Zipper Assembly of SHJ Photosystems: Focus on Red Naphthalenediimides, Optoelectronic Finetuning and Topological Matching

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Supplementary Information

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1. Materials and methods

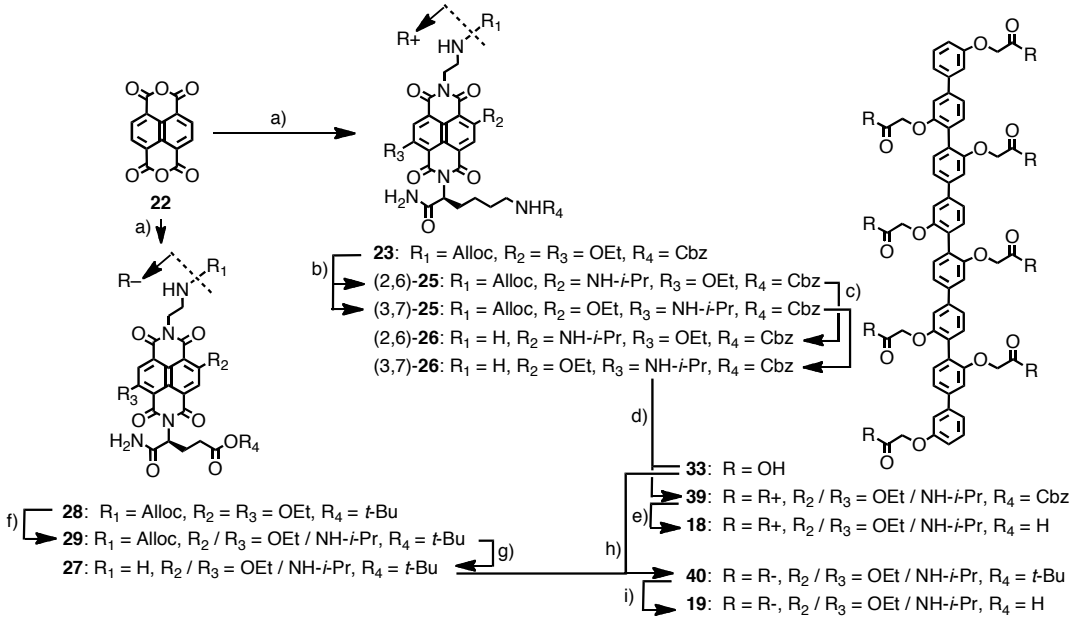
As in ref. S1, Supplementary Information. Briefly, reagents for synthesis were purchased from Fluka, amino acid derivatives from Novabiochem and Bachem, HATU from Applied Biosystems, buffers, and salts from Sigma or Fluka-Aldrich. All reactions were performed under N_2 or argon atmosphere. Unless stated 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 *m/z* (%). MALDI-TOF MS were performed on a Axima CFR^+ (Shimadzu) and are reported as *m/z* (%). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Sciex QSTAR Pulsar mass spectrometer. 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) and $\Delta\varepsilon$ (in $mM^{-1}cm^{-1}$). ^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 ($\delta = 0$). 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; *en*: Ethylenediamine; Fc: Ferrocene; *FF*: Fill factor; FU: Fluorescence up-conversion; Fwhm: Full-width at half-maximum; *Gla*: Glycolic acid; Glu: L-Glutamic acid; HATU: N-[(Dimethylamino)-1*H*-1,2,3 -triazolo[4,5-b]pyridin-1-ylmethylene]-N-methylmethanammonium hexafluorophosphate N-oxide; IPCE: Incident photon to current conversion efficiency; LBL: layer-by-layer assembly; NDA: 1,4,5,8-Naphthalenedianhydride; NDI: 1,4,5,8-Naphthalenediimide; NTE: 1,4,5,8-Naphthalenetetraester; OPE: Oligophenylethynyl; POP: *p*-Oligophenyl; rt: Room temperature; TA: Transient absorption; TCSPC: Time-correlated single photon-counting technique; TEA: Triethylamine; TEOA: Triethanolamine; TFA: Trifluoroacetic acid; TFE: 2,2,2-Trifluoroethanol.

2. Synthesis

2.1. Synthesis of POP propagators



Scheme S1. (a) as in ref. S1. (b) *i*-PrNH$_2$, 77 % ((2,6)-**25**: 21%; (3,7)-**25**: 57%). (c) PdCl$_2$(PPh$_3$)$_4$, PhSiH$_3$ (crude). (d) HATU, di-tBu-pyridine, TEA, DMF (53% from **25**). (e) HBr, thioanisole, pentamethylbenzene, TFA (quant). (f) *i*-PrNH$_2$, 42%. (g) PdCl$_2$(PPh$_3$)$_4$, PhSiH$_3$ (crude). (h) HATU, di-tBu-pyridine, TEA, DMF (52% from **29**). (i) TFA (quant).

***O,O*-NDI 23**. This compound was prepared from commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride **22** following the reported procedures.[S1]

(2/3,6/7)-*O,N*-NDI 25. *O,O*-NDI **23** (140 mg, 0.188 mmol) was dissolved in 25 ml isopropylamine/dichloromethane mixture (1.5:1). The resulting orange solution was stirred for 4 h

and then evaporated to dryness at room temperature. The pink residue obtained was purified by preparative thin layer chromatography (CH_2Cl_2/MeOH 93:7). The pink band was extracted affording the desired **25** as a mixture of two isomers (110 mg, 77%). Mp: 119-120 °C; CD (CH_2Cl_2): 270 (1.04); IR: 3354 (m), 2930 (m), 1979 (m), 1679 (s), 1640 (s), 1585 (s), 1526 (m), 1499 (m), 1455 (s), 1298 (m), 1259 (m), 1215 (m), 1140 (m), 1024 (m), 792 (m), 749 (m); ^{1}H NMR (400 MHz, $CDCl_3$, N/N = regioisomeric equivalents, Fig. S1): 9.65/9.56 (d, ^3J (H,H) = 7.3/7.3 Hz, 1H), 8.15/8.07 (s, 1H), 7.89/8.05 (s, 1H), 7.23 - 7.25 (m, 5H), 6.67 (br.s, 1H), 5.92 (br.s, 1H), 5.87 - 5.75 (m, 1H), 5.71 - 5.67/5.66 - 5.62 (m, 1H), 5.24 - 5.09 (m, 2H), 4.96/4.95 (s, 2H), 4.87/4.83 (br.s, 1H), 4.54 - 4.44 (m, 2H), 4.26 - 4.21 (m, 2H), 4.13 - 4.06 (m, 1H), 3.40 (br.s, 2H), 3.13 (br.s, 2H), 2.44 - 2.09 (m, 2H), 1.72 (br.s, 2H), 1.62 – 1.59 (m, 2H), 1.58/1.56 (t, ^3J (H,H) = 7.3/6.8 Hz, 3H), 1.46/1.43 (d, ^3J (H,H) = 6.3/6.1 Hz, 6H); MS (ESI, +ve): 757 (80, $[M + H]^+$), 740 (100, $[M – NH_2]^+$); HR-MS (ESI, +ve): Calcd for $C_{39}H_{45}O_{10}N_6^+$: 757.3191, Found: 757.3136.

