.4 (s), 107.8 (s), 79.5 (s), 65.7 (t), 64.6 (t), 52.1 (d), 39.4 (t), 32.0 (t), 29.6 (t),

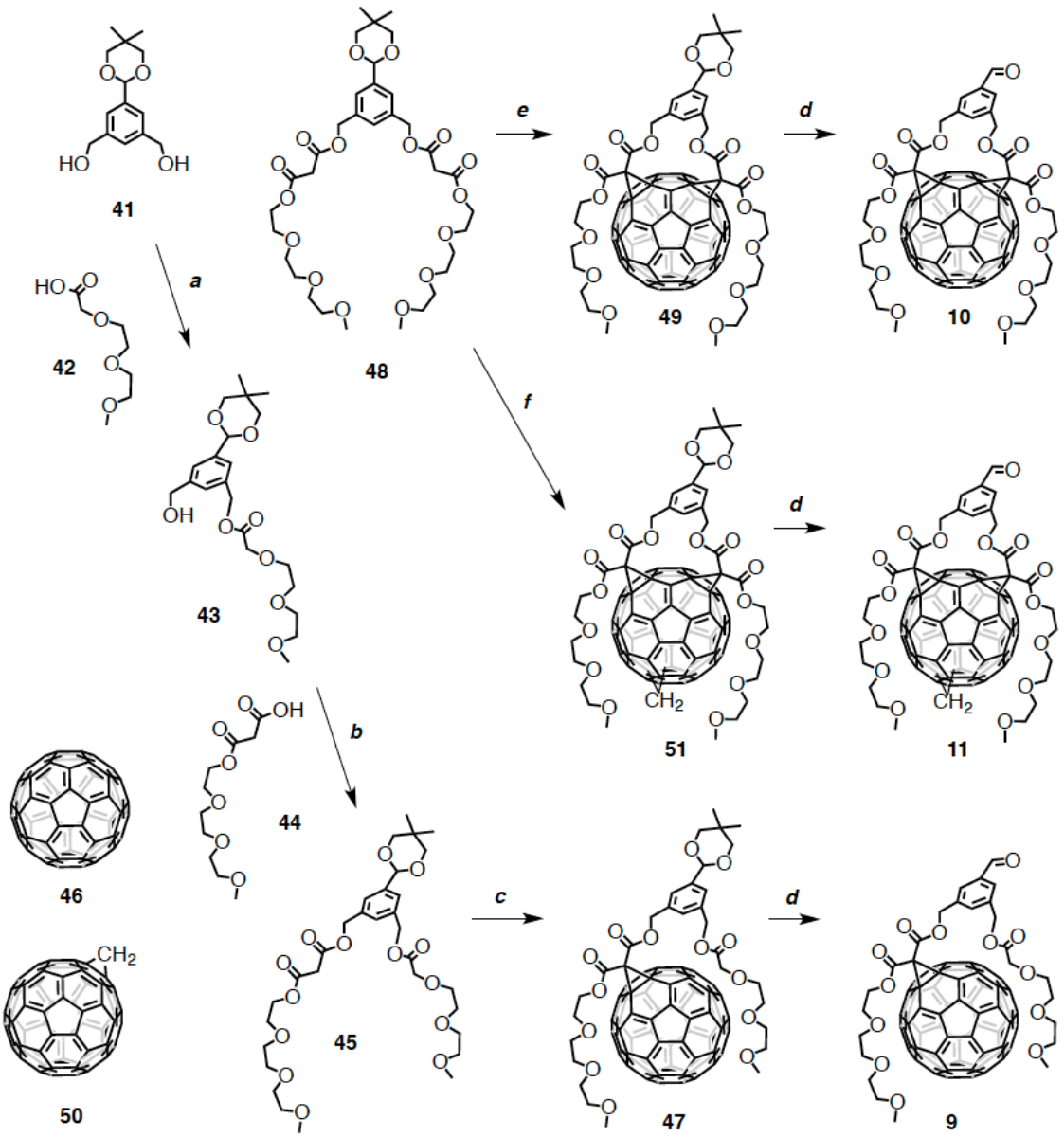
28.5 (q), 23.4 (t); MS (ESI, MeOH/DCM 1:1): 1188 (62, $[M+H]^+$), 1055 (97, $[M\text{-BocNHNH+H}]^+$), 956 (100, $[M\text{-2Boc-NHNH+H}]^+$).

Compound 40. A solution of **39** (200 mg, 0.17 mmol), $PhSiH_3$ (0.21 ml, 1.7 mmol) and *p*-nitorophenol (240 mg, 1.7 mmol) in DCM/MeOH 3:1 (40 ml) was stirred at rt for 0.5 h. The mixture was concentrated, and the residue was washed with diethyl ether. The residue was diluted with DMF (4.0 ml) and the pH of the solution was adjusted to about 8 by the addition of TEA. To the mixture was added **34** (170 mg, 0.69 mmol). The mixture was stirred for 40 min, then diluted with DCM and washed successively with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography of the residue (DCM/MeOH 95:4, $R_f = 0.2$) gave product **40** (0.15 g, 69%) as an orange solid. Mp: 176-177 °C; CD (DCM/MeOH 1:1): 458 (–1.37), 414 (1.14), 288 (–0.80); IR (neat): 3271 (w), 2929 (w), 1728 (w), 1618 (m), 1540 (s), 1512 (m), 1476 (s), 1435 (s), 1362 (s), 1302 (m), 1237 (s), 1157 (s), 1077 (s), 935 (w), 884 (w), 811 (w), 745 (w), 610 (w), 570 (w), 554 (w); ^{1}H NMR (500 MHz, DMSO-d_6): 9.74 (br s, 2H), 8.75 (br s, 2H), 8.47 (d, ^3J (H,H) = 8.8 Hz, 2H), 8.10 (t, ^3J (H,H) = 5.7 Hz, 2H), 7.87 (d, ^3J (H,H) = 4.0 Hz, 2H), 7.87 (d, ^3J (H,H) = 4.0 Hz, 2H), 4.47 (br s, 8H), 4.45 – 4.39 (m, 2H), 3.29 – 3.27 (m, 2H), 3.10 – 3.02 (m, 10H) 1.71 – 1.68 (m, 4H), 1.44 – 1.37 (m, 26H); ^{13}C NMR (125 MHz, DMSO-d_6): 171.4 (s), 170.1 (s), 160.9 (s), 155.1 (s), 138.4 (s), 138.1 (s), 137.5 (s), 136.7 (s), 129.2 (d), 122.7 (d), 108.9 (s), 107.3 (s), 79.1 (s), 65.2 (t), 51.6 (d), 51.4 (d), 42.0 (t), 38.6 (t), 31.5 (t), 28.5 (t), 28.0 (q), 22.9 (t); MS (ESI, MeOH/DCM 1:1): 1151 (100, $[M\text{-BocNHNH+H}]^+$), 1283 (79, $[M+H]^+$), 1183 (54, $[M\text{-Boc+H}]^+$).

Compounds 8. A solution of **40** (56 mg, 0.043 mmol) and thioanisole (0.70 ml, 6.2 mmol) in TFA (0.70 ml) and DCM (2.0 ml) was stirred for 1 h at rt. To the mixture was added benzaldehyde (0.54 g, 5.1 mmol). After 1 h of stirring, the mixture was diluted with DCM, washed with sat.

