Supplementary Material (ESI) for Energy & Environmental Science

Toward polymerized artificial photosystems with supramolecular n/p-heterojunctions and antiparallel redox gradients

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Supplementary Information

1. Materials and methods

As in reference S1 and S2, Supplementary Information. Briefly, reagents for synthesis were purchased from Fluka, amino acid derivatives from Novabiochem and Bachem, HATU from Applied Biosystems, buffers, and salts from Sigma or Fluka-Aldrich. All

reactions were performed under N_2 or argon atmosphere. 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. HPLC was performed using either Jasco HPLC system (PU-980, UV-970, FP-920) or an Agilent 1100 series apparatus with a photo diode array detector. $[\alpha]^{20}_D$ values were recorded on a Jasco P-1030 Polarimeter, melting points (m.p.) on a heating table from Reichert (Austria), 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). ESI-MS were performed on a Finnigan MAT SSQ 7000 instrument or a ESI API 150EX and are reported as mass-per-charge ratio *m/z* (intensity in %, [assignment]). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Sciex QSTAR Pulsar mass spectrometer, MALDI-TOF on a Axima CFR+ (Shimadzu). 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 $M^{-1}cm^{-1}$). Circular dichroism (CD) spectra were obtained using JASCO J-815 spectropolarimeter and are reported as maximal wavelength λ (in nm) and Δε (in $M^{-1}cm^{-1}$). ^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), quartet (q) and quintet (quint) with coupling constants (*J*) given in Hz, or multiplet (m).

Broad peaks are marked as br. ^{1}H 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). 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; Cbz: (Benzyloxy)carbonyl; CV: Cyclic voltammetry; DMF: N,N-Dimethylformamide; DMI: 1,3-dimethyl-2-imidazolidinone; DTBP: 2,6-Di-*tert*-butylpyridine; *en*: Ethylenediamine; Fc: Ferrocene; *FF*: Fill factor; *Gla*: Glycolic acid; Glu: L-Glutamic acid; HATU: N-[(Dimethylamino)-1*H*-1,2,3-triazolo[4,5-b]pyridin-1-ylmethylene]-Nmethylmethanammonium hexafluorophosphate N-oxide; HFIP: 1,1,1,3,3,3-Hexafluoro-2-propanol; IPCE: Incident photon to current conversion efficiency; LBL: layer-by-layer assembly; NDI: 1,4,5,8-Naphthalenediimide; OPE: Oligophenylethynyl; POP: *p*-Oligophenyl; rt: Room temperature; TEA: Triethylamine; TEOA: Triethanolamine; TFA: Trifluoroacetic acid; TFE: 2,2,2-Trifluoroethanol.

2. Supporting text

2.1. Synthesis

2.1.1. Synthesis of short-tail cationic propagator 6 (Scheme S1)

Compound 18. This compound was prepared from compound **22** in overall two steps following previously reported procedures.[S1]

Compound 23. To a solution of **18** (320 mg, 0.40 mmol) in DMI (20 mL) was added 3-butene-1-amine **12**,[S3] and the mixture was stirred for 4 h at rt. The reaction mixture was diluted with EtOAc (100 mL) and the organic layer was washed with 0.1 M aq HCl (100 mL) and water (100 mL). The organic layer was dried over Na_2SO_4 and solvent was evaporated to dryness. The resultant residue was purified by column chromatography (CH_2Cl_2:CH_3OH 95:5; R_f = 0.32) affording **23** (245 mg, 76%) as a red solid. mp: 104.5–105.5 °C; UV/vis (CH_2Cl_2): 534 (12400), 368 (11000), 350 (9300); IR: 3324 (m), 2924 (m), 1671 (s), 1637 (s), 1582 (s), 1441 (s), 1312 (s), 1214 (s), 1137 (m), 992 (m), 789 (m); ^{1}H NMR (400 MHz, $CDCl_3$, N/N = regioisomeric equivalents): 9.99/9.89 (t, ^3J (H,H) = 5.56 Hz, 1H / br t, 1H), 8.70/8.60 (s, 1H), 8.23/8.12 (s, 1H), 7.27 (m, 5H), 6.30 (br s, 1H), 5.96–5.84 (m, 1H), 5.83–5.73 (m, 1H), 5.65/5.60 (dd, ^3J (H,H) = 9.24/8.72 Hz, ^3J (H,H) = 5.08/5.56 Hz, 1H), 5.32–5.08 (m, 4H), 4.97 (s, 2H), 4.87–4.80 (m, 1H), 4.43 (dd, ^3J (H,H) = 14.3 Hz, ^3J (H,H) = 5.56 Hz, 2H), 4.21 (br s, 2H), 3.66–3.63 (m, 2H), 3.47 (br s, 2H),

3.17–3.12 (m, 2H), 2.58 (q, ^{3}J (H,H) = 6.80 Hz, 2H), 2.30–2.21 (m, 2H), 1.60–1.49 (m, 2H), 1.43–1.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.0, 171.5, 165.7, 165.4, 162.0, 161.8, 161.5, 161.4, 156.8, 156.7, 156.6, 151.9, 151.7, 138.7, 138.4, 136.7, 134.15, 134.10, 133.0, 132.9, 128.7, 128.2, 128.1, 127.4, 126.9, 123.4, 123.2, 122.82, 122.78, 121.6, 121.3, 120.8, 120.7, 119.0, 118.9, 117.8, 99.8, 99.5, 66.7, 65.8, 55.3, 54.4, 43.0, 42.9, 40.83, 40.78, 40.65, 39.9, 39.7, 39.4, 37.9, 33.7, 33.5, 29.8, 29.7, 28.3, 28.1, 23.9, 23.8; MS (ESI, +ve, largest of isotopic peaks): 803 (100, $[M + H]^+$), 786 (95, $[M – NH_2]^+$).

Compound 24. A solution of **23** (244 mg, 0.30 mmol) in CH_2Cl_2 (60 ml) was treated at rt with $PhSiH_3$ (0.30 ml, 2.4 mmol) followed by $Pd(PPh_3)_4$ (21 mg, 6 mol%) and stirred for 1 h. The amount of solvent was reduced to approximately 2 ml *in vacuo* and then loaded on a silica gel column, which was in prior neutralized by washing with 1% Et_3N in CH_2Cl_2. The product was eluted from the column with 1% CH_3OH and Et_3N in CH_2Cl_2 and concentrated to afford **24** (185 mg, 86%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ 6:1, N/N = regioisomeric equivalents): 10.0/9.95 (br t, 1H), 8.78/8.75 (s, 1H), 8.26/8.22 (s, 1H), 7.27–7.24 (m, 5H), 5.92–5.82 (m, 1H), 5.67–5.58 (m, 1H), 5.27–5.15 (m, 2H), 4.96 (br s, 2H), 4.33–4.30 (m, 2H), 3.68–3.62 (m, 2H), 3.33 (s, 2H), 3.10 (s, 2H), 2.54 (br q, ^{3}J (H,H) = 6.40 Hz, 2H), 2.25–2.23 (m, 2H), 1.53–1.47 (m, 2H), 1.40–1.35 (m, 2H); MS (ESI, +ve, largest of isotopic peaks): 721 (100, $[M + H]^+$), 743 (65, $[M + Na]^+$), 704 (95, $[M – NH_2 + H]^+$).

