Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Three-component zipper assembly of photoactive cascade architectures with blue, red and colorless naphthalenediimide donors and acceptors

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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 in 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. ^{1}H 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; DMF: N,N-Dimethylformamide; *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]-N-methylmethanammonium hexafluorophosphate N-oxide; NDI: Naphthalenediimide; rt: Room temperature; TEA: Triethylamine; TEOA: Triethanolamine; TFA: Trifluoroacetic acid; TFE: 2,2,2-Trifluoroethanol.

2. Supplementary text

2.1. Synthesis of anionic rNDI initiator *r* and octamer *R*

Alloc-*en*-*Cl,Cl*-NDI-Glu(*t*-Bu)-NH_2 (1). This compound was prepared from pyrene following the procedures published in ref. [S2].

Alloc-*en*-*N,Cl*-NDI-Glu(*t*-Bu)-NH_2 (2). A solution of Alloc-*en*-*Cl,Cl*-NDI-Glu(*t*-Bu)-NH_2 **1** (96 mg, 0.15 mmol) in isopropylamine (2 ml) was stirred for 5 min at rt. The resulting red solution was concentrated in *vacuo*. Purification by column chromatography (CH_2Cl_2/acetone 8 : 1) gave **2** (87 mg, 87%) as a red solid. MP: 121-122 °C; $[\alpha]^{20}_D$ = +97.0 (c = 0.01 in MeOH); IR: ν 3356 (m), 2974 (m), 2929 (m), 1672 (s), 1638 (s), 1584 (s), 1523 (m), 1497 (m), 1444 (s), 1311 (s), 1263 (s), 1216 (s), 1147 (s), 992 (m), 920 (m), 790 (s), 733 (s); ^{1}H NMR (400 MHz, $CDCl_3$, N/N = regioisomeric equivalents): δ 9.96/9.91, (d, ^3J(H,H) = 7.6/7.2 Hz, 1H), 8.49/8.35 (s, 1H), 8.26/8.14 (s, 1H), 6.65 - 6.35 (br m, 1H), 6.20 - 6.05 (br m, 1H), 5.89 - 5.75 (m, 1H), 5.73/5.66 (dd, ^3J(H,H) = 4.8/4.8 Hz, ^3J(H,H) = 8.8/9.0 Hz, 1H), 5.26 - 5.09 (m, 3H), 4.45/4.41 (d, ^3J(H,H) = 5.6/5.3 Hz, 2H), 4.20 (br t, ^3J(H,H) = 5.6 Hz, 2H), 4.21 - 4.13 (m, 1H), 3.55 - 3.40 (m, 2H), 2.78 - 2.60 (m, 1H), 2.50 - 2.25 (m, 3H), 1.49 - 1.46 (m, 6H), 1.37/1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, N/N = regioisomeric equivalents): δ 172.3/172.2 (s),171.7/171.3 (s), 165.7/165.5 (s), 162.2/162.1 (s), 161.5/161.3 (s), 156.8/156.7 (s), 151.1/151.0 (s), 135.3/135.0 (d), 133.3/133.2 (s), 133.0/132.9 (d), 128.6/128.4 (s), 127.6/127.0 (s), 123.6/123.0 (s), 121.6/121.5 (d), 121.3/121.0 (s), 117.8 (t), 99.4/99.1 (d), 81.1/81.0 (s), 65.8 (t), 54.9 (d), 54.0 (d), 45.2 (d), 40.7 (t), 39.9/39.8 (t), 32.8/32.7 (t), 28.2/28.2 (q), 24.0/23.9 (t), 23.4/23.4 (q); MS (ESI, +ve): *m/z* (%) 692 (19 $[M + Na]^+$), 670 (43 $[M + H]^+$), 615 (66 $[M - C_4H_7]^+$), 598 (100 $[M - C_4H_7 - NH_3]^+$).