$NaHCO_3$ aq. and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was washed with diethyl ether (solid-liquid extraction) to give compound **8** (30 mg, 55%) as an orange solid (DCM/MeOH 95:5, R_f = 0.35). Mp: 177-178 °C; CD (DCM/MeOH 1:1): 474 (+2.71), 430 (–0.19), 402 (+1.12), 378 (+0.53), 356 (+0.98), 312 (–1.08), 286 (+6.70); IR (neat): 3287 (w), 2932 (w), 1667 (w), 1642 (m), 1612 (w), 1538 (w), 1479 (w), 1435 (m), 1361 (w), 1264 (w), 1111 (s), 1084 (s), 996 (m), 937 (m), 886 (w), 852 (w), 808 (w), 757 (w), 693 (m), 637 (s), 614 (s), 571 (m), 540 (m); ^{1}H NMR (500 MHz, DMSO-d_6): 11.7 (s, 1H), 11.4 (s, 1H), 8.69 (d, ^3J (H,H) = 7.8 Hz, 1H), 8.56 (d, ^3J (H,H) = 8.1 Hz, 1H), 8.27 (s, 1H), 8.13 (t, ^3J (H,H) = 5.8 Hz, 1H), 8.03 (s, 1H), 7.93 – 7.91 (m, 2H), 7.71 – 7.68 (m, 4H), 7.49 – 7.42 (m, 6H), 7.27 (d, ^3J (H,H) = 3.9 Hz, 2H), 5.33 – 5.29 (m, 1H), 4.49 (br s, 8H), 4.47 – 4.43 (m, 1H), 3.37 – 3.34 (m, 2H), 3.18 – 3.04 (m, 10H), 1.81 – 1.76 (m, 4H), 1.56 – 1.39 (m, 8H); ^{13}C NMR (125 MHz, DMSO-d_6): 173.4 (s), 170.2 (s), 170.1 (s), 168.4 (s), 161.2 (s), 161.1 (s), 147.0 (d), 143.3 (d), 138.5 (s), 138.4 (s), 138.2 (s), 138.1 (s), 137.5 (s), 136.8 (s), 136.6 (s), 134.2 (s), 134.1 (s), 130.0 (d), 129.9 (d), 129.3 (d), 129.2 (d), 128.9 (d), 128.8 (d), 127.0 (d), 126.7 (d), 122.7 (d), 108.9 (s), 107.4 (s), 107.3 (s), 65.2 (t), 52.5 (d), 51.6 (d), 49.8 (d), 42.0 (t), 38.6 (t), 31.1 (t), 30.1 (t), 28.6 (t), 28.5 (t), 23.2 (t), 23.1 (t); MS (ESI, MeOH/DCM 1:1): 1139 (100, $[M\text{-}C_7H_7N_2+H]^+$), 1259 (50, $[M+H]^+$); MS (MALDI, DCTB): 1258 (100, $[M+H]^+$).

2.5. Synthesis of Stack Exchangers 9, 10 and 11



Scheme S3. a) **42**, EDC, DMAP, dry DCM, 18 h, 0 ºC to rt, 57%; b) **44**, EDC, DMAP, dry DCM, 18 h, 0 ºC to rt, 66%; c) **46**, DBU, I_2, dry PhMe, 1 h, rt, 64%; d) TFA, H_2O, DCM, 4 h, rt, **9**: 52%, **10**: 50%, **11**: 56%; e) **46**, DBU, I_2, dry PhMe, 12 h, rt, 39%; f) **50**, DBU, I_2, dry PhMe, 10 min, 0 ºC to rt, 40%; *Note*: **11**, and **51** are mixtures of regioisomers.[S11]

These compounds were prepared as described in ref. S11.

3. Absorption, Emission and Redox Potentials

UV-vis absorption spectra and emission spectra of **23**, **36** and **38** were recorded in dichloromethane (Fig. S2).

Oxidation and reduction potentials of **23**, **36** and **38** were determined using cyclic voltammetry (scan rate 100 mV/s) and DPV *vs* Fc^+/Fc in dichloromethane (Fig. S3, supporting electrolyte: 100 mM Bu_4NPF_6, working electrode: Pt disk, counter electrode: Pt wire, reference electrode: Ag/AgCl). HOMO and LUMO energies *vs* vacuum were calculated from the $E_{1/2}$ of oxidation waves using equation (S1).[S12]

$$E_{\mathrm{HOMO/LUMO}} = -5.1\ \mathrm{eV} - E_{1/2}\ \mathrm{vs}\ (\mathrm{Fc}^+/\mathrm{Fc}) \qquad \text{(S1)}$$

The optical bands gap E_g^{opt} were estimated from intersection ($\lambda_{\mathrm{intersection}}$) of normalized UV-vis absorption and emission spectra using the equation (S2).

$$E_{\mathrm{g}}^{\mathrm{opt}} = 1240 / \lambda_{\mathrm{intersection}}\,(\mathrm{nm}) \qquad \text{(S2)}$$

These results are summarized in the Table S1 together with the previously reported spectroscopic and electrochemical data for **9**, **10** and **11**.

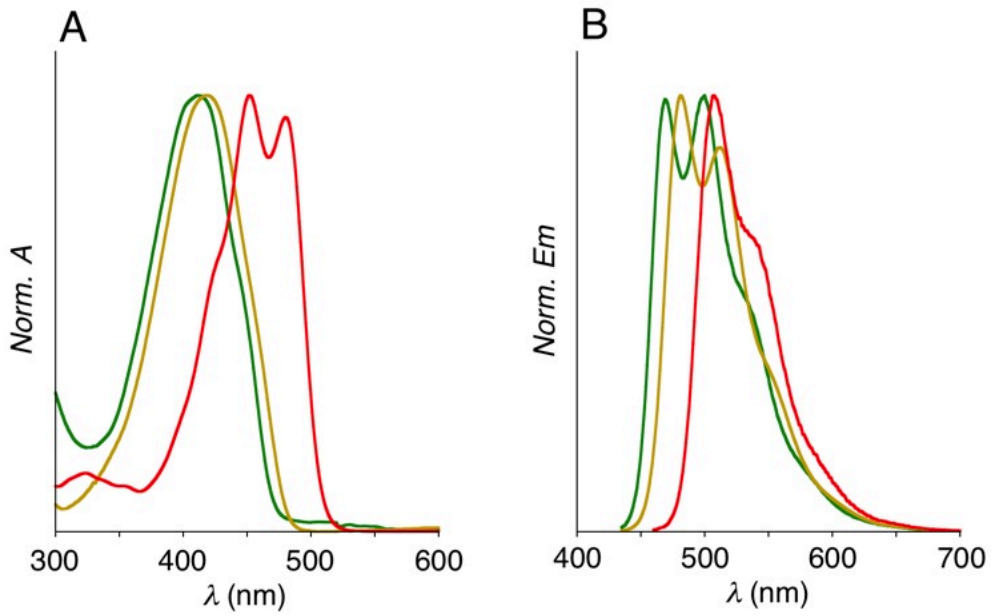


Figure S2. Normalized (A) absorption and (B) emission spectra of **23** (green line), **36** (yellow line), and **38** (red line).