Compound 15. This compound was prepared following previously reported procedures.[S2]

Compound 25. To a solution of **15** (2.8 mg, 2.3 μmol), HATU (13 mg, 34 μmol) and DTBP (60 μL, 267 μmol) in distilled DMF (0.5 mL) was added a mixture of **24** (72 mg, 100 μmol) and TEA (30 μL, 214 μmol) in DMF (1.0 mL) at rt. After stirring at rt for 12 h, DMF was removed under high vacuum. The residue was dissolved in a mixture of CH_2Cl_2 and CH_3OH (CH_2Cl_2:CH_3OH 9:1) and the solution was poured into CH_3OH (100 mL). The resultant red precipitates were collected by centrifugation. Purification by PTLC (CH_2Cl_2:CH_3OH 90:10; R_f = 0.46) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, CH_2Cl_2/CH_3OH 90:10, 2.0 ml/min, R_t = 6.6 min) **25** (3.6 mg, 19%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 5:1): 9.92–9.71 (m, 10H), 8.66–8.00 (m, 20H), 7.19 (br s, 50H), 6.66 (br m, 12H), 5.82–5.51 (m, 20H), 5.29–5.14 (m, 20H), 4.91–4.89 (m, 20H), 4.40–4.24 (m, 40H), 3.59–3.54 (m, 40H), 3.04 (br s, 20H), 2.48 (br s, 20H), 2.16 (br s, 20H), 1.48–1.22 (m, 40H); MS (MALDI, +ve linear, HABA): 8253 (100, $[M + Na]^+$).

Compound 6. A catalytic amount of thioanisole and pentamethyl benzene were added to a solution of **25** (2.6 mg, 0.3 μmol) in TFA (1 mL), and this red solution was stirred for 3 h at 35 °C. After this time, the red solution was evaporated to dryness by N_2 gas. Impurities were removed by solid-liquid extraction with ether (2 x 20 mL) and hexane (2 x 20 mL), to yield analytically pure (RPHPLC, Nucleosil 100-7 c18 250 x 8 mm, CH_3OH (with 1% TFA, 1.0 mL/min, R_t = 4.8 min) **6** (2 mg, quantitative) as a red solid. ^{1}H NMR (400 MHz, TFA-D): 8.86–8.36 (m, 20H), 7.31–6.92 (m, 12H), 5.95–5.86 (m, 20H), 5.22–5.13 (m,

20H), 4.87 (m, 40H), 3.86–3.66 (m, 40H), 3.18 (br s, 20H), 2.53–2.32 (m, 40H), 1.86 (br s, 20H), 1.60–1.36 (m, 20H).

2.1.2. Synthesis of short-tail anionic propagator 7 (Scheme 1)

Compound 11. This compound was prepared from compound **22** in over all two steps following previously reported procedures.[S4]

Compound 13. To a solution of **11** (350 mg, 0.48 mmol) in DMI (24 mL) was added 3-butene-1-amine **12**[S3] (410 μL, 4.8 mmol) and the mixture was stirred for 4 h at rt. The reaction mixture was diluted with EtOAc (75 mL) and the organic layer was washed with water (100 mL x 2). The organic layer was dried over Na_2SO_4 and solvent was evaporated to dryness. The resultant residue was purified by column chromatography (CH_2Cl_2:CH_3OH 95:5; R_f = 0.39) affording **13** (316 mg, 91%) as a red solid. mp: 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$, N/N = regioisomeric equivalents): 10.0/9.96 (t, ^3J (H,H) = 5.28 Hz / br t, 1H), 8.78/8.68 (s, 1H), 8.29/8.19 (s, 1H), 6.46 (br s, 1H), 6.01–5.91 (m, 1H), 5.90–5.80 (m, 1H), 5.76/5.71 (dd, ^3J (H,H) = 8.88/8.96 Hz, ^3J (H,H) = 4.44/4.68 Hz, 1H), 5.37–5.14 (m, 4H), 4.49 (dd, ^3J (H,H) = 15.4 Hz, ^3J (H,H) = 5.36 Hz, 2H), 4.28 (br t, 2H), 3.71 (q, ^3J (H,H) = 6.08 Hz, 2H), 3.56–3.51 (m, 2H), 2.65 (br q, 2H), 2.55–2.28 (m, 4H), 1.41 (s, 5H), 1.40 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.34, 172.26, 171.7, 171.4, 165.6, 165.5, 162.0, 165.5, 162.0, 161.8, 161.5, 161.4, 156.8, 156.7, 151.8, 151.7, 138.6, 138.4, 134.2, 134.1, 133.0, 132.9, 128.6, 128.4, 127.5, 126.7, 123.5, 123.4, 122.7, 122.6, 121.5, 121.3, 121.2,

121.0, 120.8, 119.0, 118.9, 117.8, 99.86, 99.32, 81.03, 80.88, 65.80, 54.99, 54.08, 43.07, 42.92, 40.89, 39.90, 39.57, 39.41, 33.67, 33.54, 32.83, 32.76, 28.19, 23.84; MS (ESI, +ve, largest of isotopic peaks): 728 (40, $[M + H]^+$), 672 (75, $[M + H - {}^tBu]^+$), 655 (100, $[M + H - {}^tBu - NH_2]^+$).