(2,6)-25 and (3,7)-25. The two regioisomers (2,6)-**25** and (3,7)-**25** were separated by preparative thin layer chromatography (CH_2Cl_2/MeOH 94:6). Three successive runs on a single plate enabled separation of the upper reddish pink band which was found to be pure (3,7)-**25** (80 mg, 57%). The bottom pink band was collected and purified again by preparative thin layer chromatography (CH_2Cl_2/MeOH 94:6) in a single run to afford pure (2,6)-**25** (30 mg, 21%). The regiochemistry of the obtained isomers were assigned by NMR analysis (Figs. S1, S2, S3). Namely, strongly downfield shifted ^{13}C signal of one of the imide carbonyls indicates the hydrogen-bonding to NH, and thus identifies it as *C1'* in (3,7)-**25**, or *C5'* in (2,6)-**25**. This hydrogen-bonding interaction was also apparent from slow proton to deuterium exchange in ^{1}H NMR. The HMBC correlations between this imide carbonyl and *H*-α in (3,7)-**25**, or *CH*$_2$ of ethylenediamine in (2,6)-**25** unambiguously place this hydrogen-bonded pair near the lysine in (3,7)-**25** and near

ethylenediamine in (2,6)-**25**. All the other correlations are compatible with these assignments. (3,7)-**25**: ^{1}H NMR (500 MHz, $CDCl_3$): 9.67 (d, ^{3}J (H,H) = 7.3Hz, 1H), 8.15 (s, 1H), 8.08 (s, 1H), 7.23 - 7.25 (m, 5H), 6.53 (br.s, 1H), 5.85 - 5.77 (m, 1H), 5.72 (dd, ^{3}J(H,H) = 9.1 Hz, ^{3}J(H,H) = 5.3 Hz, 1H), 5.20 (d, ^{3}J(H,H) = 17.3 Hz, 1H), 5.10 (d, ^{3}J(H,H) = 9.5 Hz, 1H), 5.08 (m, 1H), 4.97 (s, 2H), 4.80 (br.s, 1H), 4.46 (m, 2H), 4.34 - 4.26 (m, 2H), 4.14 - 4.06 (m, 1H), 4.12 (br.s, 2H), 3.45-3.41 (m, 2H), 3.13 (br.s, 2H), 2.38 - 2.14 (m, 2H), 1.62 - 1.59 (m, 2H), 1.58 (t, ^{3}J (H,H) = 6.9 Hz, 3H), 1.46 (d, ^{3}J (H,H) = 6.3 Hz, 3H), 1.43 (d, ^{3}J (H,H) = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.8 (s), 165.3(s), 162.6 (s), 162.5 (s), 161.1 (s), 157.7 (s), 156.4 (s), 156.3 (s), 149.8(s), 136.4 (s), 132.8 (d), 128.0 (d), 127.9 (d), 126.5 (s), 124.6 (s), 123.8 (s), 121.0(d), 117.9 (d), (d), 117.5 (t), 111.0 (s), 99.4 (s), 66.5 (t), 65.9 (t), 65.5 (t), 54.2 (d), 53.4 (d), 44.7 (d), 40.6 (t), 39.7 (t), 39.6 (t), 29.7 (t), 28.1 (t), 23.7 (t), 23.2 (q), 23.1 (q), 14.9 (q); MS (ESI, +ve): 757 (70, $[M + H]^+$), 740 (100, $[M - NH_2]^+$). (2,6)-**25**: ^{1}H NMR (500 MHz, $CDCl_3$): 9.67 (d, ^{3}J (H,H) = 7.3 Hz, 1H), 8.15 (s, 1H), 8.08 (s, 1H), 7.23 - 7.25 (m, 5H), 6.53 (br.s, 1H), 5.85 - 5.77 (m, 1H), 5.72 (dd, ^{3}J(H,H) = 9.1 Hz, ^{3}J(H,H) = 5.3 Hz, 1H), 5.20 (d, ^{3}J(H,H) = 17.3 Hz, 1H), 5.10 (d, ^{3}J(H,H) = 9.5 Hz, 1H), 5.08 (m, 1H), 4.97 (s, 2H), 4.80 (br.s, 1H), 4.46 (m, 2H), 4.34 - 4.26 (m, 2H), 4.14 - 4.06 (m, 1H), 4.12 (br.s, 2H), 3.45-3.41 (m, 2H), 3.13 (br.s, 2H), 2.38 - 2.14 (m, 2H), 1.62 - 1.59 (m, 2H), 1.58 (t, ^{3}J (H,H) = 6.9 Hz, 3H), 1.46 (d, ^{3}J (H,H) = 6.3 Hz, 3H), 1.43 (d, ^{3}J (H,H) = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.5 (s), 165.7 (s), 162.8 (s), 162.6 (s), 161.2 (s), 158.0 (s), 156.4 (s), 149.8 (s), 136.5 (s), 132.8 (d),128.5 (d, 2x) 128.4 (d, 2x), 128.0 (d), 127.9 (d), 127.0 (s), 124.6 (s), 123.9 (s), 121.2 (s), 121.1 (s), 117.9 (d), 117.5 (t), 99.4 (s), 66.5 (t), 66.0 (t), 65.6 (t), 54.3 (d), 53.4 (d), 44.7 (d), 40.5 (t), 39.7 (t), 29.5 (t), 28.2 (t), 23.6 (t), 23.2 (q), 23.1 (q), 14.8 (q); MS (ESI, +ve): 757 (80, $[M + H]^+$), 740 (100, $[M - NH_2]^+$).