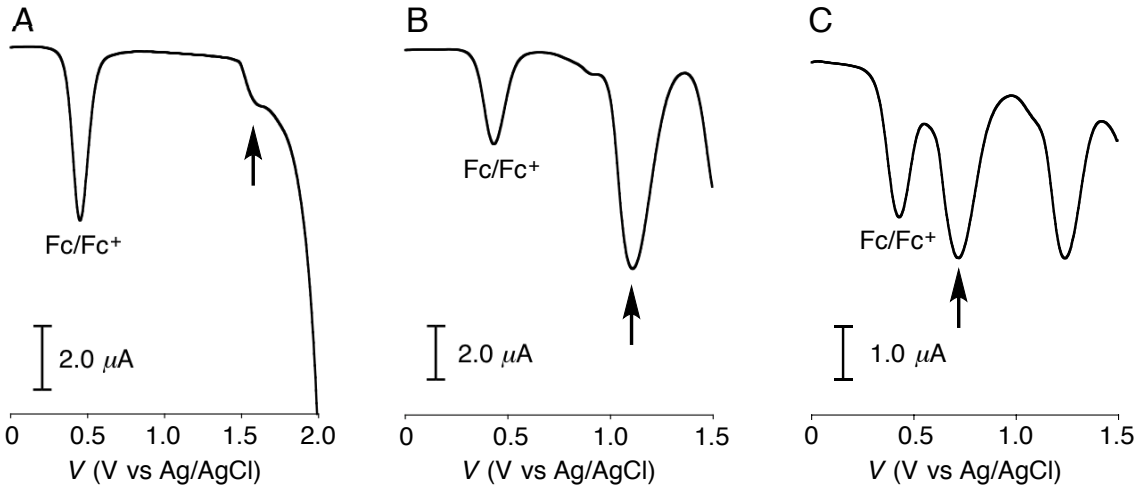


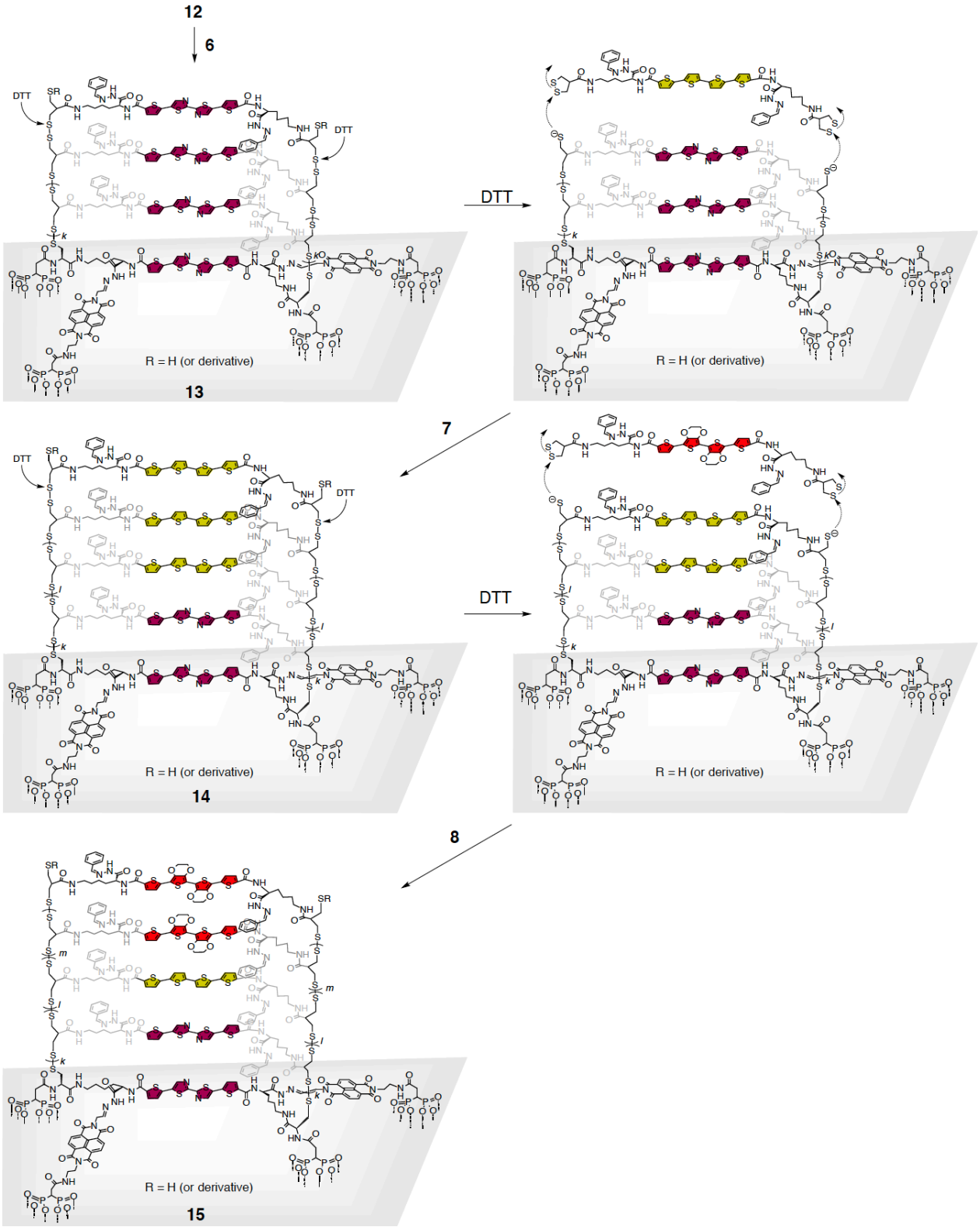
Figure S3. DPV curves of (A) **23**, (B) **36**, and (C) **38**. Black Arrows show the first oxidation potentials (E_{ox1} vs Ag/AgCl) of the compound.

Table S1. Electrochemical and spectroscopic data.

Cpd	λ_{max}/nm[a] (ε/mM^{-1}cm^{-1})	λ_{em}/nm[b]	E_{ox1} /V[c]	E_{HOMO} /eV	E_{red1} /V[c]	E_{LUMO} /eV	E_g^{opt} /eV
23	411 (43)	469 500	+1.13	-6.23[d]	–[e]	-3.50[f]	2.73
36	420 (40)	481 512	+0.68	-5.78[d]	–[e]	-3.12[f]	2.66
38	452 (45) 480 (44)	507 540 (br)	+0.29	-5.39[d]	–[e]	-2.88[f]	2.51
9[g]	328 (48)	–[e]	–[e]	–6.4[h]	–1.05	–4.05[d]	–[e]
10[i]	315 (57)	–[e]	–[e]	–6.3[h]	–1.11	–3.99[d]	–[e]
11[g]	315 (25)	–[e]	–[e]	–6.2[h]	–1.23	–3.87[d]	–[e]

[a]Wavelengths at absorption maxima in DCM; [b]Wavelengths at emission maxima in DCM by exciting at λ_{max}; [c]*V vs* Fc^+/Fc; [d]Estimated by – 5.1 + $E_{ox/red}$; [e]Not measured; [f]Estimated by $E_{HOMO} + E_g^{opt}$; [g]Taken from ref. S11; [h]Estimated by – 2.3 + E_{LUMO}; [i]Taken from ref. S21.

4. Self-Organizing Surface-Initiated Polymerization



Scheme S4. Schematic representation of SOSIP and proposed chemical structures of **13**-**15**.

4.1. Initiation

Initiator **5** was deposited on ITO electrodes as reported.[S1] Namely, ITO electrodes (~1 × 2 cm^2) were cleaned in the RCA solution (H_2O/24% NH_4OH/30% H_2O_2 5:1:1, 60 ºC, 15 min), rinsed with bidistilled water and EtOH, dried under argon flow and immersed in the solution of **5** (1 mM in DMSO). The coated electrodes were tested for pin holes by measuring CV of potassium ferricyanide (2 mM $K_3Fe(CN)_6$, 1 M KNO_3) using the covered ITO as a working electrode (Pt wire as a counter and Ag/AgCl as a reference; Fig. S4bA).[S13] Complete disappearance of the redox wave after 1 day of 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 °C to achieve better bonding between diphosphonates and ITO substrate. The CVs of the bound initiator were obtained using the ITO electrode as a working electrode, Pt wire as a counter electrode and Ag/AgCl as a reference electrode in 100 mM Bu_4NPF_6 in DCM (for oxidation potential) and in 200 mM Na_2SO_4 in H_2O (for reduction potential) (Fig. S4bB). The observed linear dependence of the peak currents to the scan rate (Fig. S4bC) confirmed the presence of redox active **5** on the electrode surface. Surface coverage Γ was estimated from the charge Q (μC/cm^2) of the oxidation wave using the equation (S3)[S14]

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

in which n is the number of electrons, F the Faraday constant and A the area of the electrode. The obtained Γ = 0.024 nmol/cm^2 (0.14 molecule/nm^2) is consistent with the nearly complete coverage of the surface by the initiator anchored with all phosphonate groups to the surface.

The electrodes were activated by a treatment with DTT (20 mM in 10 mM NH_4HCO_3aq) for 1 h at rt.

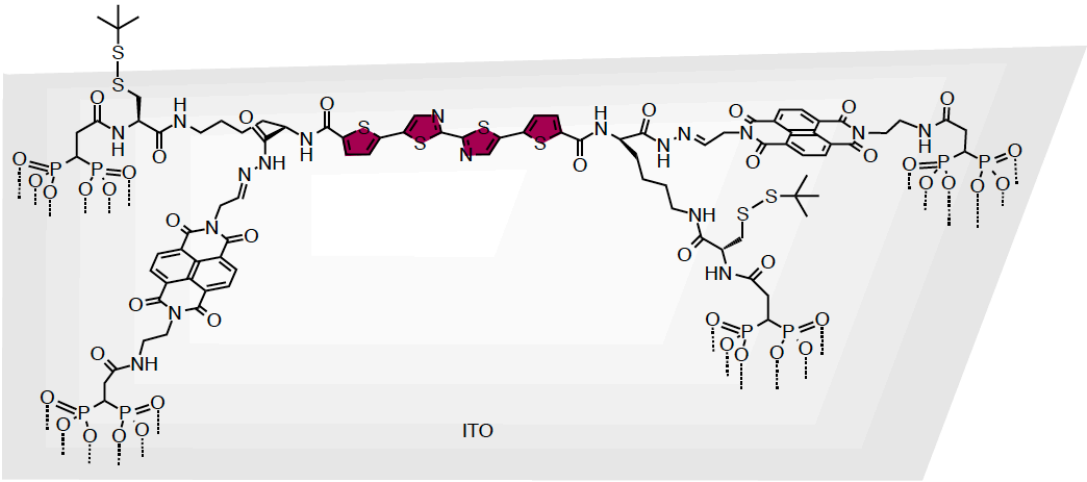


Figure S4a. Proposed chemical structure of monolayer with **5**.