H-*en*-*N*,*Cl*-NDI-Glu(*t*-Bu)-NH_2 (3). To a solution of **2** (65 mg, 97 μmol) in dry CH_2Cl_2 (35 ml) were added *p*-nitrophenol (40 mg, 0.29 mmol) and tributyltin hydride (130 μl, 0.49 mmol) followed by $Pd(PPh_3)_2Cl_2$ (7 mg, 0.001 mmol). After stirring for 0.5 h at rt, the reaction mixture was concentrated in *vacuo* and lipophilic impurities were removed by solid-liquid extraction with petroleum ether. Further purification by column chromatography (CH_2Cl_2/MeOH 9:1 then CH_2Cl_2/MeOH/TEA 8:2:0.1), followed by removal of hydrophilic impurities by solid-liquid extraction with water gave pure desired amine **3** (44 mg, 77%) as a red solid. ^{1}H NMR (300 MHz, CD_3OD, N/N = regioisomeric equivalents): δ 10.00 (d, ^3J(H,H) = 6.8 Hz, 1H), 8.51/8.44 (s, 1H), 8.34/8.28 (s, 1H), 5.75 - 5.64 (m, 1H), 4.32 - 4.25 (m, 3H), 3.12 - 3.06 (m, 2H), 2.75 - 2.52 (m, 1H), 2.52 - 2.25 (m, 3H), 1.47 (d, ^3J(H,H) = 6.1 Hz, 6H), 1.37/1.36 (s, 9H).

1^4-(2-Lipoylaminoethoxy)-1^2,2^2,3^3,4^2-tetra(*Gla*-OH)-*p*-quaterphenyl (4). This compound was prepared following previously reported procedures.[S2]

1^4-(2-Lipoylaminoethoxy)-1^2,2^2,3^3,4^2-tetra(*Gla*-*en*-*N*,*Cl*-NDI-Glu(*t*-Bu)-NH_2)-*p*-quaterphenyl (5). The tetraacid **4** (3 mg, 4 μmol) was dissolved in DMF (0.5 ml), and HATU (7 mg, 0.002 mmol), di-*tert*-butyl pyridine (40 μl, 0.18 mmol), **3** (22 mg, 38 μmol) and TEA (16 μl, 0.11 mmol) were successively added. After stirring for 24 h at rt, the mixture was concentrated *in vacuo*. Purification of the residue by PTLC (CH_2Cl_2 / MeOH 9 / 1) and HPLC (YMC-pack-SIL, 10 x 250 mm, CH_2Cl_2 / MeOH 9 / 1, 2 ml / min, R_t = 6.7 min) gave pure tetramer **5** (2 mg, 17%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$ 1/1): δ 9.98 ~ 9.80 (m, 4H), 8.35 ~ 7.90 (m, 8H), 7.38 ~ 6.75 (m, 11H), 6.70 ~ 6.45 (m, 2H), 6.32 (brs, 1H), 5.75 ~ 5.50 (m, 4H), 4.50 ~ 4.00 (m, 22H), 3.95 ~ 3.75 (m, 1H), 3.65 ~3.30 (m, 11H), 3.20 ~ 3.00 (m, 2H), 2.70 ~ 2.50 (m, 5H), 2.50 ~

2.20 (m, 14H), 1.90 ~ 1.75 (m, 1H), 1.75 ~ 1.50 (m, 6H), 1.35 (brs, 60H); MS (ESI, +ve): *m/z* (%) 1579 (100 $[M + 2NH_4]^{2+}$), 1570 (66 $[M + H + NH_4]^{2+}$), 1562 (90 $[M + 2H]^{2+}$).

1^4-(2-Lipoylaminoethoxy)-1^2,2^2,3^3,4^2-tetra(*Gla*-*en*-*N*,*Cl*-NDI-Glu-NH_2)-*p*-quaterphenyl (*r*). A solution of tetra-NDI **5** (2 mg, 0.6 μmol) in CH_2Cl_2 (0.5 ml) and TFA (0.5 ml) was stirred for 15 min at rt, and then concentrated *in vacuo* to give title compound (***r***, 2 mg, quant) as a red amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$ / CD_3OD 1 / 1): δ 8.28 ~ 7.80 (m, 8H), 7.55 ~ 6.32 (m, 13H), 5.65 ~ 5.35 (m, 4H), 4.55 ~ 3.70 (m, 22H), 3.60 ~ 3.20 (m, 11H), 3.10 ~ 2.90 (m, 2H), 2.70 ~ 2.55 (m, 4H), 2.50 ~ 2.05 (m, 15H), 1.88 ~ 1.72 (m, 1H), 1.68 ~ 1.50 (m, 6H), 1.33 (brs, 24H); MS (ESI, –ve): *m/z* (%) 1449 (100 $[M - 2H]^{2-}$).