Compound 14. A solution of **13** (140 mg, 0.19 mmol) in CH_2Cl_2 (30 ml) was treated at rt with $PhSiH_3$ (0.17 ml, 1.3 mmol) followed by $Pd(PPh_3)_4$ (19 mg, 6 mol%) and stirred for 1 h. The amount of solvent was reduced to approximately 2 ml in *vacuo* and then loaded on a silica gel column, which was in prior neutralized by washing with 1% Et_3N in CH_2Cl_2. The product was eluted from the column with 1% MeOH and Et_3N in CH_2Cl_2 and concentrated to afford **14** (95 mg, 76%) as a red solid. ^1H NMR (400 MHz, $CDCl_3/CD_3OD$ 6:1, N/N = regioisomeric equivalents): 9.84/9.79 (br t, 1H), 8.62 (s, 1H), 8.11/8.10 (s, 1H), 5.78–5.67 (m, 1H), 5.53–5.44 (m, 1H), 5.10–4.93 (m, 2H), 4.16–4.10 (m, 2H), 3.50–3.48 (m, 2H), 2.94–2.81 (m, 2H), 2.41–2.04 (m, 6H), 1.19 (s, 5H), 1.18 (s, 4H); MS (ESI, +ve, largest of isotopic peaks): 642 (100, $[M + H]^+$), 627 (95, $[M - NH_2 + H]^+$).

Compound 16. To a solution of **15**[S2] (4.2 mg, 3.5 μmol), HATU (20 mg, 52 μmol) and DTBP (100 μL, 0.45 mmol) in distilled DMF (0.9 mL) was added a mixture of **14** (95 mg, 0.15 mmol) and TEA (40 μL, 0.29 mmol) in DMF (1.8 mL) at rt. After stirring at rt for 13 h, DMF was removed under high vacuum. The residue was dissolved in a mixture of CH_2Cl_2 and CH_3OH (CH_2Cl_2:CH_3OH 9:1) and the solution was poured into CH_3OH (100 mL). The resultant red precipitates were collected by centrifugation. A preliminary purification by

PTLC (CH_2Cl_2:CH_3OH 90:10; R_f = 0.43) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, CH_2Cl_2/CH_3OH 90:10, 2.0 ml/min, R_t = 6.6 min) **16** (8.8 mg, 34%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 5:1): 9.84–9.64 (m, 10H), 8.58–7.96 (m, 20H), 6.78–6.39 (m, 12H), 5.74 (m, 10H), 5.48–5.41 (m, 10H), 5.11–5.04 (m, 20H), 4.31–4.18 (m, 40H), 3.53–3.43 (m, 40H), 2.40–2.17 (m, 60H), 1.22–1.18 (m, 90H); MS (MALDI, +ve linear, HABA): 7486 (100, $[M + Na]^+$).

Compound 7. A solution of **16** (5.8 mg, 0.78 μmol) in TFA (1 ml) and CH_2Cl_2 (1 mL) was stirred for 3 h at rt. After this time, TFA and CH_2Cl_2 were removed by N_2 gas. Impurities were removed by solid-liquid extraction with acetonitrile (20 mL), ether (20 mL) and hexane (2 x 20 mL), leaving **7** (5.7 mg, quantitative) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$/TFA 10:1): 8.71–7.98 (m, 20H), 7.57–6.86 (m, 12H), 5.89–5.78 (m, 20H), 5.32–5.22 (m, 20H), 4.70–4.33 (m, 40H), 3.83–3.62 (m, 40H), 2.68–2.53 (m, 60H); MS (MALDI, +ve linear, HABA): 6922 (100, $[M + Na]^+$).

2.1.3. Synthesis of long-tail cationic propagator 8 (Scheme S2)

Compound 26. To a solution of **18** (352 mg, 0.43 mmol) in DMI (22 mL) was added 3-undecenylamine **17**[S5] (910 μL, 4.3 mmol) and the mixture was stirred for 4 h at rt. The reaction mixture was diluted with EtOAc (75 mL) and the organic layer was washed with 0.1 M HCl aq. (100 mL x 2) and water (100 mL x 2). The organic layer was dried over Na_2SO_4 and solvent was evaporated. The resultant residue was purified by column

chromatography (CH_2Cl_2:CH_3OH 95:5; R_f = 0.37) affording **26** (306 mg, 79%) as a red solid. mp: 75–76 °C; UV/vis (CH_2Cl_2): 537 (15100), 368 (12800), 350 (11100); IR: 3319 (m), 2925 (m), 1689 (s), 1637 (s), 1582 (s), 1533 (s), 1444 (s), 1369 (m), 1314 (m), 1256 (s), 1157 (s), 993 (m); ^{1}H NMR (400 MHz, $CDCl_3$, N/N = regioisomeric equivalents): 9.98/9.91 (t, ^3J (H,H) = 5.28 Hz / br t, 1H), 8.67/8.59 (s, 1H), 8.22/8.10 (s, 1H), 7.27–7.25 (m, 5H), 6.33 (br s, 1H), 5.87–5.76 (m, 2H), 5.66–5.58 (m, 1H), 5.21–4.92 (m, 6H), 4.82 (m, 1H), 4.43 (dd, ^3J (H,H) = 12.3 Hz, ^3J (H,H) = 4.80 Hz, 2H), 4.21 (br s, 2H), 3.53 (m, 2H), 3.47 (br s, 2H), 3.15–3.10 (m, 2H), 2.30–2.21 (m, 2H), 2.05 (q, ^3J (H,H) = 7.08 Hz, 2H), 1.86–1.80 (m, 2H), 1.52–1.33 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.9, 171.5, 165.8, 165.5, 162.2, 162.0, 161.6, 161.5, 156.7, 156.6, 152.0, 151.9, 139.4, 138.7, 138.4, 136.70, 136.68, 133.0, 132.9, 128.7, 128.3, 128.1, 127.4, 127.0, 123.4, 123.2, 122.9, 121.6, 121.4, 121.1, 120.7, 120.5, 117.83, 117.79, 114.4, 99.6, 99.4, 66.7, 65.8, 55.3, 54.5, 43.9, 43.8, 40.8, 40.6, 39.9, 39.7, 39.5, 34.0, 29.8, 29.69, 29.66, 29.62, 29.5, 29.3, 29.1, 28.4, 28.2, 27.3, 27.2, 23.9, 23.8; MS (ESI, +ve, largest of isotopic peaks): 901 (100, $[M + H]^+$), 886 (80, $[M – NH_2]^+$).

Compound 27. A solution of **26** (150 mg, 0.17 mmol) in CH_2Cl_2 (33 ml) was treated at rt with $PhSiH_3$ (0.16 ml, 1.3 mmol) followed by $Pd(PPh_3)_4$ (20 mg, 10 mol%) and stirred for 1 h. The amount of solvent was reduced to approximately 2 ml *in vacuo* and then loaded on a silica gel column, which was in prior neutralized by washing with 1% Et_3N in CH_2Cl_2. The product was eluted from the column with 1% CH_3OH and Et_3N in CH_2Cl_2 and concentrated to afford **27** (95 mg, 70%) as a red solid. MS (ESI, +ve, largest of isotopic peaks): 820 (100, $[M + H]^+$), 843 (50, $[M + Na]^+$), 802 (50, $[M – NH_3]$).