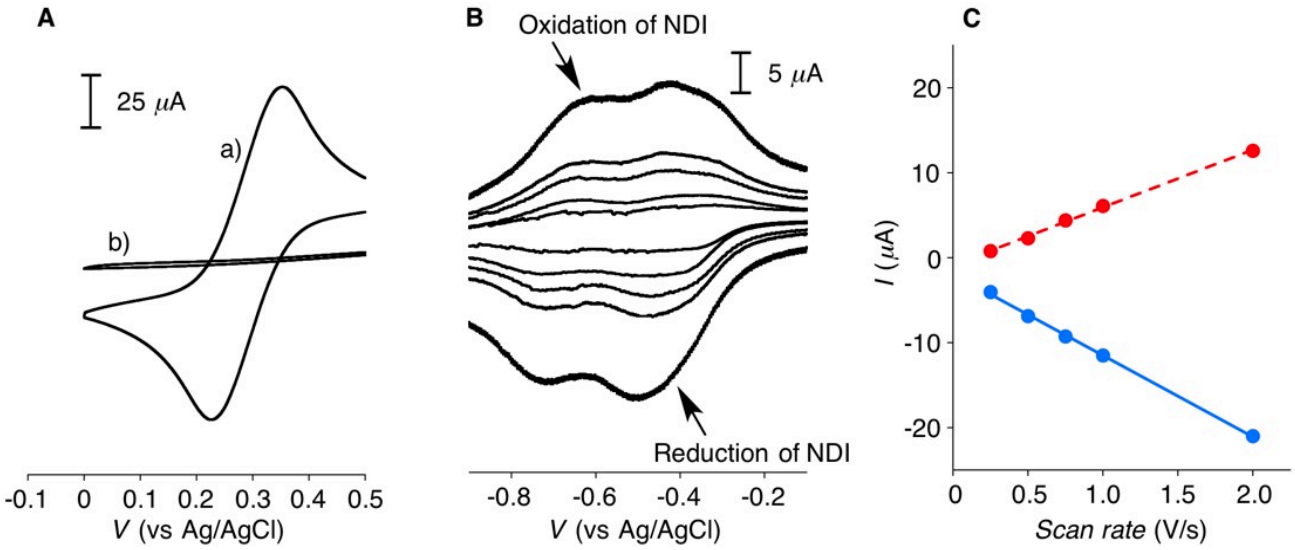


Figure S4b. (A) Cyclic voltammograms of aqueous ferricyanide measured with an ITO electrode (a) before the deposition of the initiator, (b) after 24 h in the solution of the initiator as a working electrode. (B) Cyclic voltammograms of the initiator coated ITO electrode (scan rate = 0.25, 0.5, 0.75, 1.0, 2.0 V/s). Arrows in Figure show the oxidation and reduction of NDI.[S1] (C) Peak current of the first reduction (red line) and the first oxidation (blue line) as a function of scan rates.

4.2. Propagation

ITO electrodes with or without activated initiator were placed in a deaerated solution of the propagator **6** (0.75-4.1 mM) in $CHCl_3$/MeOH 1:1 with DIPEA (100 mM), and shaken under argon atmosphere at rt (Fig. S5a). After 24 h, the electrodes were rinsed with DMSO and EtOH, and then dried under flow of argon. After the propagation, absorbance values at 414 nm (λ_{max} of **6**) of the electrodes with activated initiator **5** were recorded. On the other hand, the electrodes without activated initiator **5** showed little absorbance at 414 nm. Based on these results, the SOSIP concentration (c_{SOSIP}) of **6** under these conditions was determined to be 1-3 mM (Fig. S5b). SOSIP condition for **8** was similarly optimized with particular emphasis of finding the best solvent mixture. These SOSIP conditions for **6** and **8** are summarized in Table S2 together with previously reported one for **7**.[S9]

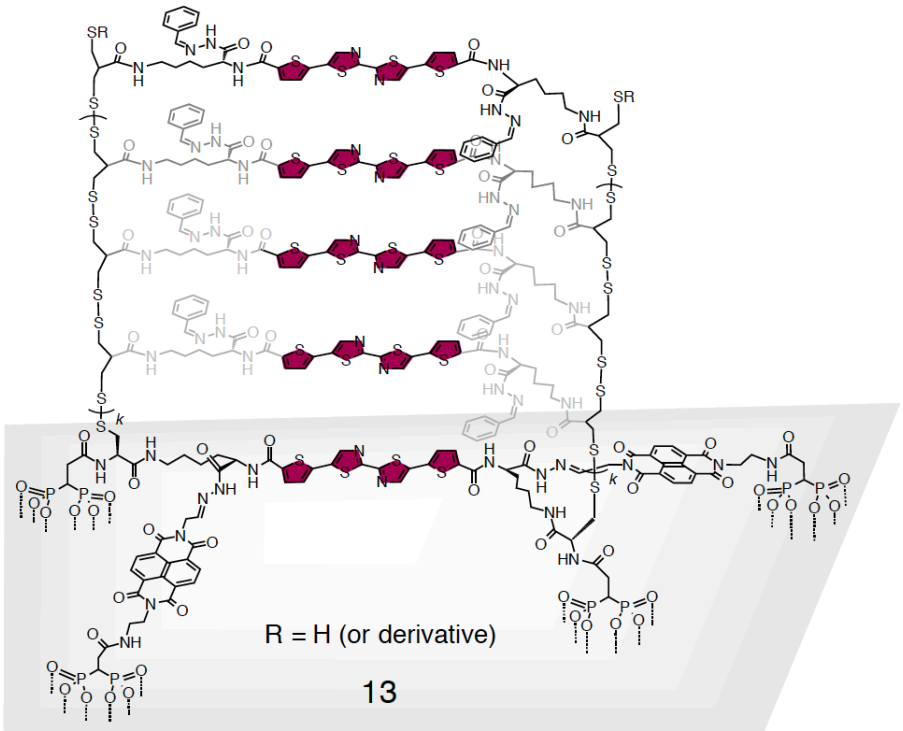


Figure S5a. Proposed chemical structure of SOSIP **13**.

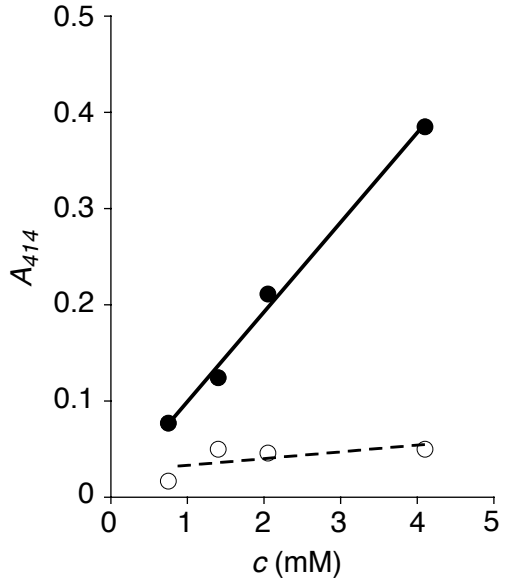


Figure S5b. Concentration dependence of SOSIP of propagator **6** on absorbance at 414 nm, filled circles: ITO electrodes coated with initiator **5**; open circles: ITO electrodes coated without initiator **5** after 24 h of incubation with propagator **6** with varied propagator concentrations at constant concentration of DIPEA (100 mM) in $CHCl_3$/MeOH 1:1.

Table S2. Summary of SOSIP conditions for **6**, **7**[a] and **8**.

Compound	Solvent	Concentration (mM)
6	$CHCl_3$/MeOH 1:1	1.5-3
7	$CHCl_3$/MeOH 3:1	2-6
8	Thioanisole/MeOH 1:3	2-5

[a]Taken from ref. S9.