1^3,2^3,3^2,4^3,5^2,6^3,7^2,8^3-Octakis(*Gla*-OH)-*p*-octiphenyl (6). This compound was prepared from Fast Blue B in overall nine steps following previously reported procedures.[S3]

1^3,2^3,3^2,4^3,5^2,6^3,7^2,8^3-Octakis(*Gla*-*en*-*N*,*Cl*-NDI-Glu(*t*-Bu)-NH_2)-*p*-octiphenyl (7). To a solution of **6** (3.3 mg, 2.8 μmol), HATU (10 mg, 0.026 mmol) and TEA (25 μl, 0.18 mmol) in DMF (0.1 ml) was added a solution of **3** (22 mg, 38 μmol) and 2,6-di-*tert*-butylpyridine (60 μl, 0.26 mmol) in DMF (0.5 ml). After stirring for 22 h at rt, the reaction mixture was concentrated in *vacuo*. Resulting crude product was purified by successive PTLCs (DCM : MeOH 9 : 1; then DCM : MeOH 85 : 15, R_f 0.73) to give **7** (4 mg, 25%) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$/CD_3OD 1:1): δ 10.0 - 9.70 (m, 8H), 8.30- 7.80 (m, 16H), 7.50 - 6.95 (m, 24H), 6.81 - 6.78 (m, 2H), 5.75 - 5.45 (m, 8H), 4.60 - 4.30 (m, 16H), 4.30 - 3.90 (m, 24H), 3.85 - 3.30 (m, 16H), 2.67 - 2.48 (m, 8H), 2.48 - 2.10 (m, 24H), 1.50 - 1.20 (m, 120H); MS (ESI, +ve): *m/z* (%) 2891 (20 $[M + 2NH_4]^{2+}$), 1924 (57 $[M + 2H + Na]^{3+}$), 1917 (100 $[M + 3H]^{3+}$).

$1^3,2^3,3^2,4^3,5^2,6^3,7^2,8^3$-Octakis(*Gla-en-N,Cl*-NDI-Glu-NH_2)-*p*-octiphenyl, TFA salt (*R*). A solution of **7** (4 mg, 0.7 μmol) in TFA (0.5 ml) and CH_2Cl_2 (0.5 ml) was stirred for 0.5 h at rt. Then the solution was concentrated *in vacuo* to give ***R*** (4 mg, ~quantitative) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$/TFA 9/1): δ 8.66 - 8.19 (m, 16H), 7.67 - 7.15 (m, 24H), 7.05 - 6.90 (m, 2H), 6.10 - 5.90 (m, 8H), 4.90 - 4.55 (m, 16H), 4.50 - 4.10 (m, 16H), 4.00 - 3.90 (m, 8H), 3.90 - 3.60 (m, 16H), 2.85 - 2.50 (m, 32H), 1.55 - 1.35 (m, 48H).

2.2. Electrochemistry

Oxidation and reduction potentials of octiphenyl **6a**, rNDI **2**, bNDI **8** and nNDI **9** were determined using differential pulse voltammetry (scan rate 10 mV/s, pulse period 0.2 s, amplitude 0.05 V) *vs* Fc/Fc^+ in dichloromethane (Figure S2, supporting electrolyte: 100 mM Bu_4NPF_6, working electrode: Pt disk, counter electrode: Pt wire, reference electrode: Ag/AgCl). Reversibility of the redox processes was assessed using cyclic voltammetry (scan rate 100 mV/s). Results are summarized in Table S1. HOMO and LUMO energies *vs* vacuum were calculated from oxidation and reduction potentials using eq (S1)[S4]

$$E_{\mathrm{HOMO/LUMO}} = -4.8\ \mathrm{eV} - E_{1/2}\ \mathrm{vs}\ (\mathrm{Fc/Fc^+}) \qquad \text{(S1)}$$

The band gaps $E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$ were converted into absorption wavelength using eq (S2)

$$\lambda_{\mathrm{calc}}\ (\mathrm{nm}) = hc / (E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}) = 1240 / (E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}) \qquad \text{(S2)}$$

and compared to the measured values λ_{max} (Table S1).

