Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2015

Electron-deficient fullerenes in triple-channel photosystems

Javier López-Andarias,^a Altan Bolag,^b Christoph Nançoz,^b Eric Vauthey,^b Carmen Atienza,^a Naomi Sakai,^b Nazario Martín^{*a} and Stefan Matile^{*b}

^aDepartamento de Química Orgánica Universidad Complutenese, Madrid, Spain

nazmar@quim.ucm.es

^bSchool of Chemistry and Biochemistry, University of Geneva, Geneva, Switzerland,

stefan.matile@unige.ch

Supplementary Information

Table of Content

| 1. | Material and Methods | | | | | |
|----|--------------------------------|---------------------|--|-----|--|--|
| 2. | Supporting Text | | | | | |
| | 2.1 | Synthesis | | | | |
| | | 2.1.1 | Synthesis of the Electron-Deficient Bingel Fullerenes | S4 | | |
| | | 2.1.2 | Synthesis of the Electron-Deficient Cyano-Ester Fullerenes | S7 | | |
| | | 2.1.3 | Synthesis of Oligothiophene-Fullerene Dyads | S12 | | |
| | 2.2 | .2 Electrochemistry | | | | |
| | 2.3 | Stack Ex | change | S16 | | |
| | 2.4 | Photosys | stem Characterization | S16 | | |
| | 2.5 | Time Re | solved Fluorescence | S17 | | |
| 3. | Supporting Schemes and Figures | | | | | |
| 4. | Supporting Tables | | | | | |
| 5. | Supporting References | | | | | |

1. Materials and Methods

As in ref. S1, Supporting Information. Briefly, reagents for synthesis were mostly purchased from Fluka, Sigma-Aldrich, and Across. Fullerene C_{60} was purchased from IoLiTec Ionic Liquids Technologies GmbH (Heilbronn, Germany). Indium tin-oxide (ITO) coated glass substrates were obtained from Präzisions Glas & Optik GmbH (Iserlohn, Germany). Reactions were performed under N₂ or Ar atmosphere when specified.

Unless stated otherwise, column chromatography was carried out on silica gel 60 (Fluka, 40-63 μ m). Analytical (TLC) and preparative thin layer chromatography (PTLC) was performed on silica gel 60 (Fluka, 0.2 mm) and silica gel GF (Analtech, 1 mm), respectively. UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller $(25 \pm 0.1 \text{ °C})$ and are reported as maximal absorption wavelength λ in nm (extinction coefficient ε in M⁻¹cm⁻¹). Melting points (m.p.) were recorded on a heating table from Reichert (Austria) and uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (ATR, Golden Gate) and are reported as wavenumbers v in cm⁻¹ with band intensities indicated as s (strong), m (medium), w (weak), br (broad). ¹H and ¹³C NMR spectra were recorded (as indicated) either on a Bruker 300 MHz, 400 MHz, 500 MHz or 700 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). ¹H and ¹³C resonances were assigned with the aid of additional information from 1D & 2D NMR spectra (H, H-COSY, DEPT 135, HSQC and HMBC). ESI-MS for the characterization of new compounds was performed on an ESI API 150EX and is reported as mass-per-charge ratio m/z (intensity in %, [assignment]). ESI-HRMS for the characterization of new compounds were performed on a QSTAR Pulsar (AB/MDS Sciex) and are reported as mass-per-charge ratio m/z calculated and observed, MALDI-TOF on 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. aq = Aqueous solution, Calcd = Calculated, DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, DCM = Dichloromethane, DCTB =*trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2propenylidene]malononitrile, DIAD = Diisopropyl azodicarboxylate, DMAP = 4-Dimethylaminopyridine, EDC = 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide, PTLC =preparative of thin layer chromatography, rt = room temperature, sat = Saturated, SOSIP = Selforganizing surface-initiated polymerization, TEOA = Triethanolamine, TFA = Trifluoroaceticacid, TSE = Templated stack exchange.

2. Supporting Text

2.1. Synthesis

2.1.1. Synthesis of the Electron-Deficient Bingel Fullerenes

The synthesis was performed as presented in Scheme S1 (see page S19).

Compound M1. This compound was prepared following the procedure in ref. S1.

1,2-Dicyano[60] fullerene. This compound was prepared following the procedure in ref. S2.