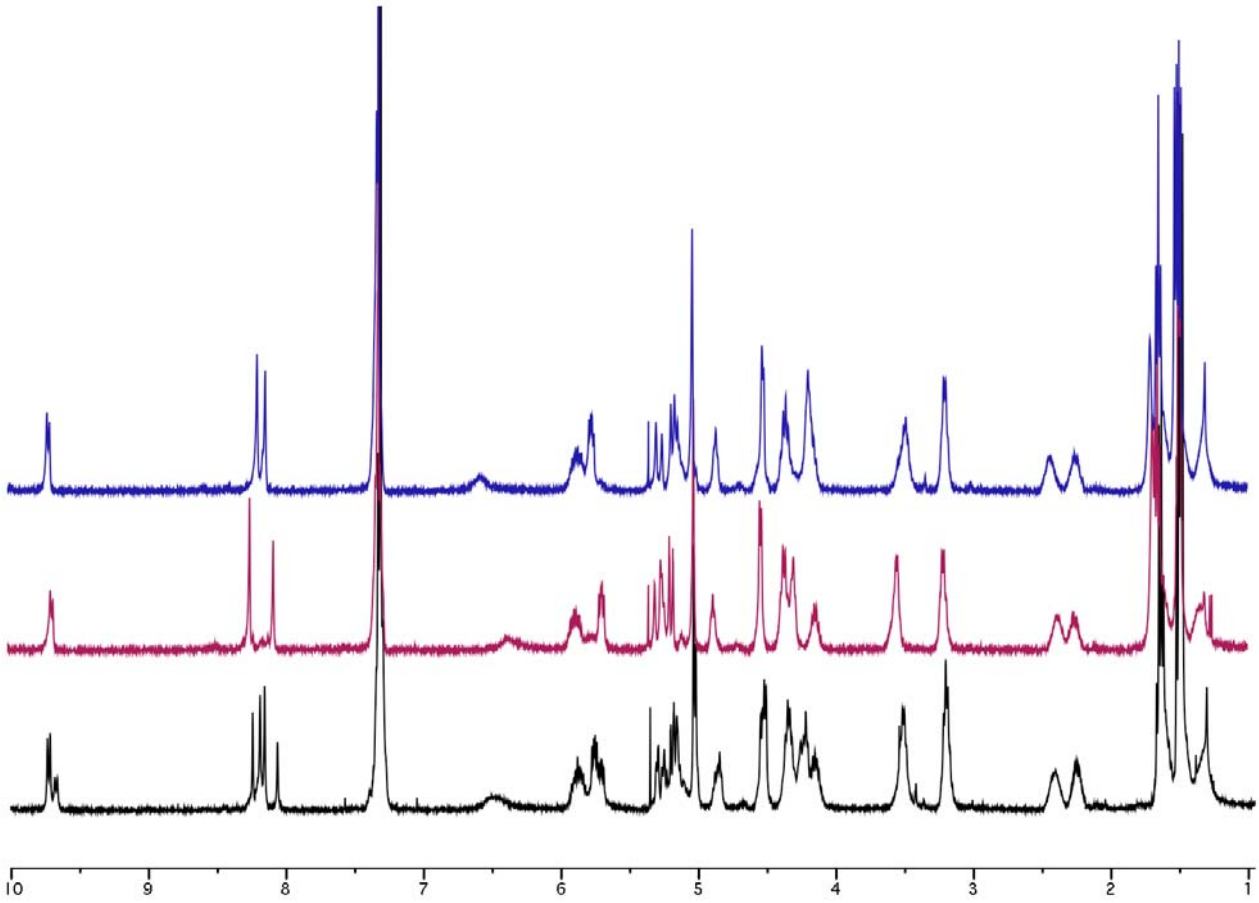


Figure S1. ^{1}H NMR spectra of *O*,*N*-NDI isomers (3,7)-**25** (blue, top), (2,6)-**25** (red, middle) and the mixture of the two (black, bottom) in $CDCl_3$.

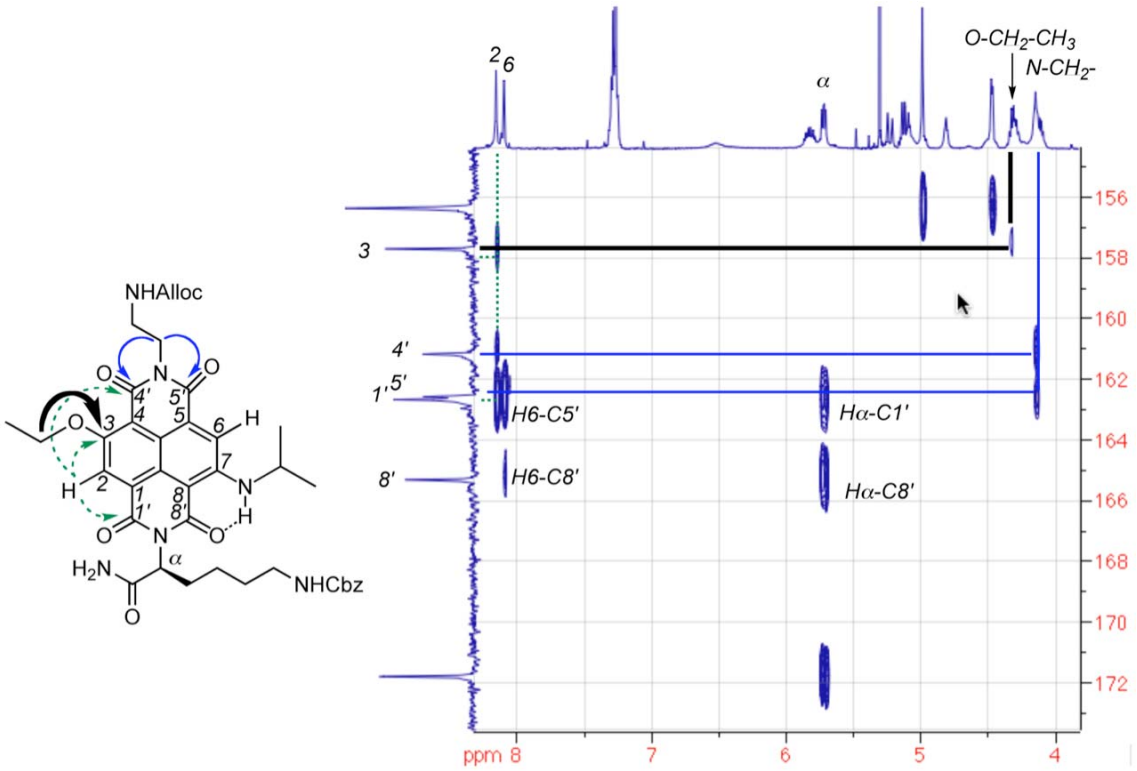


Figure S2. HMBC correlations of (3,7)-**25**.