2.3 Zipper assembly on gold electrodes

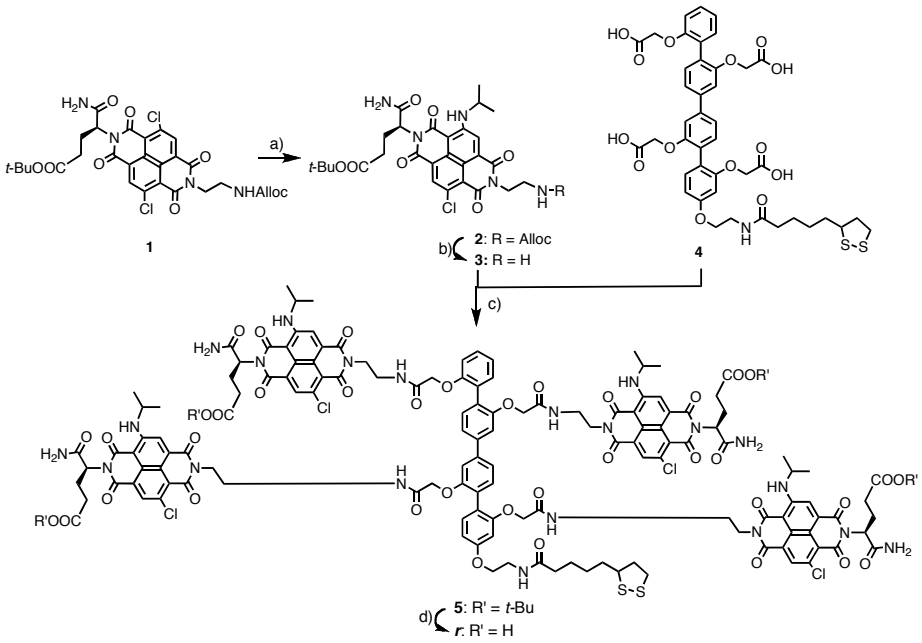
Gold electrodes. Gold electrodes were prepared as reported in ref [S2]: Gold-coated glass slides (22 x 22 mm^2) were purchased from Mivitec GmbH, Analytical μ-Systems (Germany). Before use, the plates were cut in half (~ 1 x 2 cm^2), and cleaned using 'piranha' solution (H_2SO_4 / 30 % H_2O_2 3 / 1; 35 °C for 5 min).[S5] *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.

Initiation. Zipper assembly was initiated as reported in ref [S2]: The cleaned gold plates were immersed in the solution of the initiator ***r*** (0.1 mM) in a 1:1 mixture of TFE : 1 mM sodium phosphate buffer (pH 7) for ≈ 3 days. The obtained Au-***r*** 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-***r*** as a working electrode.[S2,S6] The absence of redox waves confirmed the absence of large uncovered areas on the Au electrode.

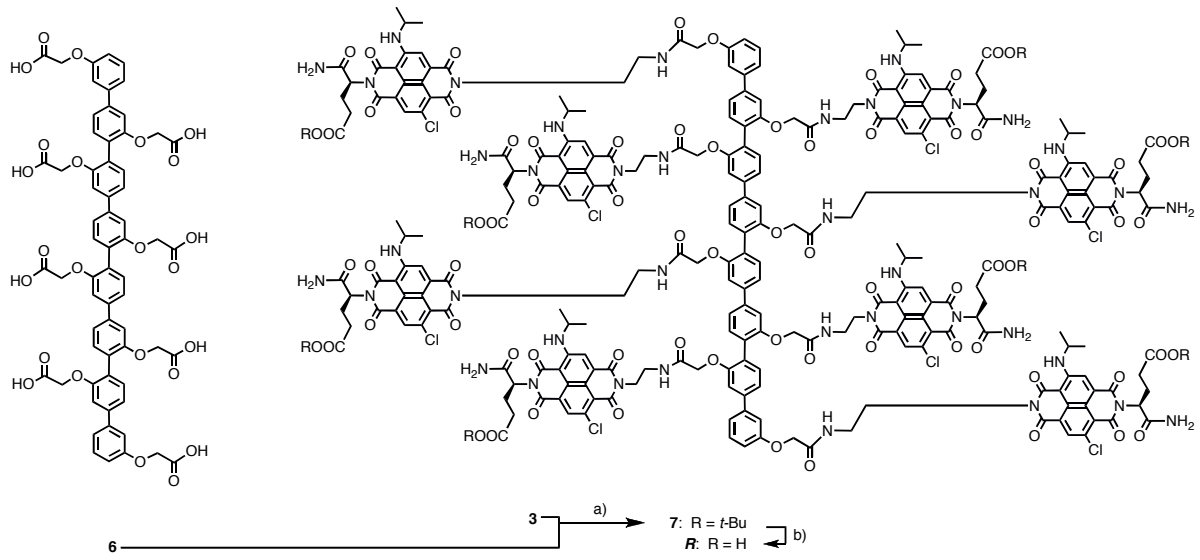
Propagation. Coated gold electrodes Au-***r*** were immersed in the solution of *cationic* octamer **B**, **R** or **N** (~10 μM) in a 1 : 1 mixture of TFE and 0.5 mM sodium phosphate, 0.5 M NaCl buffer (pH 7) for overnight. The plate was rinsed repeatedly with bidistilled water and TFE, and the photocurrent of the resulting plate was recorded. The obtained bilayer coated plate was similarly treated with *anionic* octamer ***B*** or ***R*** to give the trilayer coated plate. Mutilayers were obtained by repeating these sequences of depositions.