Dicyanomethane[60]fullerene. This compound was prepared following the procedure in ref. S3.

Compound 6a. To a solution of **M1** (115 mg, 0.18 mmol), 1,2-dicyano[60]fullerene (250 mg, 0.32 mmol) and I₂ (82 mg, 0.32 mmol) in dry toluene (120 mL) under Ar atmosphere, DBU (80 μ L, 0.54 mmol) was added at –15 °C slowly. Resulting mixture was allowed to react for 15 min and then solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (unreacted 1,2-dicyano[60]fullerene was recovered using toluene and **6a** was eluted using DCM/MeOH 30:1) followed by PTLC purification (DCM/MeOH 30:1, R_f = 0.33 with DCM/MeOH 30:1). The product **6a** (151 mg, 60%) was obtained as a brown powder. M.p.: 91-92 °C; IR (neat): 2940 (m), 2900 (m), 2242 (w), 1748 (s), 1464 (w), 1269 (m), 1141 (m), 1106 (s), 1031 (w); ¹H NMR (500 MHz, CDCl₃): 7.78-7.31 (m, 3H), 5.72-5.29 (m, 3H), 5.29-4.99 (m, 2H), 4.82-4.36 (m, 2H), 4.35-4.13 (m, 2H), 4.02-3.50 (m, 22H), 3.44-3.22 (m, 3H), 1.30-1.20 (m, 3H), 0.87-0.76 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): 170.3 (C), 162.7 (C), 162.5 (C), 149.6 (C), 149.5 (C), 149.4 (C), 148.7 (C), 148.2 (C), 147.4 (C), 146.8 (C), 144.8 (C), 144.8 (C), 144.8 (C), 144.7 (C), 144.6 (C), 144.5 (C), 144.2 (C), 144.1 (C), 143.3 (C), 143.1 (C), 143.0 (C), 142.9

(C), 142.5 (C), 141.7 (C), 141.6, (C) 141.5 (C), 141.2 (C), 139.8 (C), 139.2 (C), 139.1 (C), 137.8
(C), 137.7 (C), 136.2 (C), 135.0 (C), 129.2 (CH), 126.8 (CH), 126.8 (CH), 116.7 (C), 116.7 (C), 100.8 (CH), 77.8 (CH₂), 77.7 (CH₂), 72.0 (CH₂), 71.1 (CH₂), 70.7 (CH₂), 70.5 (C), 68.7 (CH₂), 68.6 (CH₂), 66.4 (CH₂), 66.0 (CH₂), 65.9 (CH₂), 59.2 (CH₃), 57.3 (C), 50.9 (C), 30.4 (C), 23.2 (CH₃), 21.9 (CH₃) (Comment: Because of the presence of regioisomers, too many ¹³C peaks were observed. Here only selected ¹³C peaks were listed); MS (MALDI, DCTB): 1438 (100, [M+Na]⁺).

Compound 7a. To a solution of M1 (89 mg, 0.14 mmol), dicyanomethane[60]fullerene (195 mg, 0.25 mmol) and I₂ (63 mg, 0.25 mmol) in dry toluene (100 mL) under Ar atmosphere, DBU (62 μ L, 0.41 mmol) was added at -15 °C slowly. Resulting mixture was allowed to react for 15 min and then solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (unreacted dicyanomethane[60]fullerene was recovered using toluene and 7a was eluted using DCM/MeOH 30:1) followed by PTLC purification (DCM/MeOH 30:1, Rf = 0.18 with DCM/MeOH 40:1). The product 7a (110 mg, 56%) was obtained as a dark-brown powder. M.p.: 123-124 °C; IR (neat): 2923 (s), 2854 (s), 2247 (w), 1746 (s), 1461 (m), 1232 (s), 1106 (s), 749 (m); ¹H NMR (500 MHz, CDCl₃): 7.73-7.32 (m, 3H), 5.72-5.33 (m, 3H), 5.29-5.08 (m, 2H), 4.78-4.42 (m, 2H), 4.28-4.15 (m, 2H), 4.08-3.47 (m, 22H), 3.45-3.21 (m, 3H), 1.33-1.24 (m, 3H), 0.88-0.75 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): 170.4 (C), 163.0 (C), 162.9 (C), 148.2 (C), 147.9 (C), 147.6 (C), 146.7 (C), 146.3 (C), 146.2 (C), 146.1 (C), 145.9 (C), 145.4 (C), 145.3 (C), 145.1 (C), 144.8 (C), 144.7 (C), 144.4 (C), 144.2 (C), 144.1 (C), 143.8 (C), 143.7 (C), 143.6 (C), 143.3 (C), 143.2 (C), 142.7 (C), 142.6 (C), 141.9 (C), 141.6 (C), 141.6 (C), 141.6 (C), 140.6 (C), 140.2 (C), 139.9 (C), 139.8 (C), 139.4 (C), 139.3 (C), 136.3 (C), 135.1 (C), 129.2 (CH), 126.9 (CH), 126.8 (CH), 109.9 (C), 109.8 (C), 100.9 (CH), 77.8 (CH₂), 77.2 (CH₂), 72.1 (CH₂), 71.1 (CH₂), 70.8 (CH₂), 70.7 (CH₂), 68.7 (CH₂), 67.8 (CH₂), 66.4 (CH₂), 66.0 (CH₂), 59.2 (CH₃), 51.2 (C), 30.4 (C), 23.3 (CH₃), 22.0 (CH₃) (Comment: Because of the presence of regioisomers, too