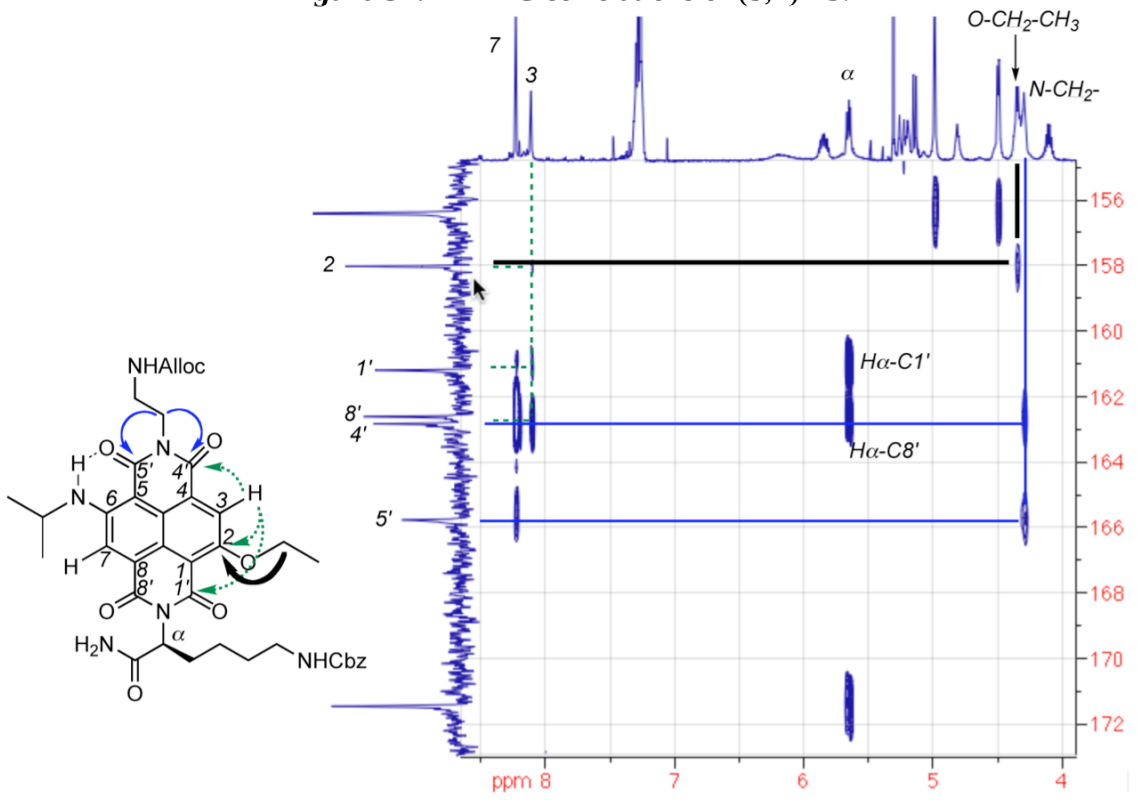


Figure S3. HMBC correlations of (2,6)-**25**.

POP 33. This compound was prepared following the reported procedures.[S2]

POP-NDI 39 (general procedure A). To a solution of **25** (71 mg, 0.20 mmol) in 4 mL CH_2Cl_2 was added $Pd(PPh_3)_4$ (5.4 mg, 4.6 μmol) followed by $PhSiH_3$ (75 μl, 0.56 mmol). The solution was stirred and monitored by TLC. After 10 min, when the consumption of the reactant **25** was observed the solvent was removed under vacuum at rt and was re-dissolved in 1 ml freshly distilled and degassed DMF to give the solution of **26**. In a separate round bottomed flask a solution of **33** (4.8 mg, 4.6 μmol), HATU (14 mg, 0.036 mmol) in dry, degassed DMF (1 ml) was stirred for 5 min. The solution of **26** in DMF was now transferred to the solution with activated **33**. To the stirred reaction mixture were added TEA (100 mg, 0.99 mmol) and 2,6,di-*tert*butylpyridine (50 mg, 0.26 mmol). The reaction mixture was stirred under inert atmosphere at rt for 16 h, following which the reaction mixture was evaporated to dryness. In a solid-liquid extraction process, the solid crude product was washed with water and methanol. Two successive PTLCs (CH_2Cl_2/MeOH 9:1, R_f = 0.5) of the residue were performed and a non-fluorescent pink band was collected to give **39** (11 mg, 53%) as a pink solid. HPLC: YMC-Pack SIL 10x250 mm, CH_2Cl_2/MeOH 9:1, 2 ml/min, R_t = 6.37 min; ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD 9:1): 9.51 (br.s, 8H), 8.21 - 7.63 (m, 24H), 7.18 (br.s, 40H), 7.04 - 6.65(m, 14H), 6.90 - 6.66 (m, 2H), 5.64 - 5.09 (m, 16H), 5.09 - 5.03 (br.s, 16H), 4.69 - 4.57 (m, 16H), 4.13 - 3.74 (m, 16H), 3.73 - 3.13 (m, 16 H), 3.13 - 2.35 (m, 16H), 2.94 (br.s, 16H), 2.35-1.86 (m, 16H), 1.52 - 1.48 (m, 24H), 1.48 - 1.10 (m, 48H); MS (MALDI, +ve linear, dithranol): 6463 (100, $[M + Na]^+$), 6419 (80, $[M – NH_2]^+$).

POP-NDI (3,7)-39. Following the general procedure A, (3,7)-**39** (16 mg, 69%) was obtained using (3,7)-**25** (90 mg, 0.118 mmol), $Pd(PPh_3)_4$ (6.8 mg, 5.8 μmol), $PhSiH_3$ (75 μl, 0.555 mmol), **33** (6.0 mg, 4.9 μmol), HATU (14 mg, 0.036 mmol), TEA (200 mg, 1.9 mmol) and 2,6,di-

*tert*butylpyridine (100 mg, 0.522 mmol). Analytical data are identical to those obtained with **39**.

POP-NDI (2,6)-39. Following the general procedure A, (2,6)-**39** (1 mg, 16%) was obtained using (2,6)-**25** (25 mg, 0.033 mmol), $Pd(PPh_3)_4$ (2.0 mg, 1.7 μmol), $PhSiH_3$ (75 μl, 0.56 mmol), **33** (1.7 mg, 1.4 μmol), HATU (14 mg, 9.0 μmol), TEA (100 mg, 0.98 mmol) and 2,6,di-*tert*butylpyridine (50 mg, 0.26 mmol). Analytical data are identical to those obtained with **39**.

POP-NDI 18 (general procedure B). To a solution of 2 mg **39** in 1 ml TFA was added 2 mg pentamethyl benzene and 5 μl thioanisole. To this red solution was added 5 μl of HBr in acetic acid and the resultant light yellow reaction mixture was stirred at room temperature for 4 h. The reaction mixture was then evaporated to dryness and washed repeatedly with ether affording the desired product **18** as a pink solid in quantitative yield. ^{1}H NMR (400 MHz, CD_3OD + TFA*d*): 8.14 - 6.72 (m, 42H), 5.75 - 5.36 (m, 8H), 4.63 - 3.82 (m, 40H), 3.15 - 2.82 (m, 16H), 2.28 - 2.18 (m, 16H), 2.16 - 1.97 (m, 16H), 1.93 - 1.72 (m, 48H), 0.91-0.88 (m, 24H); MS (ESI, +ve): 1790 (5, $[M + 3H]^{3+}$), 1342 (25, $[M + 4H]^{4+}$), 1074 (75, $[M + 5H]^{5+}$), 896 (100, $[M + 6H]^{6+}$), 767 (10, $[M + 7H]^{7+}$); MS (MALDI, +ve linear, dithranol): 5365 (100, $[M]^+$), 5344 (70, $[M - NH_2]^+$), 5321 (80, $[M - OEt]^+$).

POP-NDI (3,7)-18. Following the general procedure B, (3,7)-**18** was prepared from (3,7)-**39**. The analytical data are identical to those of **18**.

POP-NDI (2,6)-18. Following the general procedure B, (2,6)-**18** was prepared from (3,7)-**39**. The analytical data are identical to those of **18**.