Compound 28. To a solution of **15** (4.0 mg, 3.3 μmol), HATU (19 mg, 50 μmol) and DTBP (90 μL, 0.40 mmol) in a mixture of distilled DMF (0.4 mL) and CH_2Cl_2 (0.4 mL) was added a mixture of **27** (95 mg, 0.12 mmol) and TEA (37 μL, 0.26 mmol) in a mixture of distilled DMF (0.8 mL) and CH_2Cl_2 (0.8 mL) at rt. After stirring at rt for 9 h, the solvents were removed under high vacuum. The residue was dissolved in a mixture of CH_2Cl_2 and CH_3OH (CH_2Cl_2:CH_3OH 9:1) and the solution was poured into CH_3OH (100 mL). The resultant red precipitates were collected by centrifugation. A preliminary purification by PTLC (CH_2Cl_2:CH_3OH 93:7; R_f = 0.48) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, CH_2Cl_2/CH_3OH 90:10, 2.0 mL/min, R_t = 6.0 min) **28** (16.5 mg, 54%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD 5:1): 9.89–9.71 (m, 10H), 8.63–7.99 (m, 20H), 7.16 (br s, 50H), 6.90–6.66 (m, 12H), 5.74–5.33 (m, 30H), 4.94–4.80 (m, 40H), 4.38–4.22 (m, 40H), 3.66–3.39 (m, 40H), 3.01 (br s, 20H), 2.15–1.95 (m, 40H), 1.73–1.19 (m, 170H); MS (MALDI, +ve linear, HABA): 9240 (100, $[M + Na]^+$).

Compound 8. A catalytic amount of thioanisole and pentamethyl benzene were added to a solution of **28** (4.3 mg, 0.47 μmol) in TFA (1 mL), and this red solution was stirred for 4 h at 35 °C. After this time, the red solution was evaporated to dryness by N_2 gas. Impurities were removed by solid-liquid extraction with ether (2 x 20 mL) and hexane (2 x 20 mL), to yield analytically pure (RPHPLC, Nucleosil 100-7 c18 250 x 8 mm, CH_3OH (with 1% TFA, 1.0 mL/min, R_t = 4.3 min) **8** (4.5 mg, quantitative) as a red solid. ^{1}H NMR (400 MHz, TFA-D): 8.84–8.39 (m, 20H), 7.73–7.19 (m, 12H), 5.98–5.91 (m, 10H),

5.38–4.58 (m, 50H), 3.89–3.62 (m, 40H), 3.21 (br s, 20H), 2.42–2.34 (m, 20H), 1.86–1.35 (m, 200H).

2.1.4. Synthesis of long-tail anionic propagator 9 (Scheme S3)

Compound 29. To a solution of **11** (406 mg, 0.55 mmol) in DMI (28 mL) was added 3-undecenylamine **17**[S5] (1.2 mL, 5.7 mmol) and the mixture was stirred for 4 h at rt. The reaction mixture was diluted with EtOAc (100 mL) and the organic layer was washed with 0.1 M HCl aq. (100 mL) water (100 mL). The organic layer was dried over Na_2SO_4 and solvent was evaporated to dryness. The resultant residue was purified by column chromatography (CH_2Cl_2:CH_3OH 95:5; R_f = 0.33) affording **29** (367 mg, 80%) as a red solid. mp: 78–79 °C; IR: 3362 (m), 2927 (m), 1674 (s), 1638 (s), 1583 (s), 1522 (m), 1441 (s), 1366 (m), 1313 (s), 1257 (s), 1215 (s), 1150 (s), 993 (s), 789 (s); ^{1}H NMR (400 MHz, $CDCl_3$, N/N = regioisomeric equivalents): 9.98 (t, ^3J (H,H) = 5.04 Hz, 1H), 8.75/8.68 (s, 1H), 8.24/8.15 (s, 1H), 6.35 (br s, 1H), 5.86–5.5.76 (m, 2H), 5.72/5.66 (dd, ^3J (H,H) = 8.96/9.00 Hz, ^3J (H,H) = 5.04/4.80 Hz, 1H), 5.24–5.11 (m, 3H), 5.09–4.92 (m, 2H), 4.44 (dd, ^3J (H,H) = 12.8 Hz, ^3J (H,H) = 5.56 Hz, 2H), 4.28 (br t, 2H), 3.54 (br m, 4H), 2.71–2.29 (m, 4H), 2.05 (q, ^3J (H,H) = 6.80 Hz, 2H), 1.82 (m, 2H), 1.62–1.33 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.33, 172.26, 171.7, 171.3, 165.7, 165.5, 162.3, 162.1, 162.0, 161.6, 161.5, 156.8, 156.7, 152.0, 151.9, 139.4, 138.6, 138.4, 133.0, 132.9, 128.7, 128.6, 127.5, 126.8, 123.5, 123.3, 122.7, 121.6, 121.3, 121.2, 121.0, 120.7, 120.6, 117.8, 117.7, 114.4, 99.6, 99.3, 81.1, 80.9, 65.8, 55.0, 54.1, 45.3, 43.83, 43.76, 40.86, 39.9, 39.7, 39.5, 34.0, 32.83, 32.76, 31.77, 29.7, 29.5, 29.3, 29.1, 28.2, 27.3, 27.2, 23.9; MS (ESI, +ve,

largest of isotopic peaks): 826 (40, $[M + H]^+$), 769 (60, $[M + H - {}^tBu]^+$), 753 (100, $[M + H - {}^tBu - NH_2]^+$).

Compound 30. A solution of **29** (132 mg, 0.16 mmol) in CH_2Cl_2 (32 ml) was treated at rt with $PhSiH_3$ (0.16 ml, 1.3 mmol) followed by $Pd(PPh_3)_4$ (18 mg, 10 mol%) and stirred for 1.5 h. The amount of solvent was reduced to approximately 2 ml *in vacuo* and then loaded on a silica gel column, which was in prior neutralized by washing with 1% Et_3N in CH_2Cl_2. The product was eluted from the column with 1% CH_3OH and Et_3N in CH_2Cl_2 and concentrated to afford **30** (78 mg, 67%) as a red solid. ^1H NMR (400 MHz, $CDCl_3/CD_3OD$ 5:1, N/N = regioisomeric equivalents): 9.91–9.83 (m, 1H), 8.68 (s, 1H), 8.158/8.149 (s, 1H), 5.72–5.50 (m, 2H), 4.86–4.76 (m, 2H), 4.26–4.22 (m, 2H), 3.46–3.44 (m, 2H), 3.04–3.00 (m, 2H), 2.50–2.12 (m, 4H), 1.92–1.86 (m, 2H), 1.70–1.66 (m, 2H), 1.37–1.17 (m, 23H); MS (ESI, +ve, largest of isotopic peaks): 742 (100, $[M + H]^+$), 726 (60, $[M - NH_2 + H]^+$).