4.3. Synthesis of Gradient SOSIP Systems

For the synthesis of photosystem **15**, ITO electrodes **12** covered with DTT-activated initiator **5** were dipped in a solution of **6** (3 mM) in $CHCl_3$/MeOH 1:1 with 100 mM DIPEA for 24 h. The electrodes were rinsed with DMSO and EtOH, and dried under argon flow. The resulting electrodes **13** were briefly treated with DTT (20 mM in 10 mM NH_4HCO_3aq, 10 sec), rinsed with water and EtOH, dried under argon flow, and dipped in a deaerated solution of **7** (4 mM $CHCl_3$/MeOH 3:1) with 100 mM DIPEA. After shaking for 12 h under argon atmosphere, the electrode was rinsed with DMSO and EtOH, and dried under argon flow. The resulting electrodes **14** were again briefly treated with DTT (20 mM in 10 mM NH_4HCO_3aq, 10 sec), rinsed with water and EtOH, dried, and dipped in a deaerated solution of **8** (4 mM thioanisole/MeOH 1:3) with 100 mM DIPEA. After shaking for 12 h under argon atmosphere, the electrode was rinsed with DMSO and EtOH, and dried to give electrodes **15** (Fig. 2a, Fig. S6). The absorption spectra of the electrodes were recorded after each propagation step with **6**, **7** and **8** (Fig. 2b). Increased absorbance was clearly observed after each propagation step with **6**, **7** and **8**, indicating successful gradient SOSIP formation on the electrode. Note that thickness of the layer strongly depends on the concentration of SOSIP solution and reaction time.[19] These parameters were carefully adjusted to give electrodes with similar absorbance. It should be noted here that slightly red-shifted (~15 nm) absorption spectrum was obtained after incubation with **8** on electrode **14**. This is due to the optical property of **8** and this result also supports the successful gradient SOSIP formation.

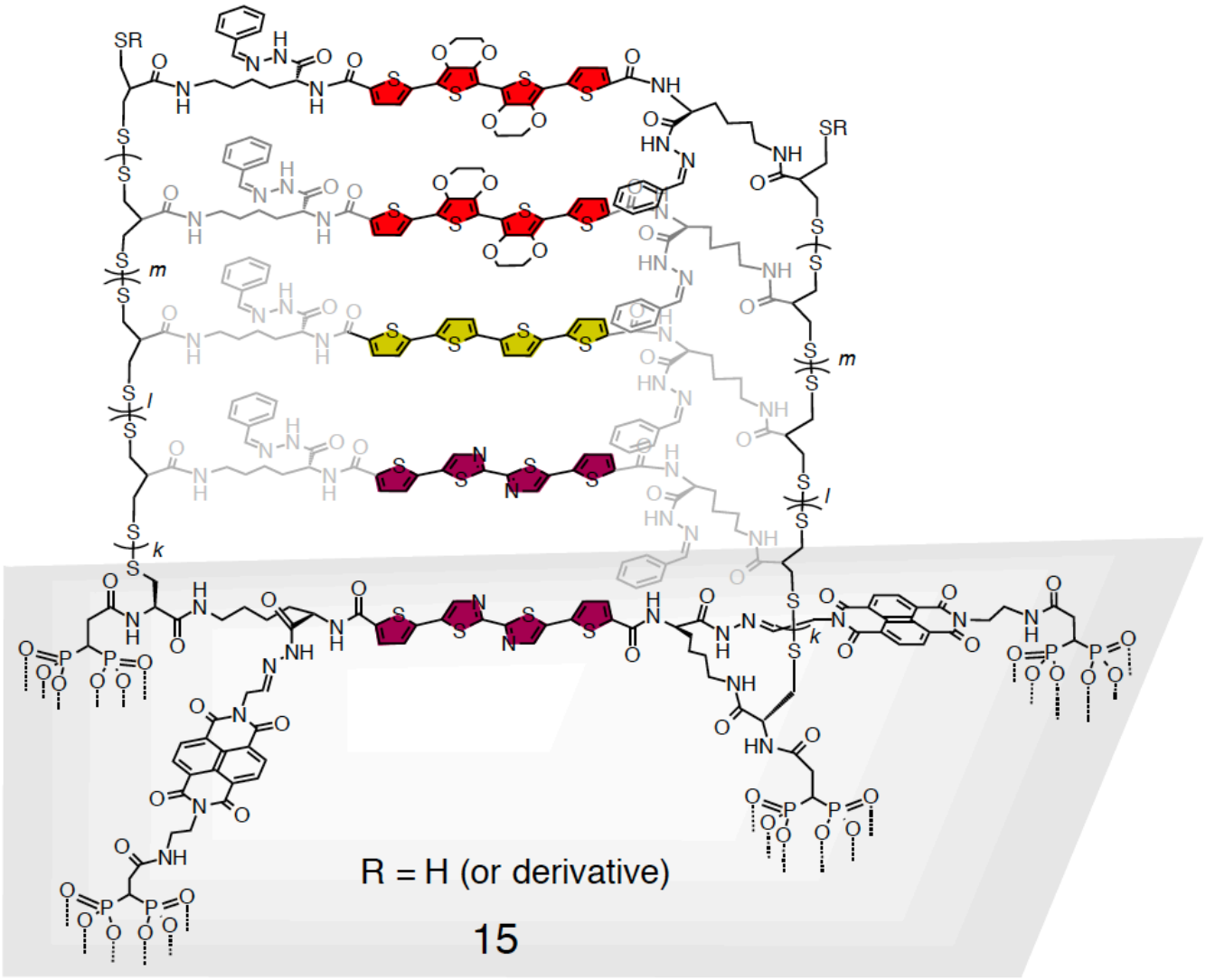
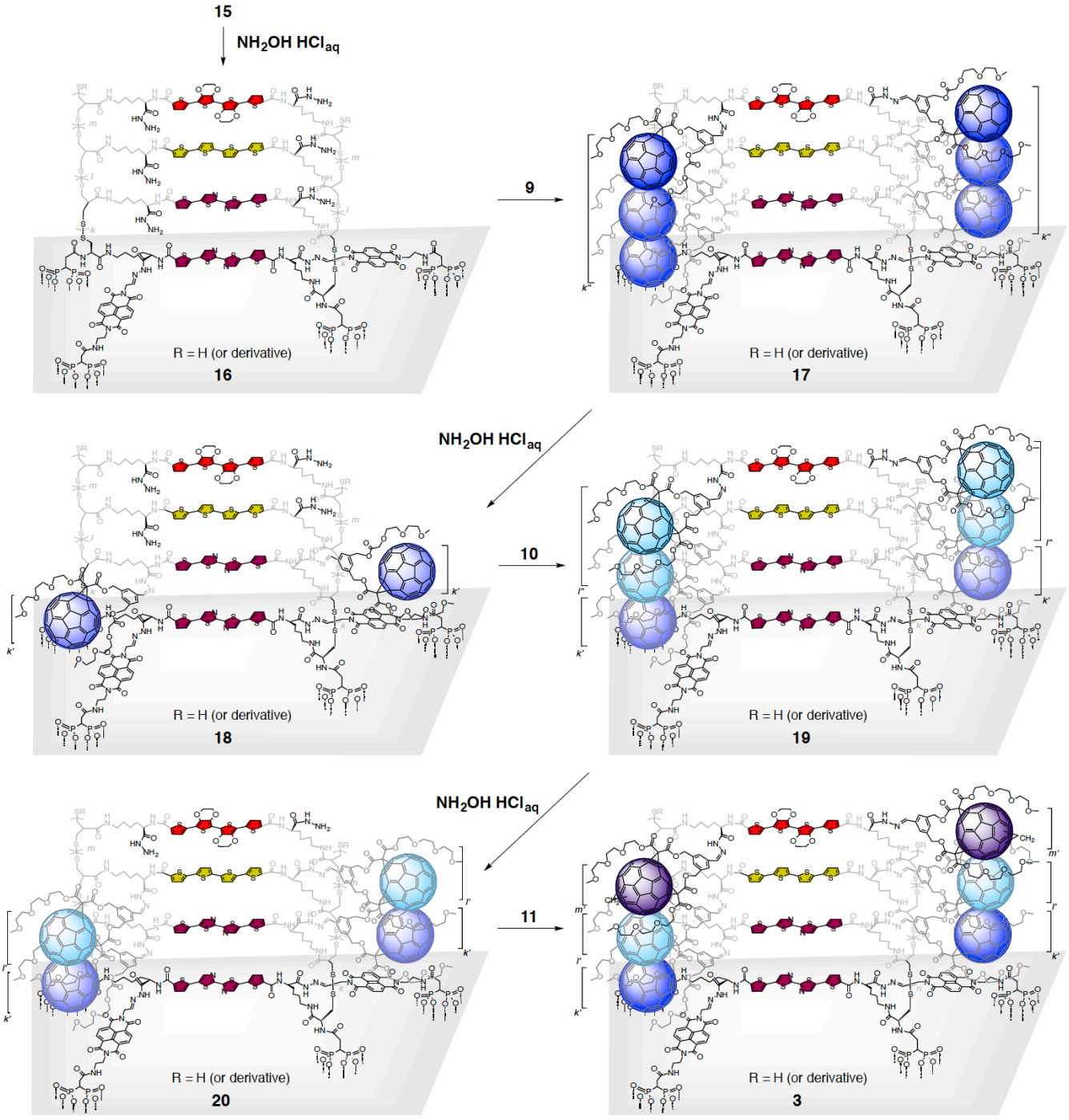


Figure S6. Proposed chemical structure of **15**.