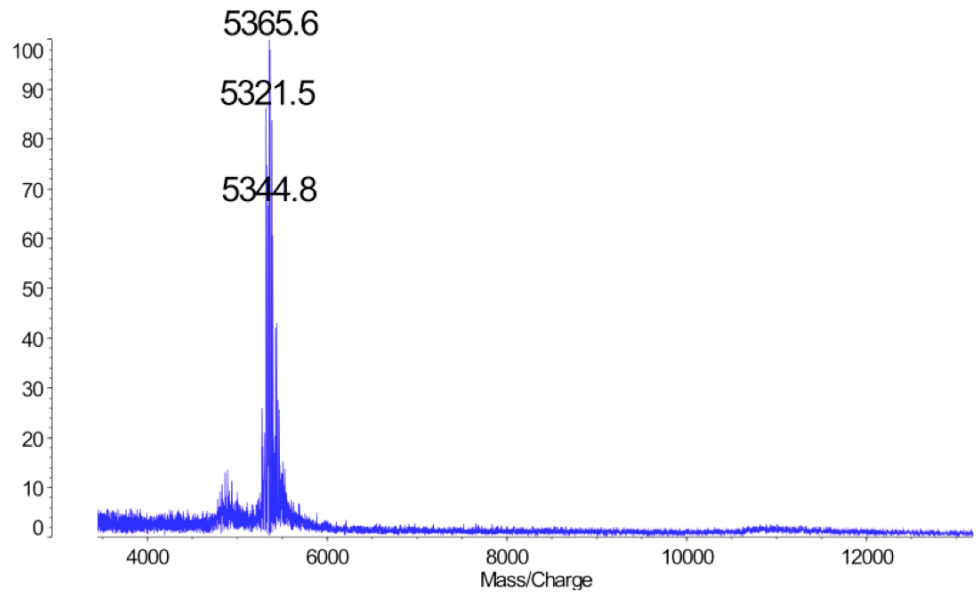


Figure S4. MALDI-MS of **18.**

***O,O*-NDI 28**. This compound was prepared from commercially available 1,4,5,8-naphthalenetetracarboxylic dianhydride **22** following the reported procedures.[S1]

***O,N*-NDI 29**. *O,O*-NDI **28** (70 mg, 0.11 mmol) was taken in 25 ml isopropylamine/dichloromethane mixture (3:2). The reaction mixture was stirred for 4 h and then evaporated to dryness at rt. The pink residue obtained was purified by preparative thin layer chromatography (CH_2Cl_2/MeOH 93:7). The pink bands were retained and extracted affording the desired **29** as a mixture of two isomers (30 mg, 42%). Mp: 189 - 190 °C; CD (CH_2Cl_2): 266 (1.57); IR: 3472 (m), 2967 (m), 1984 (m), 1690 (m), 1637 (s), 1584 (s), 1498 (m), 1459 (m), 1390 (m), 1300 (m), 1258 (m), 1215 (s), 1142 (m), 1082 (m), 932 (m), 847 (m), 792 (m); ^{1}H NMR (400 MHz, $CDCl_3$, N/N = regioisomeric equivalents): 9.69/9.63 (d, ^3J (H,H) = 7.6/7.8 Hz, 1H), 8.18/8.13 (s, 1H), 8.09/7.98 (s, 1H), 6.64 (br.s, 1H), 5.89 - 5.79 (m, 1H), 5.77 - 5.73/5.70 - 5.67 (m, 1H), 5.26 -

5.10 (m, 2H), 4.49 - 4.46 (m, 2H), 4.33 - 4.27 (m, 2H), 4.16 - 4.08 (m, 3H), 3.45 (br.s, 2H), 3.19 (br.s, 2H), 2.71 - 2.27 (m, 4H), 1.72 (br.s, 2H), 1.61/1.59 (t, ^{3}J (H,H) = 6.8/6.6 Hz, 3H); 1.47/1.45 (d, ^{3}J (H,H) = 6.28/6.32 Hz, 6H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$), N/N = regioisomeric equivalents): 172.4/172.3 (s), 171.7/171.6 (s), 165.6/165.5 (s), 163.6/162.8 (s), 162.7/161.5 (s), 161.4/158.0 (s), 157.9/157.8 (s), 133.1/133.0 (d), 127.5/127.4 (s), 125.0/124.9 (s), 121.2/121.1 (d, 2x), 120.9 (s), 118.1/117.8 (t), 117.7/117.6 (d, 2x), 112.0 (s), 99.6 (s), 80.8 (s), 66.3/66.2 (t), 65.8/65.7 (t), 54.2/54.0 (t), 44.9/44.9 (d), 39.8/39.7 (t), 32.9/32.8, 28.2 (q, 3x) 24.1/23.5 (t), 23.4/23.3 (q, 2x), 15.0/14.9 (q); MS (ESI, +ve): 698 (25, $[M + NH_4]^+$), 680 (80, $[M + H]^+$), 621 (100, $[M - OBu^t]^+$); HR-MS (ESI, +ve): Calcd for $C_{34}H_{42}O_{10}N_5^+$: 680.2926, Found: 680.2950.

POP-NDI 40. Following the general procedure A, **40** (11 mg, 52%) was obtained from **29** (69 mg, 0.10 mmol), $Pd(PPh_3)_4$ (6.6 mg, 5.7 μmol), $PhSiH_3$ (120 μl, 0.89 mmol), **33** (6 mg, 4.9 μmol), HATU (14 mg, 0.036 mmol), TEA (200 mg, 2.0 mmol) and 2,6,di-*tert*butylpyridine (40 mg, 0.21 mmol). HPLC: YMC-Pack SIL 10x250 mm, CH_2Cl_2/MeOH 9:1, 2 ml/min, R_t = 6.37 min; ^{1}H NMR (400 MHz, $CDCl_3$): 9.59 (br.s, 8H), 8.37 - 7.75 (m, 16H), 7.71 - 7.32 (m, 16H), 7.19 - 6.53 (m, 8H), 5.83 - 5.43 (m, 8H), 4.79 - 3.80 (m, 54H), 3.80 - 3.16 (m, 18H), 2.91 - 2.51 (m, 8H), 2.51 - 2.10 (m, 16H), 2.08 - 1.60 (m, 24H), 1.56 - 0.97(m, 120H); MS (MALDI, +ve linear, HABA): 5847 (100, $[M + Na]^+$).

POP-NDI 19. A solution of **40** (7 mg, 1.2 μmol) in TFA (1 ml) was stirred for 1 h at rt. The mixture was concentrated in *vacuo*, and the residue washed with CH_2Cl_2 (solid-liquid extraction) to give **19** (6.5 mg, quant.) as a pink solid. ^{1}H NMR (300 MHz, $CDCl_3$ / TFA-*d* 4:1): 8.48 – 8.00 (m, 16H), 7.67 – 7.11 (m, 24H), 7.00 – 6.89 (m, 2H), 6.07 – 5.87 (m, 8H), 4.82 – 4.05 (m, 56H), 3.97 – 3.57 (m, 16H), 2.82 – 2.45 (m, 32H), 1.63 – 1.29 (m, 72H); MS (MALDI, +ve linear, HABA):

5396 (100, $[M + Na]^+$).