Compound 31. To a solution of **15** (3.8 mg, 3.1 μmol), HATU (19 mg, 50 μmol) and DTBP (90 μL, 0.40 mmol) in a mixture of distilled DMF (0.4 mL) and CH_2Cl_2 (0.4 mL) was added a mixture of **30** (78 mg, 0.11 mmol) and TEA (40 μL, 0.29 mmol) in DMF (1.8 mL) at rt. After stirring at rt for 12 h, the solvents were removed under high vacuum. The residue was dissolved in a mixture of CH_2Cl_2 and CH_3OH (CH_2Cl_2:CH_3OH 9:1) and the solution was poured into CH_3OH (100 mL). The resultant red precipitates were collected by centrifugation. A preliminary purification by PTLC (CH_2Cl_2:CH_3OH 93:7; R_f = 0.40)

yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, CH_2Cl_2/CH_3OH 90:10, 2.0 mL/min, R_t = 6.1 min) **31** (14.6 mg, 56%) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ 5:1): 10.0–9.81 (m, 10H), 8.69–8.07 (m, 20H), 6.96–6.73 (m, 12H), 5.81–5.53 (m, 20H), 4.97–4.83 (m, 20H), 4.44–4.30 (m, 40H), 3.73–3.44 (m, 40H), 2.54–2.28 (m, 40H), 2.01–1.98 (m, 20H), 1.73–1.30 (m, 230H); MS (MALDI, +ve linear, HABA): 8469 (100, $[M + Na]^+$).

Compound 9. A solution of **31** (4.0 mg, 0.47 μmol) in TFA (1 ml) and CH_2Cl_2 (1 mL) was stirred for 3.5 h at rt. After this time, TFA and CH_2Cl_2 were removed by N_2 gas. Impurities were removed by solid-liquid extraction with ether (20 mL) and hexane (2 x 20 mL), leaving **9** (3.7 mg, quantitative) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$/TFA-D 10:1): 8.69–8.02 (m, 20H), 7.55–6.91 (m, 12H), 5.81 (br s, 10H), 5.44 (br s, 10H), 5.13–4.31 (m, 60H), 3.74–3.53 (m, 40H), 2.68–2.52 (m, 40H), 2.00 (br s, 20H), 1.85–1.66 (m, 40H), 1.50–1.36 (m, 100H).

2.2. Photocurrent generation

Gold electrodes. Gold electrodes were prepared as reported previously.[S6] Gold-coated glass slides (22 x 22 mm^2) were purchased from Mivitec GmbH, Analytical μ-Systems (Germany). Before use, the plates were cut in half (~ 1 x 2 cm^2), and cleaned using 'piranha' solution (H_2SO_4/30% H_2O_2 3/1; 35°C for 5 min).[S7] *Caution: piranha solution reacts violently with organic compounds. It should be handled with extreme care.* After the

treatment with piranha solution, the plates were thoroughly rinsed with water and EtOH, and used immediately.

Zipper initiation. Zipper assembly was initiated as reported in reference S2: The cleaned gold plates were immersed in the solution of the anionic initiator **10** (0.3 mM) in a 1:0.4 mixture of DMF:water for 7 days. The obtained Au-**10** electrodes were tested for defects using the standard procedure in which reduction-oxidation of $K_3Fe(CN)_6$ (2 mM in 1 M aqueous KNO_3) was measured by cyclic voltammetry using Au-**10** as working electrode.[S2,S8] The absence of redox wave confirmed the absence of large uncovered areas on the Au electrode.

LBL initiation. For LBL assembly, the gold electrodes were coated with lipoic acid. Namely, the cleaned gold plates were immersed in the solution of lipoic acid **19** (10 mM) in 0.5 mM sodium phosphate, 0.5 M NaCl, 50% aqueous TFE buffer pH 7, for 1 day. The obtained Au-**19** electrodes were tested for defects as described above.

Propagation. Typical procedure of preparation of the zipper assemblies or LBL on gold electrodes is described below. Coated gold electrodes Au-**10** or Au-**19** were immersed in the solution of *cationic* OPE **6** (5 μM) in a mixture of water (75%) and TFE (25%) with 0.5 mM sodium phosphate, 0.5 M NaCl buffer (pH 7) for two days, unless stated. The plate was rinsed repeatedly with bidistilled water and TFE, and the photocurrent of the resulting plate was recorded. The obtained bilayer coated plate was similarly treated with *anionic*

OPE **7** to give the trilayer coated plate. Multilayers were obtained by repeating these sequences of depositions. Results obtained under varied conditions for Au-**10**-(**6**-**7**-)$_n$-**6**, and Au-**10**-(**8**-**9**-)$_n$-**8** are summarized in Tables S1 and S2.

Photocurrent measurements. Coated gold 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 = ~0.9 cm^2). Changes in current upon on-off switching of irradiations (20 seconds each) were measured at +0.4 V *vs* Ag/AgCl unless stated. The power of irradiation for experiments in Table S1 and S2 was 66 mW cm^{-2}. For the other experiments, Hoya ND8 (neutral filter) was used to reduce power of irradiation to 8.91 mW cm^{-2}.

2.3. Covalent capture of zippers on gold surface

Cross-linking of zippers.[S9] Typical procedure of cross-linking of zippers on gold electrodes is described below. Coated gold electrodes Au-**10**-(**6**-**7**-)$_n$-**6** were immersed in the solution of Grubbs catalyst first or second generation (10 mM) in CH_2Cl_2 or toluene (2 mL) at rt for time periods between 10 min and 8 h. In parallel, a negative control eletrode was incubated into identical sloutions without catalyst. The plates were then rinsed repeatedly with CH_2Cl_2, and the photocurrent of the resulting plate was recorded. The same

zipper propagation as described in the above "propagation" section was carried out after cross-linking (see Figure 6-8).