5. Templated Stack Exchange

5.1. Synthesis of Triple-Gradient [3+3] Photosystem 3



Scheme S5. Schematic representation of TSE and proposed chemical structures of **3** and **16**-**20**.

After the formation of gradient SOSIP system, the resulting electrode **15** was immersed in an aqueous solution of NH_2OH HCl (1 M, pH 3) for 1 day at 40 ºC, rinsed with water and EtOH, dried under argon flow to give **16** (Fig. 2a). The electrode was immersed in a solution of **9** (23 mM in DMSO/$CHCl_3$/AcOH 72:8:15) for 12 h at 40 ºC, rinsed with DMSO/$CHCl_3$ 1:1, EtOH, dried under argon flow to give **17** (Fig. S7). The electrode was immersed in an aqueous solution of NH_2OH HCl (1 M, pH 3) for 6 h at 40 ºC, rinsed with water, DMSO/$CHCl_3$ 1:1, EtOH, and dried under argon flow to give **18** (Fig. 2a). The electrode was immersed in a solution of **10** (12 mM in DMSO/AcOH 9:1) for 2 h at 40 ºC, rinsed with DMSO/$CHCl_3$ 1:1, EtOH, and dried under argon flow to give **19** (Fig. 2a, 2c, Fig. S8). The electrode was immersed in an aqueous solution of NH_2OH HCl (1 M, pH 3) for 1 h at 40 ºC, rinsed with water, DMSO/$CHCl_3$ 1:1, EtOH, and dried under argon flow to give **20** (Fig. 2a). The electrode was immersed in a solution of **11** (12 mM in DMSO/AcOH 9:1) for 0.5 h at 40 ºC, rinsed with DMSO/$CHCl_3$ 1:1, EtOH and dried under argon flow to give triple-gradient [3+3] photosystem **3** (Fig. 2c, Fig. S9). The absorption spectra of the electrode were recorded before and after NH_2OH HCl treatments and following TSEs with stack exchangers **9** (Fig. S7), **10** (Fig. 2c) and **11** (Fig. S9). Note that absorbance values from 300-400 nm, where stack exchangers **9**, **10** and **11** strongly absorb, decreased after each NH_2OH HCl treatment, and increased after each treatment with stack exchangers **9**, **10** and **11**. The extent of decrease in absorbance could be simply controlled by changing the time for NH_2OH HCl treatment. Subsequent hydrazone formation was followed until no more changes in absorption spectra were observed. These results indicate that a part of the fullerene stacks in photosystem was successfully removed and the resulting pores in photosystem were subsequently filled with the next stack exchangers (Fig. 2d), i.e., successful formation of triple-gradient [3+3] photosystem **3**.

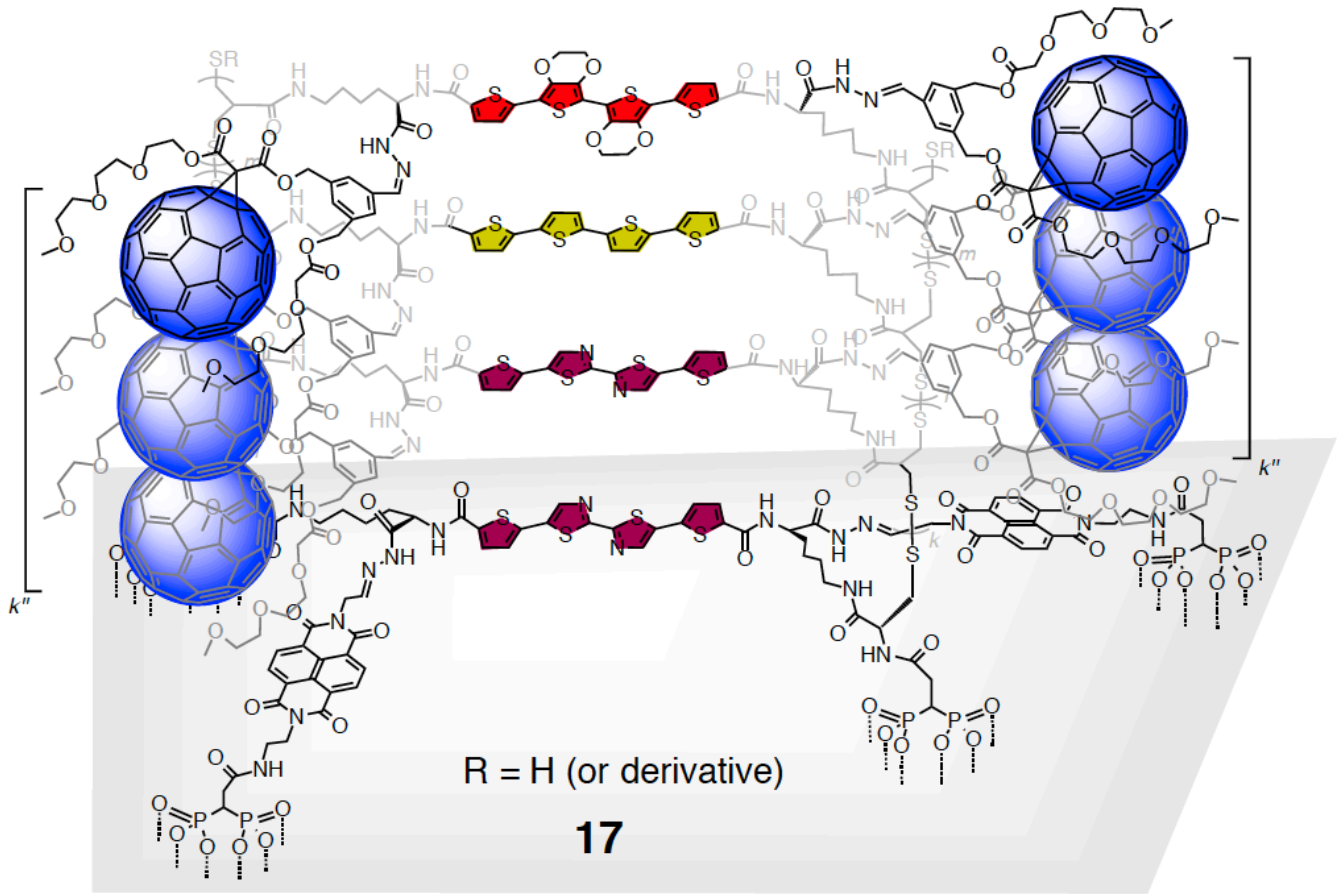


Figure S7a. Proposed chemical structure of **17**.

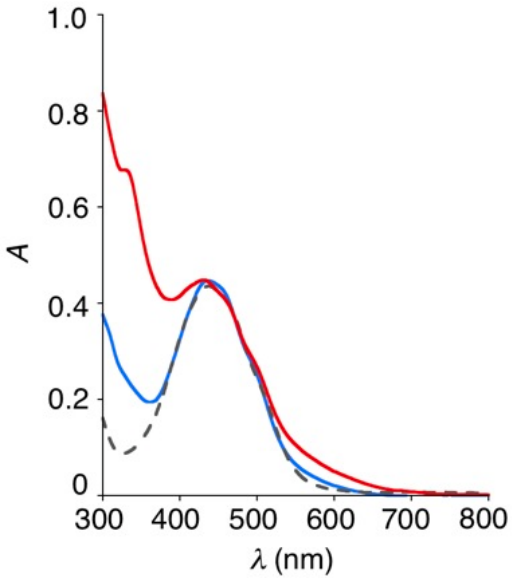


Figure S7b. Absorption spectra of SOSIP architecture (**15**, blue solid line), after NH_2OH HCl treatment (**16**, gray dashed line), and after stack exchange (**17**, red solid line) with **9**.