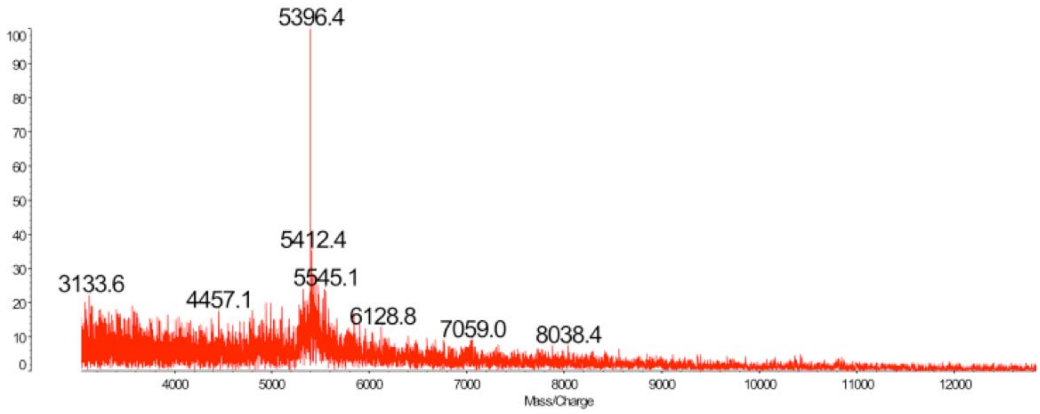
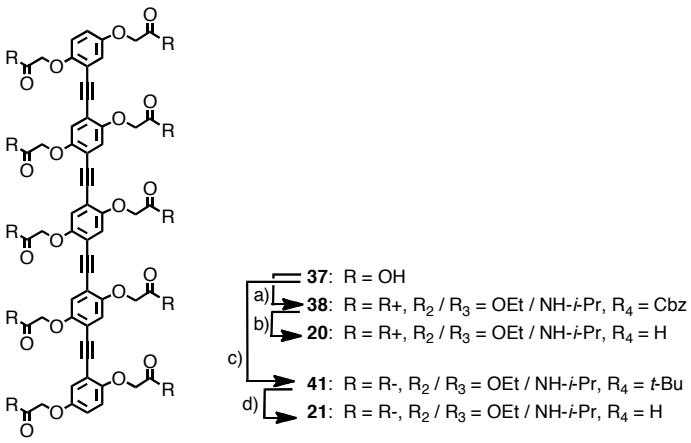


Figure S5. MALDI-MS of **19**.

2.2. Synthesis of OPE propagators



Scheme S2. (a) HATU, di-tBu-pyridine, TEA, DMF (28%). (b) Thioanisole, pentamethylbenzene, TFA (quant). (c) HATU, di-tBu-pyridine, TEA, DMF (43%). (d) TFA (quant).

OPE 37. This compound was prepared following a literature procedure.[S3]

OPE-NDI 38. To a solution of **25** (80 mg, 0.105 mmol) in 20 ml CH_2Cl_2, was added $Pd(PPh_3)_4$ (7.2 mg, 0.0062 mmol) followed by $PhSiH_3$ (105 μL, 0.845 mmol). The solution was stirred at rt and monitored by TLC. After 15 min, when the consumption of the reactant compound **25** was observed then the solvent was removed under vacuum at rt and impurities were removed by solid-liquid extraction with ether (3 x 10 ml) and CH_2Cl_2 (3 x 10 ml), yielded **26** (71 mg, quantitative) as a red solid. Crude **26** (69 mg, 0.10 mmol) was dissolved with **37** (3.2 mg, 2.6 μmol), HATU (15 mg, 39 μmol), DTBP (70 μl, 0.31 mol) and TEA (28 μl, 0.21 mol) in freshly distilled and degassed DMF (1 ml), and stirred at rt for 16 h. DMF was removed under high vacuum. A preliminary purification by column chromatography (CH_2Cl_2/MeOH 9:1) was followed

by PTLC (CH_2Cl_2/MeOH 9:1, R_f = 0.5) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, CH_2Cl_2/MeOH 92:8, 2 ml/min, R_t = 7.29 min) compound **38** (5.6 mg, 28%) as a red solid. ^{1}H NMR (500 MHz, $CDCl_3$/CD_3OD 5:1): 9.57 (br.s, 10H), 8.17 - 7.65 (m, 20H), 7.20 (br.s, 50H), 7.03 - 6.75(m, 12H), 5.55 - 5.51 (m, 10H), 4.99 - 4.89 (br.s, 20H), 4.47 - 3.99 (m, 70H), 3.72 - 3.61 (m, 20 H), 3.15 - 2.99 (m, 20H), 2.26 - 2.14 (m, 20H), 1.52 - 1.51 (m, 20H), 1.34 - 1.24 (m, 110H); MS (MALDI, +ve linear, dithranol): 7789 (100, $[M+Na]^+$), 7748 (45, $[M-NH_3]^+$).

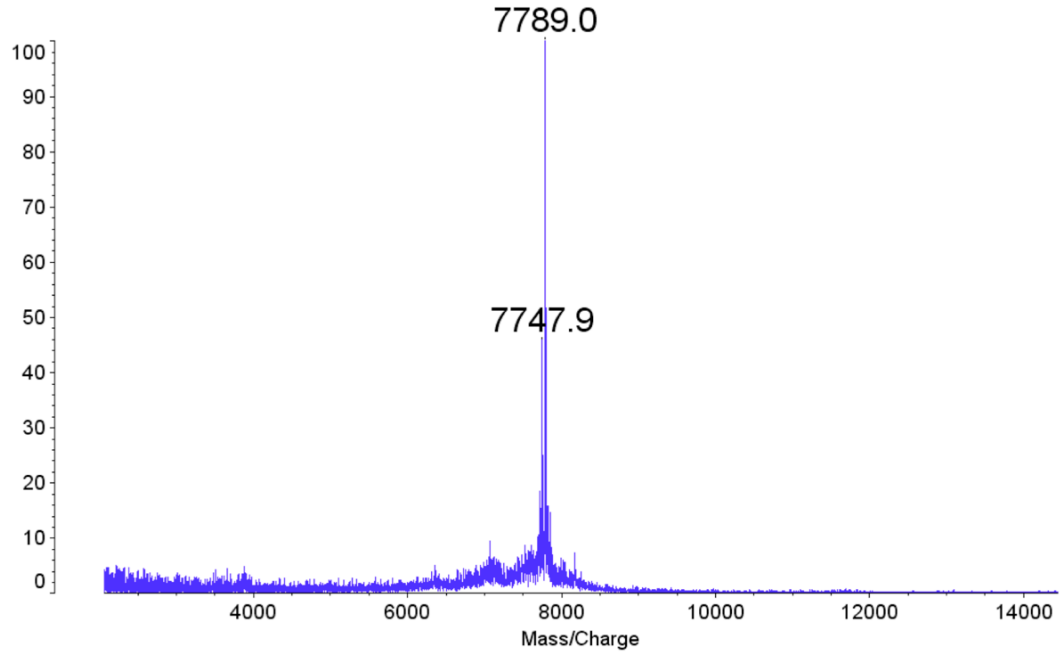


Figure S6. MALDI MS of **38**.