many ¹³C peaks were observed. Here only selected ¹³C peaks were listed); MS (MALDI, DCTB): 1450 (100, [M+Na]⁺).

Compound 6. A mixture of 6a (46 mg, 31 µmol), DCM (2 mL), TFA (1 mL) and H₂O (1 mL) was stirred at rt for 2 h. The organic layer was then washed with H₂O, dried over Na₂SO₄ and solvent evaporated. PTLC purification (DCM/MeOH 25:1, $R_{\rm f} = 0.57$ with DCM/MeOH 19:1) followed by washing firstly with MeOH and then with hexane gave 6 (25 mg, 58%) as a brown powder. M.p.: 84-85 °C; IR (neat): 2923 (m), 2873 (m), 2241 (w), 1747 (s), 1699 (m), 1457 (w), 1244 (m), 1144 (m), 1106 (m); ¹H NMR (500 MHz, CDCl₃): 10.16-9.97 (m, 1H), 8.22-7.81 (m, 2H), 7.81-7.55 (m, 1H), 5.82-5.38 (m, 2H), 5.37-5.15 (m, 2H), 4.85-4.38 (m, 2H), 4.37-4.15 (m, 2H), 3.88-3.50 (m, 18H), 3.43-3.23 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): 191.3 (CH), 170.3 (C), 162.7 (C), 162.5 (C), 149.5 (C), 149.4 (C), 149.3 (C), 148.7 (C), 148.2 (C), 147.5 (C), 146.9 (C), 146.6 (C), 146.5 (C), 146.0 (C), 145.8 (C), 145.7 (C), 145.5 (C), 145.3 (C), 145.3 (C), 145.2 (C), 144.9 (C), 144.8 (C), 144.7 (C), 144.6 (C), 144.2 (C), 143.3 (C), 143.2 (C), 143.0 (C), 142.5 (C), 142.4 (C), 141.8 (C), 141.7 (C), 141.6 (C), 141.2 (C), 141.1 (C), 139.1 (C), 137.8 (C), 137.7 (C), 137.6 (C), 137.3 (C), 136.4 (C), 135.0 (C), 134.0 (CH), 129.8 (CH), 129.4 (CH), 116.6 (C), 77.4 (CH), 77.2 (CH₂), 72.0 (CH₂), 71.2 (CH₂), 71.0 (CH₂), 70.8 (CH₂), 70.7 (CH₂), 70.4 (CH₂), 68.7 (CH₂), 67.9 (CH₂), 66.5 (CH₂), 65.4 (CH₂), 65.3 (CH₂), 59.2 (CH₃), 57.3 (C), 50.7 (C); MS (MALDI, DCTB): 1352 $(100, [M+Na]^+).$

Compound 7. A mixture of **7a** (52 mg, 36 μ mol), DCM (2 mL), TFA (1 mL) and H₂O (1 mL) was stirred at rt for 2 h. The organic layer was then washed with H₂O, dried over Na₂SO₄ and solvent evaporated. PTLC purification (DCM/MeOH 25:1, $R_f = 0.55$ with DCM/MeOH 19:1) followed by washing firstly with MeOH and then with hexane gave **7** (28 mg, 56%) as a reddish brown powder. M.p.: 117-118 °C; IR (neat): 2924 (s), 2855 (m), 2248 (w), 1747 (s), 1699 (m), 1460 (m), 1233 (s),