2.4. Supplementary references

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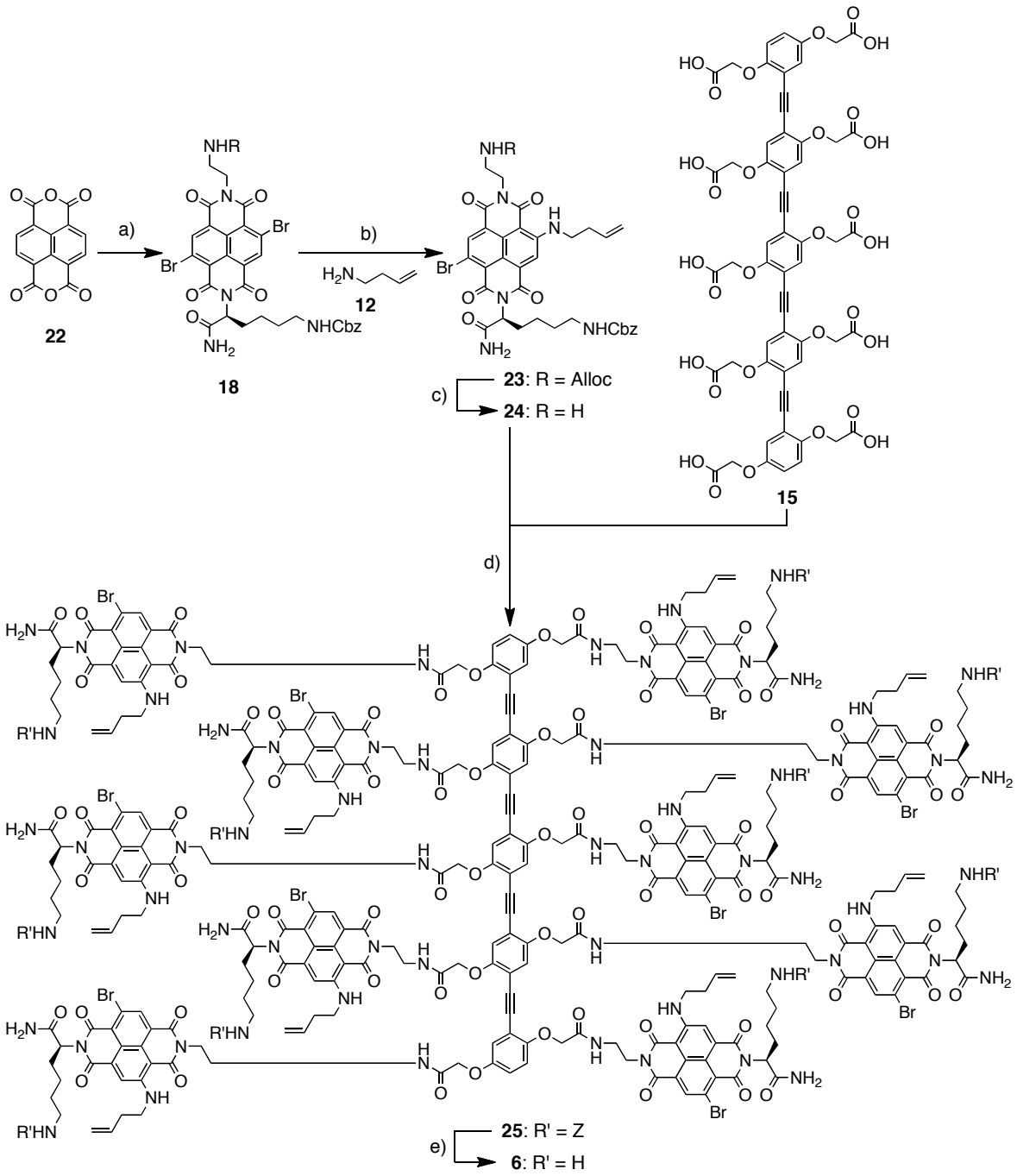
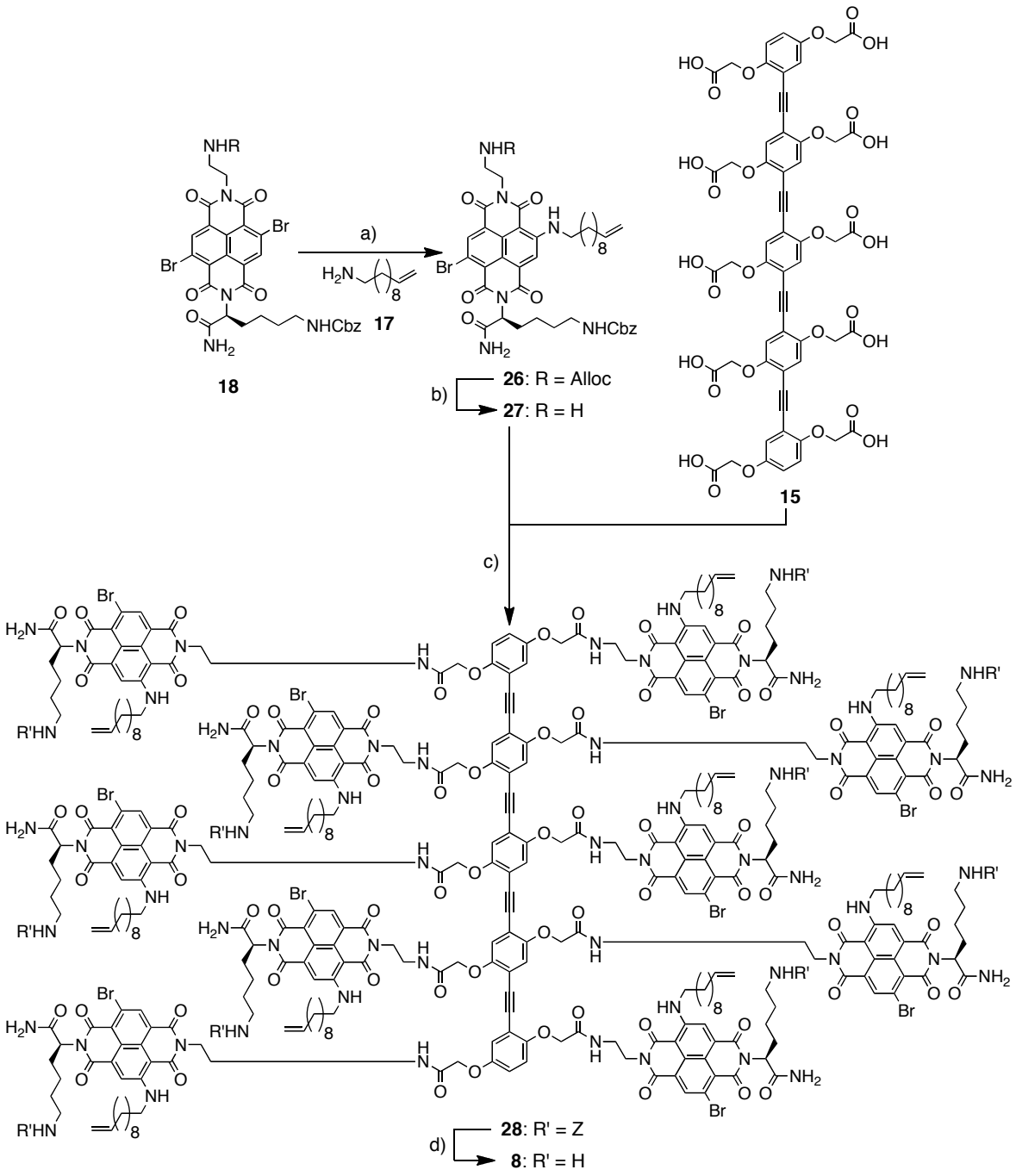
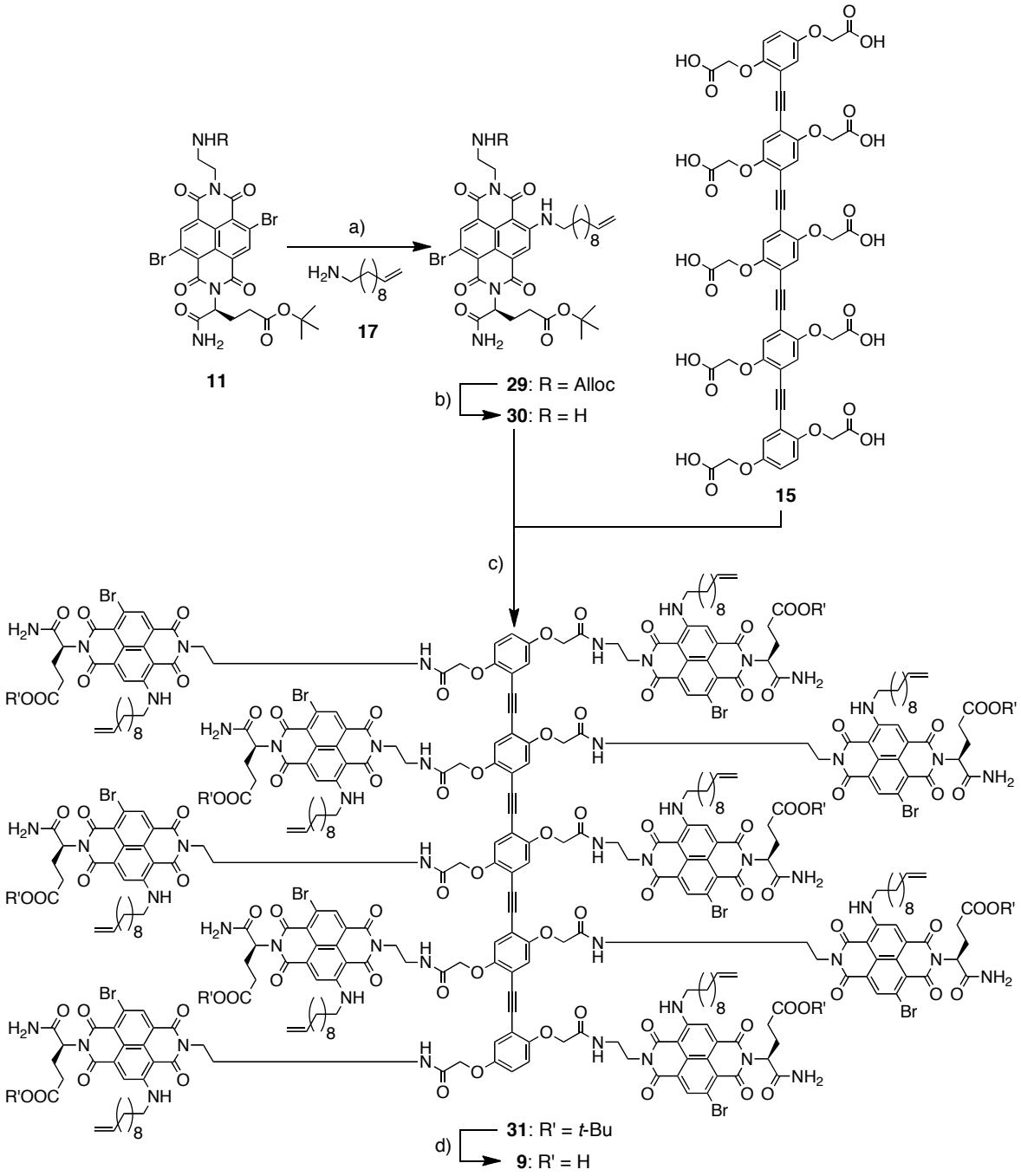