OPE-NDI 20. Thioanisole (14 μl) and a catalytic amount of pentamethyl benzene were added to a solution of compound **38** (2 mg, 0.25 μmol) in TFA (1 ml) and this red solution was stirred for 3 h at 50 ˚C. After this time, the red solution was evaporated to dryness under reduced pressure. Impurities were removed by solid-liquid extraction with ether (3 x 2 ml) and CH_2Cl_2 (3 x 2 ml), to yield analytically pure (RP-HPLC, Nucleosil 100-7 c18 250 X 8 mm, MeOH (with 1% TFA)/H_2O 80:20, 1 ml/min, R_t = 5.86 min) compound **20** (2 mg, quantitative) as a red solid. ^{1}H NMR (400

MHz, $CDCl_3/CD_3OD$ 1:1): 8.51 – 8.43 (m, 20H), 6.81 - 6.63 (m, 12H), 5.88 - 5.67 (m, 10H), 4.58 – 4.40 (m, 50H), 4.18 – 4.10 (m, 20H), 3.84 – 3.72 (m, 20H), 3.15 – 3,14 (m, 20H), 2.38 - 2.28 (m, 20H), 1.91 – 11.79 (m, 20H), 1.53 – 1.52 (m, 50H), 1.42 – 1.40 (m, 60H); MS (MALDI, +ve linear, HABA): 6443 (100, $[M+NH_4]^+$).

OPE-NDI 41. To a solution of **29** (67.6 mg, 0.099 mmol) in 20 ml CH_2Cl_2, was added $Pd(PPh_3)_4$ (6.8 mg, 0.0046 mmol) followed by $PhSiH_3$ (98 μl, 0.555 mmol). The solution was stirred at rt and monitored by TLC. After 15 min, when the consumption of **29** was observed then the solvent was removed under vacuum at rt and impurities were removed by solid-liquid extraction with ether (3 x 10 ml) and CH_2Cl_2 (3 x 10 ml), yielded compound **27** (58 mg, quantitative) as a red solid. Crude **31** (38 mg, 63.7 μmol) was dissolved with **37** (2.5 mg, 1.6 μmol), HATU (9.1 mg, 23.9 μmol), DTBP (43 μl, 0.192 mmol) and TEA (18 μl, 0.128 mmol) in freshly distilled and degassed DMF (1 ml), and stirred at rt for 16 h. DMF was removed under high vacuum. A preliminary purification by column chromatography (CH_2Cl_2/MeOH 9:1) was followed by PTLC (CH_2Cl_2/MeOH 9:1, R_f = 0.5) yielded analytically pure (HPLC, YMC-Pack SIL 250 X 4.6 mm, CH_2Cl_2/MeOH 92:8, 2 ml/min, R_t = 6.98 min) compound **41** (5.1 mg, 43%) as a red solid. ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ 9:1): 9.55 (br.s, 10H), 8.19 - 7.70 (m, 20H), 6.96 - 6.65 (m, 12H), 5.66 - 5.60 (m, 10H), 4.56 - 3.95 (m, 70H), 3.65 - 3.50 (m, 20H), 2.58 - 2.17 (m, 40H), 1.46 - 1.31 (m, 180H); MS (MALDI, +ve linear, HABA): 7021 (100, $[M+Na]^+$).

OPE-NDI 21. A solution of **41** (3.5 mg, 0.5 μmol) in TFA (1 ml) was stirred for 3 h at rt. After this time, the red solution was evaporated to dryness under reduced pressure. Impurities were removed by solid-liquid extraction with ether (3 x 2 ml) and CH_2Cl_2 (3 x 2 ml), leaving **21** (3.3 mg, quantitative) as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$/TFA 9:1): 8.49 - 8.31 (m, 20H), 7.22 -

6.96 (m, 12H), 6.09 - 5.85 (m, 10H), 4.81 - 4.75 (m, 20H), 4.54 - 4.39 (m, 40H), 4.19 - 4.17 (m, 20H), 3.83 - 3.73 (m, 20H), 2.73 - 2.51 (m, 40H), 1.60 - 1.53 (m, 30H), 1.48 - 1.36 (m, 60H); MS (MALDI, +ve linear, HABA): 6479 (50, $[M+K]^+$), 6458 (100, $[M+Na]^+$).

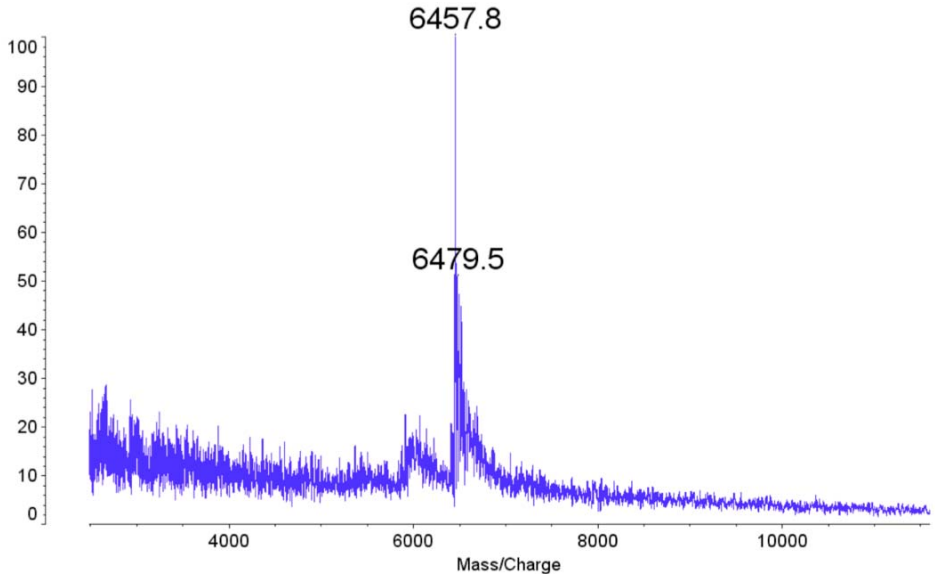


Figure S7. MALDI MS of **21**.

3. Electrochemistry

Oxidation and reduction potentials of (3,7)-**25** were determined using cyclic voltammetry (scan rate 100 mV/s) *vs* Fc/Fc^+ in dichloromethane (Figure 4, supporting electrolyte: 100 mM Bu_4NPF_6, working electrode: Pt disk, counter electrode: Pt wire, reference electrode: Ag/AgCl, internal reference: ferrocene). Results are summarized in Table 1. HOMO and LUMO energies *vs* vacuum were calculated from the onset of oxidation and reduction waves using eq (S1)[S4]

$$E_{\mathrm{HOMO/LUMO}} = -4.8\ \mathrm{eV} - E_{\mathrm{onset}}\ \mathrm{vs}\,(Fc/Fc^+) \qquad \text{(S1)}$$

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

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

and compared to the band gaps obtained from CV (E_g^{CV}, Table 1).

4. Femtosecond fluorescence and transient absorption spectroscopy

Samples. If not specified, all measurements were performed with the NDIs in the cationic form. As solvents methanol (MeOH, spectroscopic grade) and DMF (spectroscopic grade) were used. For steady-state and time-correlated single photon counting studies, the concentration in terms of NDI units was on the order of 10 μM. For fluorescence up-conversion and transient absorption experiments, they amounted to about 1 mM and to 300 μM, respectively.