1143 (m), 1110 (m); ¹H NMR (500 MHz, CDCl₃): 10.28-9.89 (m, 1H), 8.19-7.62 (m, 3H), 5.78-5.41 (m, 2H), 5.34-5.18 (m, 2H), 4.81-4.41 (m, 2H), 4.31-4.17 (m, 2H), 3.38-3.49 (m, 18H), 3.41-3.28 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): 191.3 (CH), 170.3 (C), 161.0 (C), 162.8 (C), 148.1 (C), 147.9 (C), 147.8 (C), 147.6 (C), 146.7 (C), 146.6 (C), 146.3 (C), 146.2 (C), 146.1 (C), 146.1 (C), 145.9 (C), 145.8 (C), 145.6 (C), 145.4 (C), 145.1 (C), 145.0 (C), 144.8 (C), 144.7 (C), 144.5 (C), 144.4 (C), 144.3 (C), 144.2 (C), 144.1 (C), 144.0 (C), 143.7 (C), 143.6 (C), 143.5 (C), 143.4 (C), 143.3 (C), 142.7 (C), 142.3 (C), 142.0 (C), 141.6 (C), 141.5 (C), 141.4 (C), 140.6 (C), 140.4 (C), 140.3 (C), 139.9 (C), 139.5 (C), 139.4 (C), 139.3 (C), 139.2 (C), 137.6 (C), 137.3 (C), 136.5 (C), 134.1 (CH), 134.0 (CH), 129.7 (CH), 129.6 (CH), 109.9 (C), 109.8 (C), 77.4 (CH), 77.2 (CH₂), 72.0 (CH₂), 71.2 (CH₂), 71.1 (CH₂), 70.8 (CH₂), 70.7 (CH₂), 70.2 (CH₂), 68.7 (CH₂), 67.9 (CH₂), 66.5 (CH₂), 65.3 (CH₂), 59.2 (CH₃), 51.0 (C); MS (MALDI, DCTB): 1364 (100, $[M+Na]^+$), 1300 (38, $[M-C(CN)_2+Na]^+$).

2.1.2. Synthesis of the Electron-Deficient Cyano-Ester Fullerenes

The synthesis was performed as presented in Scheme S2 (see page S20).

Compound 5a. This compound was prepared following the procedure in ref. S4.

Compound 5b. To a solution of dimethyl 5-hydroxyisophthalate (550 mg, 2.61 mmol), **5a** (1.04 g, 2.61 mmol) and triphenylphosphine (753 mg, 2.87 mmol) in 25 mL of dry DCM at 0 °C and under Ar atmosphere, DIAD (0.57 mL, 2.87 mmol) was added dropwise. The resulting mixture was stirred at rt overnight. After solvent evaporation under reduced pressure, the crude mixture was purified by flash chromatography on silica gel (DCM/MeOH/Acetone 40:1:2, $R_f = 0.39$ with DCM/MeOH 19:1). The product **5b** (750 mg, 50%) was obtained as a colorless oil. IR (neat): 2871 (br), 1724 (s), 1595 (w), 1435 (m), 1339 (m), 1240 (s), 1100 (s) 1046 (m), 759 (m); ¹H NMR (300

MHz, CDCl₃): 8.24 (t, ${}^{4}J$ (H,H) = 1.3 Hz, 1H), 7.73 (d, ${}^{4}J$ (H,H) = 1.3 Hz, 2H), 4.10 (d, ${}^{3}J$ (H,H) = 5.6 Hz, 2H), 3.92 (s, 6H), 3.66-3.55 (m, 24H), 3.55-3.47 (m, 4H), 3.35 (s, 6H), 2.47-2.36 (m, 1H); ${}^{13}C$ NMR (75 MHz, CDCl₃): 166.3 (C), 159.3 (C), 131.8 (C), 123.0 (CH), 119.9 (CH), 72.0 (CH₂), 70.8 (CH₂), 70.7 (CH₂), 70.6 (CH₂), 69.3 (CH₂), 66.7 (CH₂), 59.1 (CH₃), 52.5 (CH₃), 40.0 (CH); HRMS (ESI, +ve): calcd for C₂₈H₄₆O₁₃Na [M+Na]⁺: 613.2830, found: 613.2834.