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 ~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 0.15 W cm^{-2}.

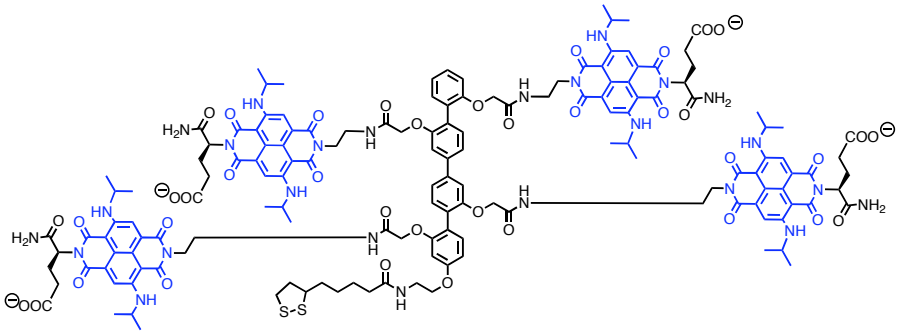
3. Supplementary schemes and figures



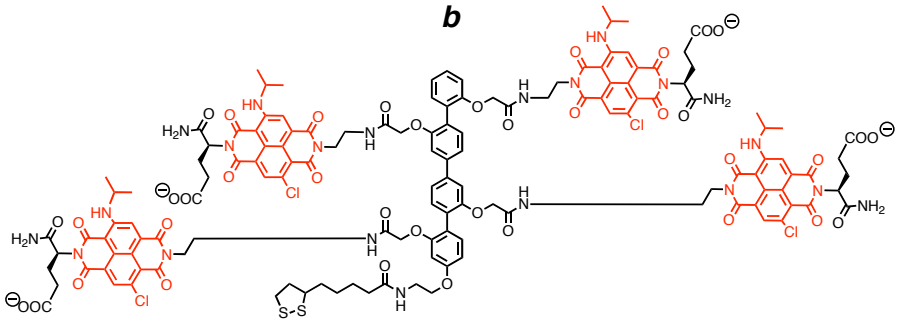
Scheme S1. a) *i*-$PrNH_2$ (87%); b) $PdCl_2(PPh_3)_4$, Bu_3SnH, *p*-nitrophenol (77%); c) HATU, di-*t*-Bu-pyridine, TEA, DMF (17%); d) TFA, CH_2Cl_2 (quant). *Note, **5** and **r** contain both regioisomers (2,6- and 3,7-) of rNDIs.*