Steady-state measurements. Absorption spectra were recorded on a Cary 50 spectrophotometer, whereas fluorescence and excitation spectra were measured on a Cary Eclipse fluorimeter. All fluorescence spectra were corrected for the wavelength-dependent sensitivity of the detection.

Time-resolved fluorescence. Fluorescence lifetime measurements on the nanosecond timescale were performed using the time-correlated single photon-counting technique (TCSPC) as described in detail elsewhere.[S5] Excitation was carried out at 469 nm with a laser diode (Picoquant model LDH-P-C-470) generating ~60 ps pulses at 10 MHz. The instrument response function had a full-width at half-maximum (fwhm) of about 200 ps.

The excited-state dynamics of OPE-R_O was additionally measured by fluorescence up-conversion (FU). As already discussed before,[S6] excitation was achieved at 400 nm with the frequency-doubled output of a Kerr lens mode-locked Ti:Sapphire laser (Mai Tai, Spectra-Physics). The polarization of the pump pulses was at magic angle relative to that of the gate pulses at 800 nm. The pump intensity on the sample was of the order of 5 $\mu J \cdot cm^{-2}$ and the fwhm of the instrument response function was ca. 210 fs. The sample solutions were located in a 0.4 mm rotating cell and had an absorbance of about 0.1 at 400 nm.

Transient absorption (TA). The experimental setup was the same as that described before.[S7, S8] Excitation was performed either at 400 nm with the frequency-doubled output of a standard 1 kHz amplified Ti:Sapphire system (Spectra-Physics) or at 550 nm with a home-built two-stage non-collinear optical parametric amplifier. The pump intensity on the sample was ca. 1-2 $mJ \cdot cm^{-2}$. The polarization of the probe pulses was at magic angle relative to that of the pump pulses. All spectra were corrected for the chirp of the white-light probe pulses. The fwhm of the response function was ca. 150 fs. The sample solutions were placed in a 1 mm thick quartz cell and were continuously stirred by N_2 bubbling. Their absorbance at the excitation wavelength was around 0.3.

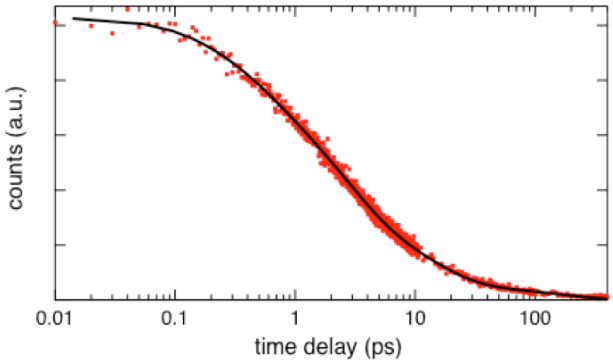


Figure S8: FU time-profile measured at 595 nm with OPE-R_O in MeOH upon 400 nm excitation and best multiexponential fit.

Table S1 Time constants (with relative amplitudes) obtained from the analysis of the fluorescence time profiles and fluorescence quantum yields.

Cpd	τ_{f1}	τ_{f2}	τ_{f3}	τ_{f4}	$\langle\tau_f\rangle$	Φ_f
25 (R_o)	10.5 ns					0.57
18 (POP-R_o)	8.3 ns (0.09)	0.24 ns (0.91)			0.97 ns	0.005
20 (OPE-R_o)	10 ns (0.02)	20.5 ps (0.20)	2.9 ps (0.45)	0.5 ps (0.33)	0.2 ns	0.01

[a]Up-conversion measurements not performed, faster decay components not resolved.

5. Zipper assembly on gold electrodes

Gold electrodes. Gold electrodes were prepared as reported in ref S9: 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). *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.

POP-Zipper initiation. POP-zippers were initiated as reported in ref S1: The cleaned gold plates were immersed in the solution of the initiator **11** (1 mM) in 0.5 mM sodium phosphate, 0.5 M NaCl, 50 % aqueous TFE buffer pH 7, for 7 days. The obtained Au-**11** 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-**11** as a working electrode.[S9,S10] The absence of redox waves confirmed the absence of large uncovered areas on the Au electrode.

OPE-Zipper initiation. Zipper initiation was done as reported in ref S3: The cleaned gold plates were immersed in the solution of the anionic initiator **17** (0.3 mM) in a 1:0.4 mix of DMF/Water for 4 days. The obtained Au-**17** electrodes were tested for defects as described above.

LBL initiation. For LBL assembly, the gold electrodes were coated with lipoic acid **12**. Namely, the cleaned gold plates were immersed in the solution of lipoic acid (**12**, 10 mM) in 0.5 mM sodium phosphate, 0.5 M NaCl, 50 % aqueous TFE buffer pH 7, for 1 day. The obtained Au-**12** electrodes were tested for defects as described above.

POP-zipper propagation. Coated gold electrodes Au-**11** were immersed in the solution of *cationic* octamer **18** (5 μM) in a 50 % aqueous TFE with 0.5 mM sodium phosphate, 0.1 M NaCl buffer (pH 7) for three 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* octamer **19** to give the trilayer coated plate. Mutilayers were obtained by repeating these sequences of depositions.

OPE-zipper propagation. The initiated Au-**17** electrodes were immersed in the solution of cationic propagator **20** (10 μM) in a 1:1 mixture of TFE and 0.5 mM sodium phosphate, 1 M NaCl buffer, pH 7, for two days. The plate was rinsed with bidistilled water and TFE, and the photocurrent of the resulting plate was recorded. Obtained Au-**17**-**20** electrodes were similarly treated with anionic propagator **21** to give Au-**17**-**20**-**21** electrodes. The same sequences were repeated using alternately charged propagators (**21** and **21**) to build up the Au-**17**(-**20**-**21**)$_n$ zipper assembly.

LBL propagation. The initiated Au-**12** electrodes were treated with the solution of cationic propagator **18** or **20**, and then with that of anionic propagator **19** or **21** under the conditions used for the zipper assembly to build Au-**12**(-**18**-**19**)$_n$ POP-LBL or Au-**12**(-**20**-**21**)$_n$ OPE-LBL, respectively.

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 = ~0.7 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 was 66 mW cm^{-2}.

***I-V* measurements**. Short circuit current (I_{sc}) and open circuit voltage (V_{oc}) of zipper and LBL assemblies were determined by *I-V* measurements. Experimental conditions are as described in the above "photocurrent measurements", but with 100 mW cm^{-2} of irradiation for POP-LBL assemblies. Fill factors (*FF*) were calculated from the maximum power (P_m), I_{sc} and V_{oc} using equation (S3).[S11]

$$FF = P_m / I_{sc} V_{oc} \qquad \text{(S3)}$$

Action Spectra. Photocurrent densities ($J_{sc} = I_{sc} / a$) were measured at 0 V *vs* Ag/AgCl upon excitation by monochromatic light (150 W Xe lamp with Oriel 1/8 m monochromator). Obtained current densities were converted into incident photon to current conversion efficiencies (IPCEs) by using the equation (S4).[S12]

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

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