Compound 5c. To a solution of **5b** (657 mg, 1.11 mmol) in 5 mL of dry THF at 0 °C under Ar atmosphere, LiAlH₄ (170 mg, 4.48 mmol) was added portionwise. After 5 h stirring at rt, some drops of methanol and then water were added carefully at 0 °C. The mixture was filtered through a pad of celite using ethyl acetate as eluent. After solvent removal, the crude mixture was purified by flash chromatography on silica gel (DCM/MeOH 15:1, R_f = 0.19 with DCM/MeOH 19:1), obtaining the pure compound **5c** (516 mg, 87%) as a colorless oil. IR (neat): 3444 (br), 2869 (m), 1738 (w), 1597 (m), 1453 (m), 1293 (m), 1096 (s), 1030 (m), 847 (m); ¹H NMR (300 MHz, CDCl₃): 6.88 (s, 1H), 6.87 (s, 2H), 4.63 (s, 4H), 4.08 (d, ³*J* (H,H) = 5.6 Hz, 2H), 3.67-3.55 (m, 24H), 3.52 (m, 4H), 3.36 (s, 6H), 2.45-2.33 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): 159.7 (C), 143.1 (C), 117.5 (CH), 112.2 (CH), 72.0 (CH₂), 70.8 (CH₂), 70.7 (CH₂), 70.6 (CH₂), 69.4 (CH₂), 66.1 (CH₂), 65.1 (CH₂), 59.1 (CH₃), 40.0 (CH); HRMS (ESI, +ve): calcd for C₂₆H₄₆O₁₁Na [M+Na]⁺: 557.2932, found: 557.2929.

Compound 5d. To a solution of **5c** (129 mg, 0.24 mmol), 2-cyanoacetic acid (16 mg, 0.19 mmol) and 4-dimethylaminopyridine (5 mg, 40 μ mol) in 5 mL of dry DCM at 0 °C under Ar atmosphere, EDC hydrochloride (40 mg, 0.21 mmol) was added portionwise. The resulting mixture was allowed to warm to rt and it was stirred at rt overnight under Ar atmosphere. After solvent removal, the crude mixture was separated by flash chromatography on silica gel (DCM/MeOH 30:1, $R_f = 0.25$ with DCM/MeOH 19:1), to give the pure compound **5d** (79 mg, 55%) as a colorless oil. IR (neat):

3448 (br), 2814 (m), 1748 (m), 1599 (m), 1455 (m), 1296 (m), 1094 (s), 1029 (m), 848 (m); ¹H NMR (300 MHz, CDCl₃): 6.97 (s, 1H), 6.90 (s, 1H), 6.81 (s, 1H), 5.17 (s, 2H), 4.64 (s, 2H), 4.07 (d, ³*J* (H,H) = 5.6 Hz, 2H), 3.67-3.55 (m, 24H), 3.55-3.48 (m, 6H), 3.35 (s, 6H), 2.50 (br s, 1H), 2.46-2.34 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): 163.0 (C), 159.7 (C), 143.6 (C), 135.9 (C), 119.0 (CH), 114.2 (CH), 113.1 (CH), 113.0 (C), 72.0 (CH₂), 70.8 (CH₂), 70.7 (CH₂), 70.6 (CH₂), 69.4 (CH₂), 68.4 (CH₂), 66.2 (CH₂), 64.8 (CH₂), 59.1 (CH₃), 40.0 (CH), 24.9 (CH₂); HRMS (ESI, +ve): calcd for C₂₉H₄₇NO₁₂Na [M+Na]⁺: 624.2990, found: 624.2967.