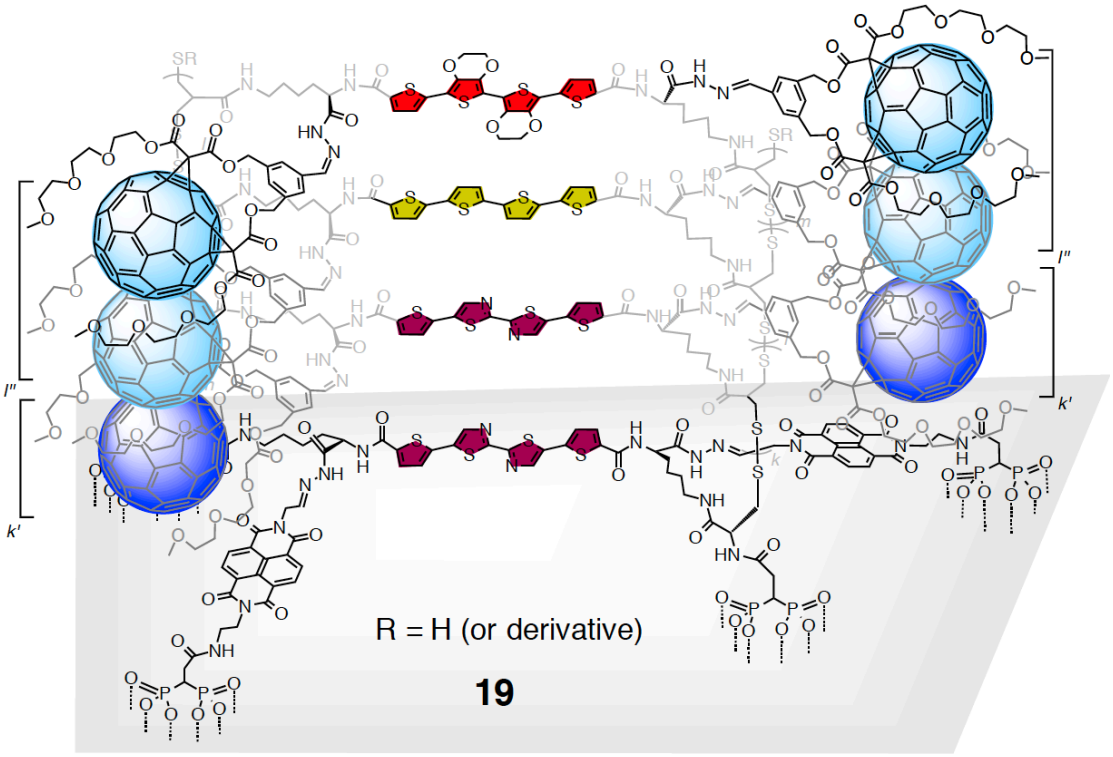


Figure S8. Proposed chemical structure of **19**.

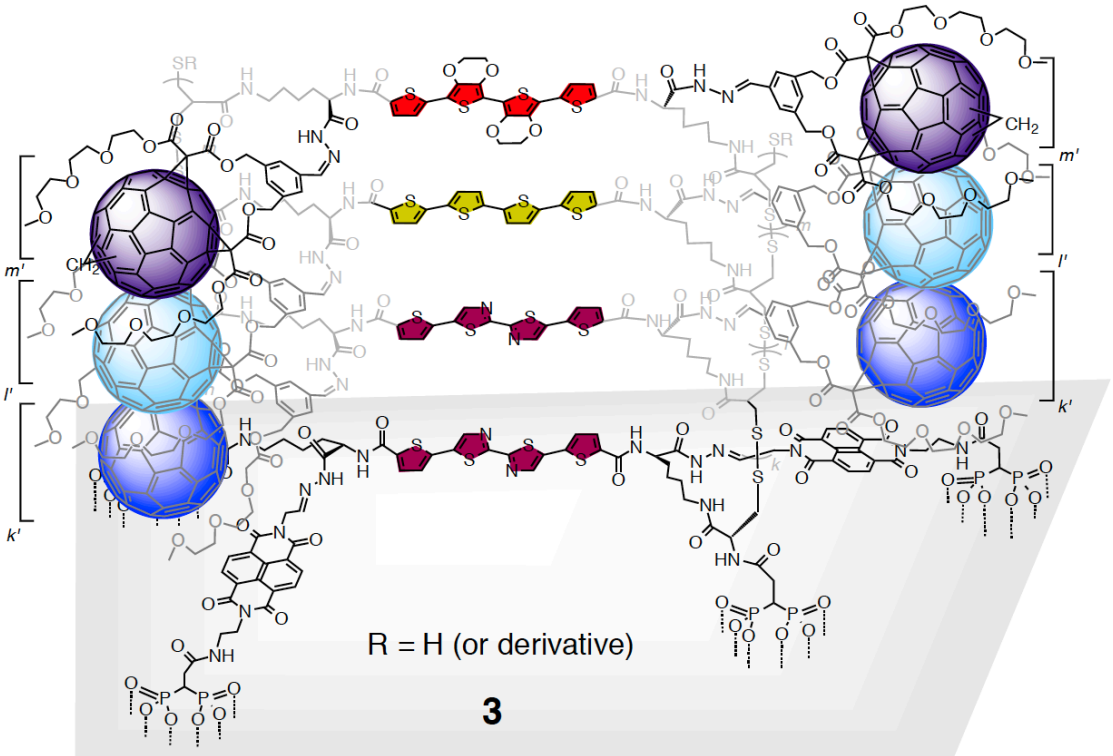


Figure S9a. Proposed chemical structure of **3**.

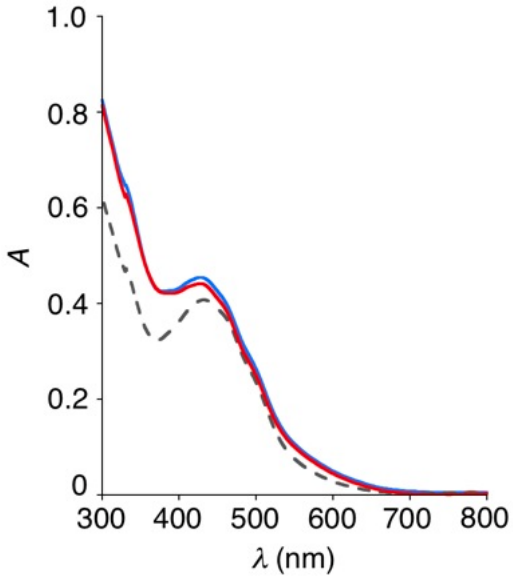


Figure S9b. (A) Absorption spectra of SOSIP architecture (**19**, blue solid line), after NH_2OH HCl treatment (**20**, gray dashed line), and after stack exchange (**3**, red solid line) with **11**.

5.2. Synthesis of Double-Gradient [2+2] Photosystem 2

The electrodes **14** were immersed in an aqueous solution of NH_2OH HCl (1 M, pH 3) for 1 day at 40 ºC, rinsed with water, DMSO/$CHCl_3$ 1:1, EtOH, and dried under argon flow. The electrodes were immersed in a solution of **9** (23 mM in DMSO/$CHCl_3$/AcOH 72:8:15) for 12 h at 40 ºC, rinsed with DMSO/$CHCl_3$ 1:1, EtOH, and dried under argon flow. The resulting electrodes were immersed in an aqueous solution of NH_2OH HCl (1 M, pH 3) for 6 h at 40 ºC, rinsed with water, DMSO/$CHCl_3$ 1:1, EtOH, and dried under argon flow. The electrodes were immersed in a solution of **10** (12 mM in DMSO/AcOH 9:1) for 2 h at 40 ºC, rinsed with DMSO/$CHCl_3$ 1:1, EtOH, dried under argon to give double-gradient [2+2] photosystem **2**. The absorption spectra of the electrodes were recorded before and after NH_2OH HCl treatments and the following treatments with **9** and **10** (Fig. S10).

For TSE experiments, the yields of stack exchange were roughly estimated from the molar ratio R of propagators **6**, **7** and **8**, and stack exchangers **9**, **10** and **11**. Quantitative yield $X = 100\%$ was assumed for a 2:1 ratio ($R = R_{9+10+11}/R_{6+7+8} = 2.0$). The propagators **6**, **7** and **8** easily polymerized and it is difficult to determine accurate ε values. Here, the absorption maxima of the propagators (**6**, **7** and **8**) are almost the same as their intermediates (**23**, **36** and **38**), therefore the ε values of **23**, **36** and **38** were used. The following values were used for **6**: ΔA411 nm, $\varepsilon = 4.3 \times 10^4$ $M^{-1}cm^{-1}$, **7**: ΔA420 nm, $\varepsilon = 4.0 \times 10^4$ $M^{-1}cm^{-1}$, **8**: ΔA452 nm, $\varepsilon = 4.5 \times 10^4$ $M^{-1}cm^{-1}$, **9**: ΔA328 nm, $\varepsilon = 4.8 \times 10^4$ $M^{-1}cm^{-1}$ (*23*), **10**: ΔA315 nm, $\varepsilon = 5.7 \times 10^4$ $M^{-1}cm^{-1}$ (*22*), and **11**: ΔA315 nm, $\varepsilon = 2.5 \times 10^4$ $M^{-1}cm^{-1}$.[S11] Judging from Fig. 2b, d, $R_{9+10+11}/R_{6+7+8} = 1.34$ ratio for triple-gradient [3+3] photosystem was obtained, resulting in TSE yield $X = 67\%$ in this case. The TSE yields for all systems are summarized in Table S3 together with the photocurrents. The obtained $X = 50$-75% ($R = 1.0$-1.5) yields are reasonable considering the three-dimensional bulk of the fullerenes.