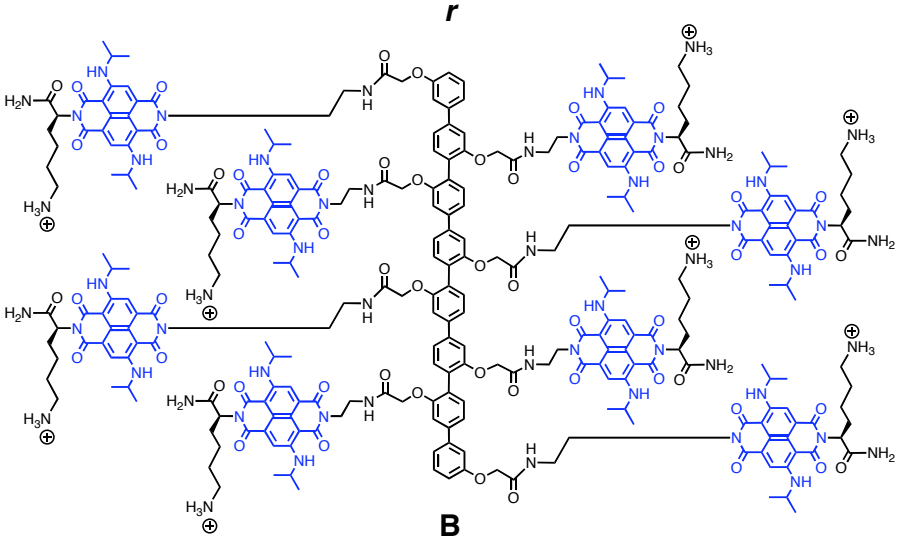
Scheme S2. a) HATU, di-*t*-Bu-pyridine, TEA, DMF (25%); e) TFA, CH_2Cl_2 (quant). *Note, **7** and **R** contain both regioisomers (2,6- and 3,7-) of rNDIs.*



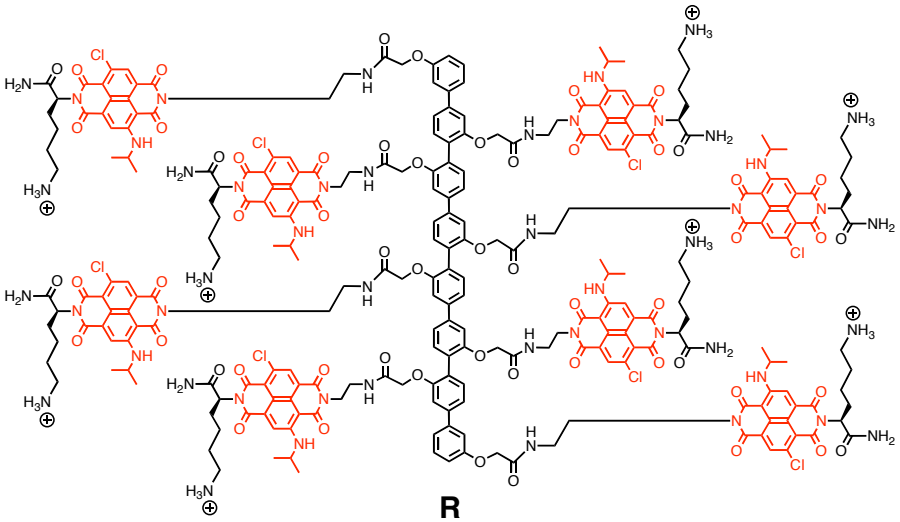
b



r



B



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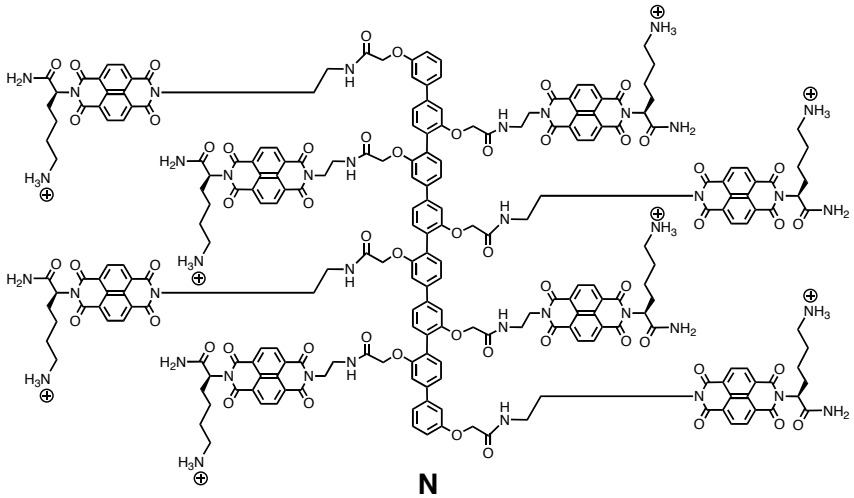