Compound 5e. To a solution of **5d** (79 mg, 131 μ mol) in 5 mL of dry DCM under Ar atmosphere, Dess-Martin periodinane (84 mg, 197 μ mol) was added portionwise. The mixture was stirred at rt overnight, filtered through a small pad of silica gel (DCM/MeOH 10:1) and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (DCM/MeOH 20:1, $R_f = 0.32$ with DCM/MeOH 19:1), obtaining the pure compound **5e** (67 mg, 85%) as a colorless oil. IR (neat): 2872 (br), 1750 (m), 1697 (m), 1597 (s), 1455 (s), 1297 (m), 1092 (w), 853 (m); ¹H NMR (300 MHz, CDCl₃): 9.96 (s, 1H), 7.45-7.42 (m, 1H), 7.40 (dd, ⁴*J* (H,H) = 2.4, 1.3 Hz, 1H), 7.20-7.16 (m, 1H), 5.25 (s, 2H), 4.11 (d, ³*J* (H,H) = 5.6 Hz, 2H), 3.67-3.56 (m, 24H), 3.57-3.49 (m, 6H), 3.36 (s, 6H), 2.47-2.36 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): 191.7 (CH), 162.9 (C), 160.1 (C), 138.3 (C), 136.9 (C), 122.5 (CH), 121.4 (CH), 114.2 (CH), 112.8 (C), 72.0 (CH₂), 70.8 (CH₂), 70.7 (CH₂), 70.6 (CH₂), 69.3 (CH₂), 67.6 (CH₂), 66.7 (CH₂), 59.1 (CH₃), 40.0 (CH), 24.9 (CH₂); HRMS (ESI, +ve): calcd for C₂₉H₄₅NO₁₂Na [M+Na]⁺: 622.2833, found: 622.2827.

Compound 5. To a solution of **5e** (65 mg, 0.11 mmol), C₆₀ fullerene (140 mg, 0.19 mmol) and I₂ (49 mg, 0.19 mmol) in dry toluene (70 mL) under Ar atmosphere, DBU (48 μ L, 0.32 mmol) was added dropwise at –15 °C. Resulting mixture was allowed to react for 15 min and then solvent was

removed under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (unreacted fullerene was recovered using carbon disulfide and **5** was eluted using DCM/MeOH 15:1) followed by PTLC purification (DCM/MeOH 20:1, $R_f = 0.39$ with DCM/MeOH 19:1). The product **5** (21 mg, 15%) was obtained as a brown powder. M.p.: 92-93 °C; IR (neat): 2956 (m), 2924 (s), 2856 (m), 2249 (w), 1754 (w), 1698 (w), 1459 (w), 1237 (m), 1136 (m), 1107 (m); ¹H NMR (500 MHz, CDCl₃): 10.03 (s, 1H), 7.66 (s, 1H), 7.48 (s, 1H), 7.41 (s, 1H), 5.62 (s, 2H), 4.17 (d, ³*J* (H, H) = 5.5 Hz, 2H), 3.71-3.59 (m, 24H), 3.57-3.52 (m, 4H), 3.38 (s, 6H), 2.46 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): 191.7 (CH), 161.5 (C), 160.3 (C), 145.8 (C), 145.7 (C), 145.6 (C), 145.5 (C), 145.4 (C), 145.3 (C), 145.0 (C), 144.9 (C), 144.7 (C), 144.6 (C), 144.5 (C), 144.2 (C), 144.1 (C), 143.6 (C), 141.3 (C), 143.3 (C), 143.2 (C), 143.1 (C), 142.4 (C), 142.3 (C), 141.8 (C), 141.7 (C), 141.5 (C), 141.3 (C), 139.1 (C), 138.5 (C), 136.6 (C), 123.0 (CH), 121.8 (CH), 114.2 (CH), 113.0 (C), 77.2 (CH₂), 72.1 (CH₂), 70.8 (CH₂), 70.7 (CH₂), 70.6 (CH₂), 69.6 (C), 69.4 (CH₂), 68.9 (CH₂), 66.9 (CH₂), 59.2 (CH₃), 40.0 (CH); MS (MALDI, DCTB): 1341 (100, [M+Na]⁺).

Compound 8. To a solution of **5e** (74 mg, 0.12 mmol), dicyanomethane[60]fullerene (155 mg, 0.20 mmol) and I₂ (56 mg, 0.22 mmol) in dry toluene (80 mL) under Ar atmosphere, a solution of DBU (55 μ L, 0.37 mmol) in 10 mL of dry toluene was added dropwise at –15 °C. Resulting mixture was allowed to react for 15 min and then solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (unreacted dicyanomethane[60]fullerene was recovered using toluene and **8** was eluted using DCM/MeOH 20:1) followed by PTLC purification (DCM/MeOH 20:1, $R_f = 0.36$ with DCM/MeOH 19:1). The product **8** (14.5 mg, 9%) was obtained as a brown powder after washing with diethyl ether. M.p.: 128-129 °C; IR (neat): 2924 (s), 2856 (m), 2248 (w), 1753 (w), 1699 (w), 1460 (w), 1254 (m), 1137 (m), 1107 (m), 747 (w); ¹H NMR (700 MHz, CDCl₃): 10.15-9.93 (m, 1H), 7.80-7.30 (m, 3H), 5.80-5.45 (m, 2H), 4.32-