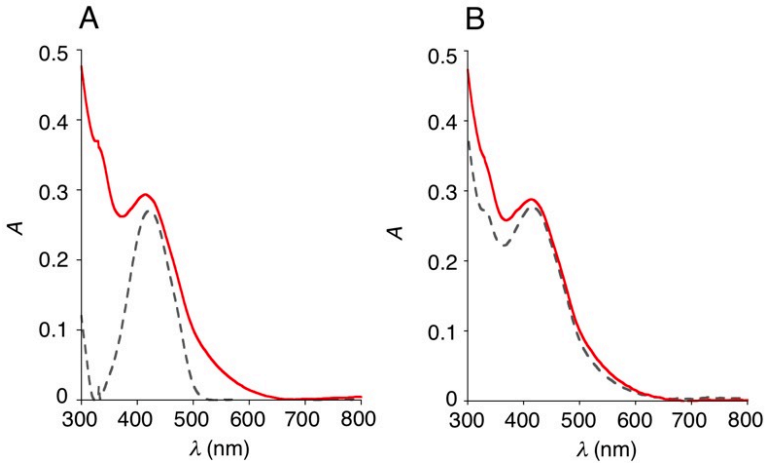


Figure S10. Absorption spectra of SOSIP architecture (A) [2+1] photosystem with propagators **6**, **7** and stack exchanger **9**, and (B) **2** before (gray dashed line) and after stack exchange (red solid line).

5.3. Synthesis of Gradient-Free [1+1] Photosystem 1

ITO electrodes **13** were shaken in an aqueous solution of NH_2OH HCl (1 M, pH 3) for 1 day at 40 ºC. The obtained electrodes were rinsed with water and EtOH, and dried under argon flow. The electrodes were placed in a solution of **9** (23 mM in DMSO/$CHCl_3$/AcOH 72:8:15) for 12 h at 40 ºC, rinsed with DMSO/$CHCl_3$ 1:1, EtOH, and dried under argon flow to give gradient-free [1+1] photosystems **1**. The absorption spectra of the electrode were recorded before and after NH_2OH HCl treatments and following treatments with **9** (Fig. S11).

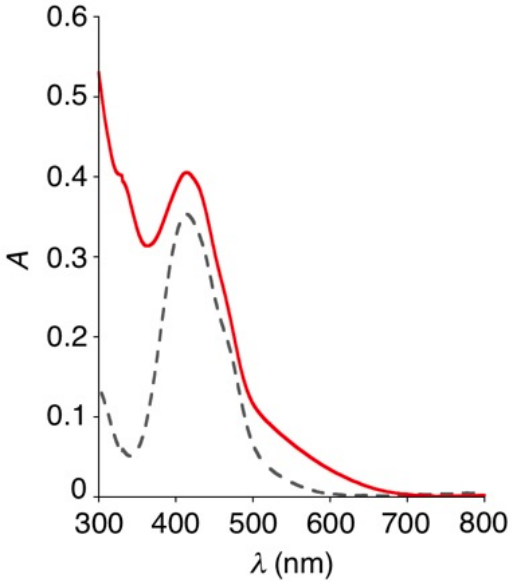


Figure S11. Absorption spectra of SOSIP architecture **1** before (gray dashed line) and after stack exchange (red solid line).

Table S3. Summary of TSE yields and photocurrent properties.

Photosystem	TSE yield (%)	J_{SC} (μA/cm^2)[a]	V_{oc} (V)[a]	FF[a]
1	50-60	2	–0.27	32
2	60-70	6	–0.41	52
3	65-75	12	–0.44	50
4	–[b]	0.24	–0.068	23

[a]Obtained from *J*-*V* curves; [b]Not measured.

6. Photocurrent Measurements

Photocurrent measurements. 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 argon gas) aqueous solution of ascorbaic acid (50 mM) and Na_2SO_4 (100 mM) and irradiated with a solar simulator (area of irradiation: a = ~1.0 cm^2). Changes in current upon on-off switching of irradiations were measured at 0 V *vs* Ag/AgCl and the power of irradiation was 100 mW cm^{-2} unless stated.

Short circuit current densities (J_{sc}, A/cm^2) and open circuit voltages (V_{oc}, V) were determined by J-V measurements. Fill factors (*FF*) were calculated from the maximum power (P_m, W/cm^2), J_{sc}, and V_{oc} using equation (S4).[S15]

$$FF = P_m / J_{sc} V_{oc} \qquad \text{(S4)}$$

Bimolecular recombination efficiencies η_{BR} were calculated from the dependence of photocurrent densities (J, A/cm^2) to the irradiation power (I, W/cm^2) using the equations S5 and S6.[S16]

$$J \propto I^{\alpha} \qquad \text{(S5)}$$

$$\eta_{BR} = \alpha^{-1} - 1 \qquad \text{(S6)}$$

Activation energies (E_a, eV) of the system were calculated from the dependence of photocurrent densities (J, A/cm^2) to the temperature (T, K) using the equation S7.[S17]

$$J\left(T, I_{light}\right) = J_{00}(I_{light})e^{\frac{-E_a}{kT}} \qquad \text{(S7)}$$

where I_{light} is the irradiation power and k is the Boltzmann constant 8.617 × 10^{-5} eV / K. I_{light} = 100 mW cm^{-2} was used for determining E_a values. These results are summarized in Table S3.

7. Dark Current Measurements

Dependence of current density to voltage was determined by measuring *J*-*V* characteristics under dark condition. Experimental conditions are as described in the above "photocurrent measurements".

Ideality factors (n) of the system were estimated from the dependence of current densities (J, A/cm^2) to the voltage (V, V) under dark condition using the equation S8.[S18-S20]

$$I = I_0\left(\exp\left(\frac{qV}{nkT}\right) - 1\right) \approx I_0\left(\exp\left(\frac{qV}{nkT}\right)\right) \qquad \text{(S8)}$$

where q is elementary charge 1.602 × 10^{-19} C, V is bias voltage, k is Boltzmann constant 1.381 × 10^{-23} J/K, and T is temperature (K).

Turn-on voltages (V_d, V) of the system were estimated by linear fitting of dark currents in the voltage region $V < -150$ mV for photosystem **1**, $V < -200$ mV for photosystem **2** and $V < -300$ mV for photosystem **3** where the dark currents increase linearly.

Comments. As described in "self-organizing surface initiated polymerization" and "templated stack exchange" parts, the thickness of layers with propagators **6**-**8** and stack exchangers **9**-**11** strongly depends on SOSIP and TSE conditions. Thus, even small differences in reaction (and environmental) conditions could significantly affect optical and photoelectrochemical properties of photosystems. To minimize batch-to-batch variations, the preparation of photosystems and the photocurrent measurements were done very carefully. First, photosystems **1**, **2** and **3** were prepared together under nearly identical conditions. Namely, for example, TA layers for electrodes **1**, **2** and **3** were prepared by dipping three electrodes **12** together in a same propagator **6** solution, and one of them was used to prepare photosystem **1** and the other two for SOSIP with propagator **7** to prepare photosystems **2** and **3**. The variability in thickness of TA for photosystems **2** and **3** was minimized with this procedure. Further, incubation times for SOSIP of propagators **6**, **7** and **8** were adjusted to give similar thickness for photosystems **1**, **2** and **3**. Photoelectrochemical properties of thus prepared photosystems did not change much if kept in dark, suggesting the high stability of the structure, probably due to strong covalent bonding. Finally, photoelectrochemical studies of a series of photosystems prepared by using the above procedure were performed within the same day to minimize the variability caused by the instrumental fluctuations. Taking these precautions, a series of photosystems prepared by using the same SOSIP solution always showed the same photoelectrochemical trend as summarized in Table 1.

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