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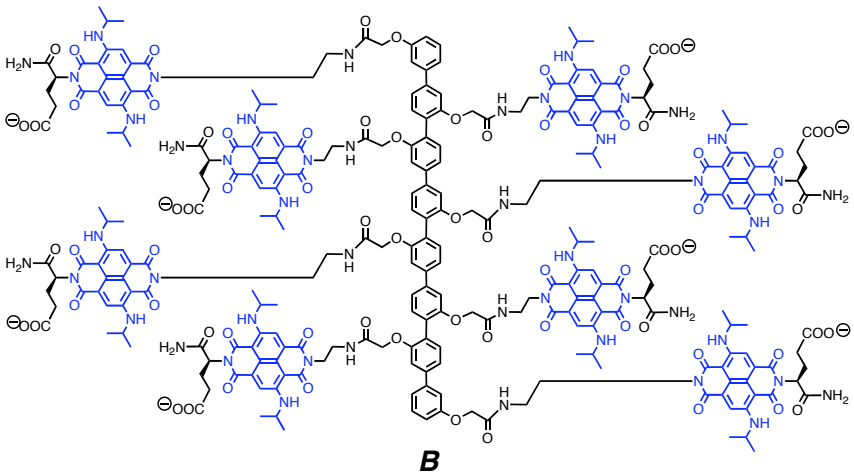

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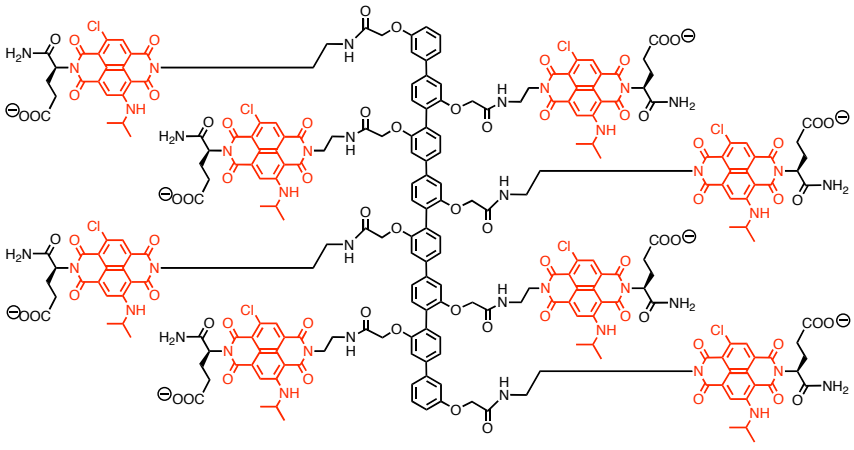

R

Figure S1. Full structures of zipper components ***b***, ***r***, **B**, **R**, **N**, ***B***, and ***R***. *Note*, ***r***, **R** *and* ***R*** *contain both regioisomers (2,6- and 3,7-) of rNDIs.*