4.08 (m, 2H), 3.97-3.47 (m, 28H), 3.39 (s, 6H), 2.59-2.37 (m, 1H); ¹³C NMR (175 MHz, CDCl₃): 191.9 (CH), 161.3 (C), 160.5 (C), 148.4 (C), 148.2 (C), 148.0 (C), 147.9 (C), 147.1 (C), 146.8 (C), 146.7 (C), 146.5 (C), 145.8 (C), 145.6 (C), 145.5 (C), 145.3 (C), 144.8 (C), 144.5 (C), 144.3 (C), 143.6 (C), 143.4 (C), 143.3 (C), 142.2 (C), 141.6 (C), 141.0 (C), 140.8 (C), 140.3 (C), 140.1 (C), 139.4 (C), 138.7 (C), 136.6 (C), 123.2 (CH), 123.1 (CH), 122.1 (CH), 122.0 (CH), 114.6 (CH), 114.5 (CH), 112.6 (C), 109.9 (C), 72.4 (CH₂), 71.1 (CH₂), 71.0 (CH₂), 70.9 (CH₂), 69.6 (CH₂), 69.3 (CH₂), 68.6 (CH₂), 68.0 (CH₂), 67.1 (CH₂), 59.5 (CH₃), 40.3 (CH); MS (MALDI, DCTB): 1405 (100, $[M+Na]^+$), 1341 (23, $[M-C(CN)_2+Na]^+$).

Compound 9. To a solution of 5e (110 mg, 0.18 mmol), 1,2-dicyano[60]fullerene (255 mg, 0.33 mmol) and I₂ (83 mg, 0.33 mmol) in dry toluene (100 mL) under Ar atmosphere, a solution of DBU (82 μ L, 0.55 mmol) in 10 mL of dry toluene was added dropwise at -15 °C. Resulting mixture was allowed to react for 15 min and then solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (unreacted 1,2-dicyano[60]fullerene was recovered using toluene and 9 was eluted using DCM/MeOH 20:1) followed by PTLC purification (DCM/MeOH 20:1, $R_f = 0.36$ with DCM/MeOH 19:1). The product 9 (40 mg, 16%) was obtained as a brown powder after washing with diethyl ether. M.p.: 101-102 °C; IR (neat): 2924 (m), 2860 (m), 2245 (w), 1751 (w), 1698 (w), 1276 (m), 1260 (m), 1108 (m), 764 (s), 750 (s); ¹H NMR (700 MHz, CDCl₃): 10.12-9.95 (m, 1H), 7.73-7.30 (m, 3H), 5.67-5.36 (m, 2H), 4.27-4.10 (m, 2H), 3.99-3.51 (m, 28H), 3.50 -3.26 (m, 6H), 2.53-2.42 (m, 1H); ¹³C NMR (175 MHz, CDCl₃): 191.5 (CH), 160.7 (C), 160.1 (C), 149.5 (C), 149.2 (C), 148.9 (C), 148.7 (C), 148.2 (C), 148.1 (C), 147.7 (C), 147.7 (C), 147.6 (C), 146.91 (C), 146.8 (C), 146.5 (C), 146.0 (C), 145.9 (C), 145.6 (C), 145.5 (C), 145.3 (C), 145.2 (C), 145.1 (C), 145.0 (C), 144.6 (C), 144.3 (C), 144.1 (C), 143.5 (C), 143.4 (C), 143.3 (C), 143.1 (C), 143.0 (C), 142.5 (C), 142.3 (C), 142.2 (C), 142.1 (C), 142.0 (C), 141.5 (C), 141.3 (C), 139.6 (C), 139.1 (C), 138.6 (C), 138.5 (C), 138.4 (C), 138.3 (C), 138.2 (C), 137.5 (C),

136.1 (C), 135.0 (C), 122.6 (CH), 122.4 (CH), 121.7 (CH), 121.1 (CH), 116.3 (C), 116.2 (C), 114.3 (CH), 113.1 (CH), 111.8 (C), 71.9 (CH₂), 70.7 (CH₂), 70.6 (CH₂), 70.5 (CH₂), 69.2 (CH₂), 69.0 (CH₂), 68.8 (CH₂), 68.1 (CH₂), 66.7 (CH₂), 66.5 (CH₂), 65.3 (CH₂), 59.1 (CH₃), 57.2 (C), 57.1 (C), 39.9 (CH); MS (MALDI, DCTB): 1393 (100, [M+Na]⁺).