Scheme S1. a) 2 steps.[S1] b) DMI, rt, 4 h, 76%. c) CH_2Cl_2, $PhSiH_3$, $Pd(PPh_3)_4$, rt, 1 h, 86%. d) HATU, DTBP, TEA, DMF, rt, 12 h, 19%. e) TFA, thioanisole, pentamethyl benzene, 35 °C, 3 h, quantitative.



Scheme S2. a) DMI, rt, 4 h, 79%. b) CH_2Cl_2, $PhSiH_3$, $Pd(PPh_3)_4$, rt, 1 h, 70%. c) HATU, DTBP, TEA, DMF, rt, 13 h, 54%. d) TFA, thioanisole, pentamethyl benzene, 35 °C, 3 h, quantitative.



Scheme S3. a) DMI, rt, 4 h, 80%. b) CH_2Cl_2, $PhSiH_3$, $Pd(PPh_3)_4$, rt, 1 h, 67%. c) HATU, DTBP, TEA, DMF, rt, 13 h, 56%. d) TFA, CH_2Cl_2, rt, 3.5 h, quantitative.

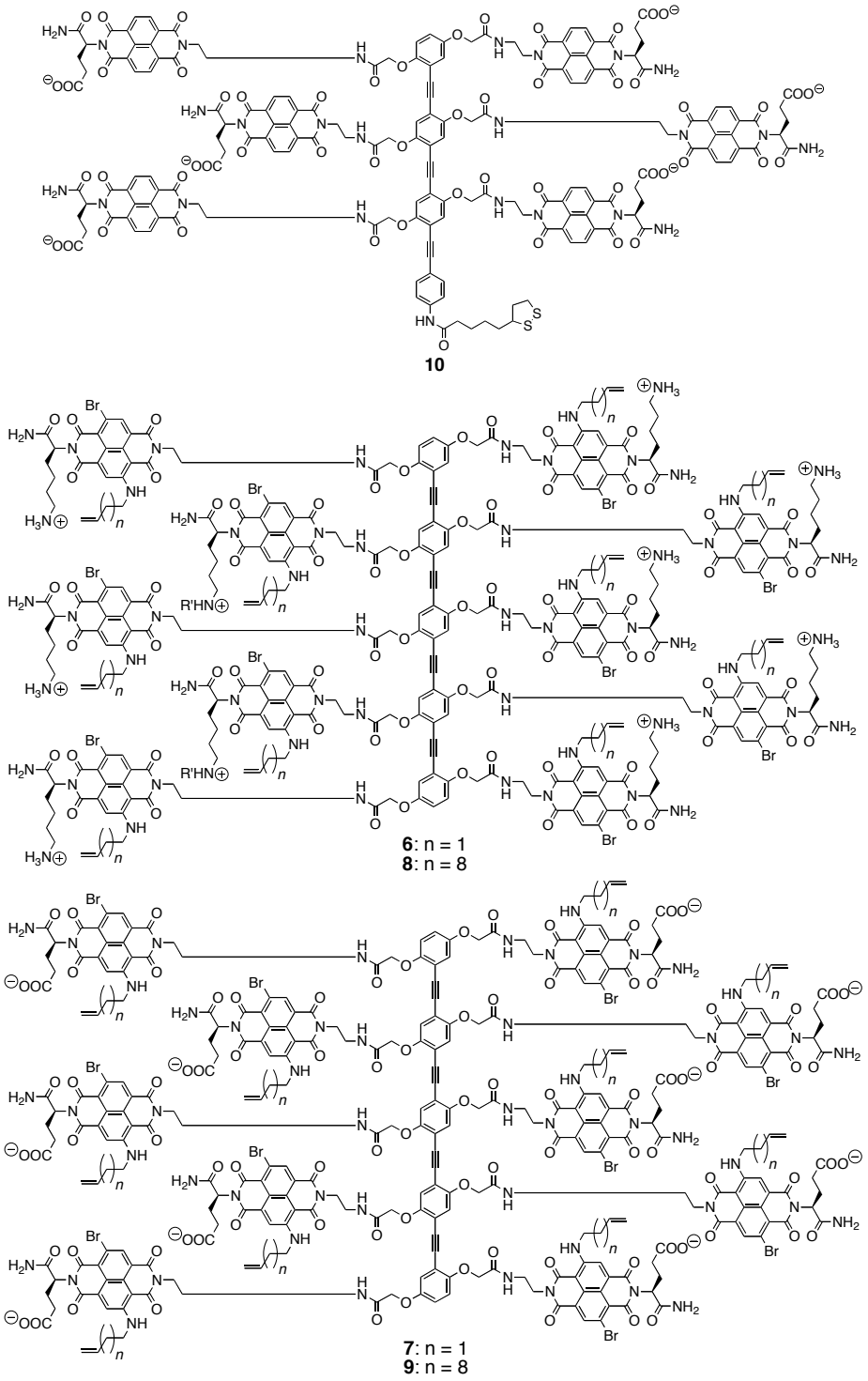


Figure S1. Full structures of zipper components **6**-**10**. *Note*, **6**-**9** *contain both regioisomers* (2,6- *and* 3,7-) *of N,Br-NDIs.*

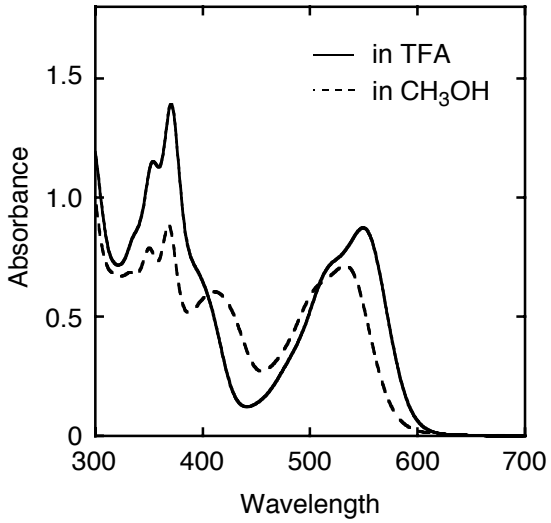


Figure S2. Absorption spectra of cationic OPE **6** having short chains measured in TFA and CH_3OH at 25 °C.

Table S1. Conditions of Zipper Assemblies Having Short Chains[a]

Entry	[OPE rod] (μM)	Solvent system	Ratio of solvents (vol/vol)	[NaCl] (M)	L_c (zippers) /L_c (LBL)[b]	J_{max} (μA/cm^2)[c]	J_{max} (zippers) /J_{max} (LBL)
1	10	TFE/water	1/1	1	3/–	5.3	–
2	10	TFE/water	½	1/0.1[d]	10/10	29	1.2
3	5	TFE/water	1/3	0.5	11/11	29	1.5
4	5	TFE/water	1/3	0.1	6/6	19	1.5
5	5	TFE/water	2/1	0.1	8/8	11	1.2
6	4	HFIP/water	1/4.6	0.36	10/7	23	1.4
7	5	HFIP/water	1/3	0.1	9/9	17	1.1
8	5	HFIP/water	½	0.1	7/7	11	1.1

[a] $[Na_nH_{3-n}PO_4]$ = 0.5 mM, pH = 7, the electrodes were dipped into the solution of OPE for 2–3 days. [b] Critical thickness in *J*–*L* curves. [c] Maximal photocurrent density in *J*–*L* curves (measured at input power P_{in} = 67 mW/cm^2). [d] [NaCl] for cationic OPE rod = 1 M, [NaCl] for anionic OPE rod = 0.1 M.

Table S2. Conditions of Zipper Assemblies Having Long Chains[a]

Entry	[OPE rod] (μM)	Solvent system	Ratio of solvents (vol/vol)	[NaCl] (M)	L_c (zippers) /L_c (LBL)[b]	J_{max} (μA/cm^2)[c]	J_{max} (zippers) /J_{max} (LBL)
1	5	TFE/water	1/1	1	9/9	25	1.1
2	5	TFE/water	½	0.1	9/9	24	1.1
3	5	TFE/water	½	1	10/8	32	1.1
4	5	TFE/water	1/3	0.1	7/5	30	1.1
5[d]	10	TFE/water	1/3	0.1	11/11	25	1.1

[a] [$Na_nH_{3-n}PO_4$] = 0.5 mM, pH = 7, the electrodes were dipped into the solution of OPE for 2–3 days. [b] Critical thickness in *J*–*L* curves. [c] Maximal photocurrent density in *J*–*L* curves (measured at input power P_{in} = 67 mW/cm^2). [d] The electrodes were dipped into the solution of OPE for 1 day.