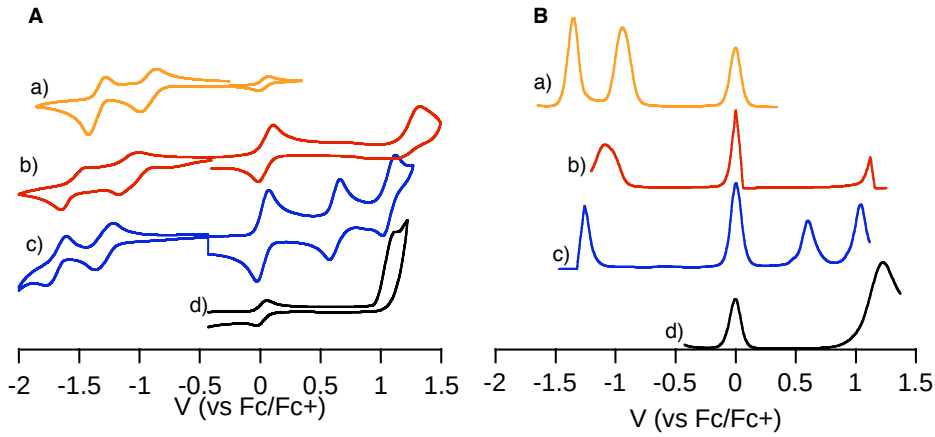

Fig. S2. Cyclic voltammograms (A) and differential pulse voltammograms (B) for nNDI **9** (a), rNDI **2** (b), bNDI **8** (c) and octiphenyl **6a** (d). Peaks at 0 V are those of ferrocene (internal standard) in dichloromethane , supporting electrolyte: 100 mM Bu_4NPF_6, working electrode: Pt disk, counter electrode: Pt wire, reference electrode: Ag/AgCl.

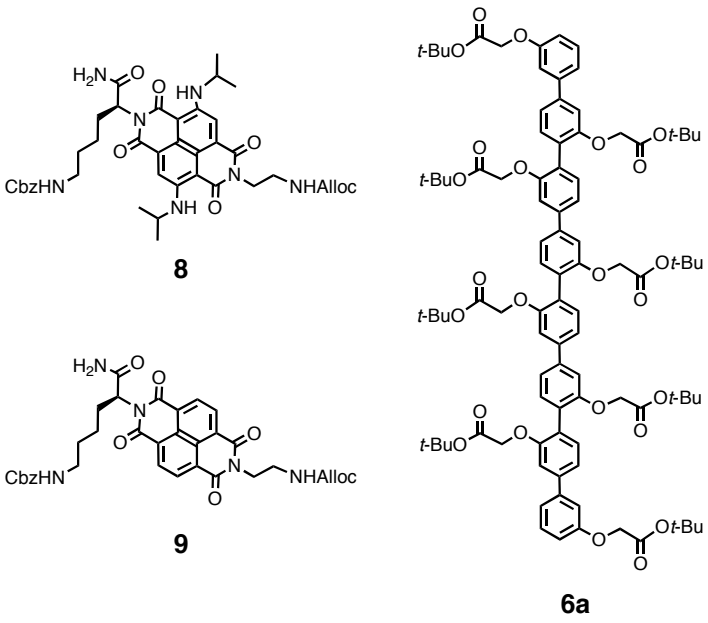

Fig. S3. Structures of octiphenyl **6a**, bNDI **8** and nNDI **9**.

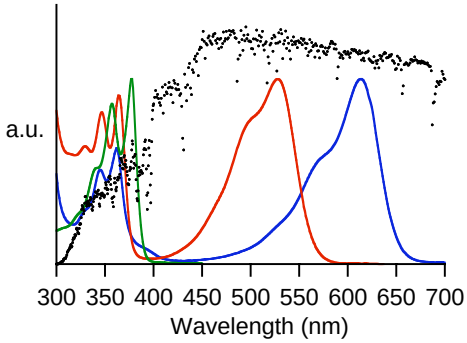

Fig. S4. UV-vis absorption spectra of bNDI (blue line), rNDI (red line) and nNDI (green line) in comparison to a solar irradiance air mass 1.5 spectrum[S7] (black dotted line).

Comment on Fig. S4: Low photocurrent generation by nNDI is reasonable as nNDI absorbs only the high-energy light, which is weak in solar spectrum.

4. Supplementary table

Table S1 Electrochemical and spectroscopic data

Dye	$E_{1/2}$ (X/X^+) V vs Fc/Fc^+	E_{HOMO} EV	$E_{1/2}$ (X/X^-) V vs Fc/Fc^+	E_{LUMO} eV	λ_{abs} (λ_{calc}) nm
8	+0.60	–5.4	–1.32	–3.5	620 (646)[a]
2	+1.12	–5.9	–1.09	–3.7	535 (561)[a]
9	nd[b]	–7.1[c]	–0.94	–3.9	380 (384)[d,e]
6a	+1.23[f]	–6.0	nd[b]	–2.5[c]	316 (350)[d,g]

[a]From ref. [S8]; [b]not detected; [c]*calculated* from absorption (see *d*); [d]estimated from the average wavelength of absorption and emission maxima; [e]from ref. [S9]; [f]irreversible; [g]from ref. [S10].

5. Supplementary references

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