2.1.3. Synthesis of Oligothiophene-Fullerene Dyads

The synthesis was performed as presented in Scheme S3 (see page S21).

Compound T₄-A was prepared following the procedure in ref. S1.

Compound 10a *(general procedure A)*. To a solution of T_4 -A (11 mg, 15 µmol) in DCM/AcOH (1 mL/100 µL) were added *n*-Bu₃SnH (50 µL, 13.2 mmol) and Pd(PPh₃)₂Cl₂ (1.3 mg, 1.71 µmol). The mixture was stirred for 30 min, and then a solution of **6** (20 mg, 15 µmol) in DCM (1 mL) was added. The mixture was stirred for 30 min, and then diluted in DCM, washed with sat. NaHCO₃ aq. and brine, dried over Na₂SO₄ and concentrated *in vacuo*. PTLC of the residue (DCM/MeOH 20:1, $R_f = 0.19$ with DCM/ MeOH 20:1) provided the product **10a** (22 mg, 73%) as a brown solid. ¹H NMR (400 MHz, CDCl₃): 8.11-8.00 (m, 1H), 7.56-7.39 (m, 5H), 7.11-7.04 (m, 8H), 6.49-6.40 (s, 1H), 5.48-5.31 (m, 2H), 5.24-5.14 (m, 2H), 4.76-4.46 (m, 4H), 4.36-4.12 (m, 4H), 3.83-3.55 (m, 22H), 3.47 (s, 6H), 3.43-3.33 (m, 6H), 2.03-1.85 (m, 3H), 1.08-0.91 (m, 6H); MS (MALDI, DCTB): 1987 (100, [M+H]⁺), 1927 (10, [M-CH₂CH₂OCH₃]⁺).

Compound 10b. Following the general procedure A, **10b** (21 mg, 69%) was obtained from **T**₄-A and **7** as a brown solid ($R_f = 0.18$ with DCM/MeOH 20:1). ¹H NMR (400 MHz, CDCl₃): 8.21-7.94 (m, 1H), 7.82-7.36 (m, 6H), 7.14-6.96 (m, 6H), 6.88-6.76 (s, 1H), 6.39-6.34 (s, 1H), 5.66-5.35 (m, 2H), 5.24-5.12 (m, 2H), 4.80-4.44 (m, 4H), 4.38-4.18 (m, 4H), 3.85-3.51 (m, 22H), 3.47 (s, 6H),

3.41-3.36 (m, 6H), 1.90-1.85 (m, 3H), 1.04-0.90 (m, 6H); MS (MALDI, DCTB): 2021 (10, [M+Na]⁺), 1999 (100, [M+H]⁺), 1939 (10, [M-CH₂CH₂OCH₃]⁺).

Compound 10c. Following the general procedure A, **10c** (11.6 mg, 78%) was obtained from **T**₄-A and **5** as a brown solid ($R_f = 0.20$ with DCM/MeOH 20:1). ¹H NMR (400 MHz, CDCl₃): 8.12 (s, 1H), 7.47-7.41 (m, 2H), 7.28-7.07 (m, 9H), 6.89 (br s, 2H), 6.50 (br s, 1H), 5.55 (s, 2H), 4.71-4.65 (m, 1H), 4.54 (t, ³*J* (H,H) = 5.2 Hz, 1H), 4.37-4.26 (m, 2H), 4.13 (d, ³*J* (H,H) = 5.2 Hz, 2H), 3.67-3.56 (m, 28H), 3.55-3.51 (m, 4H), 3.46 (s, 6H), 3.36 (m, 6H), 2.47-2.37 (m, 1H), 1.82-1.77 (m, 3H), 1.00-0.98 (m, 6H).

Compound 10d. Following the general procedure A, **10d** (6 mg, 31%) was obtained from T₄-A and **8** as a brown solid ($R_f = 0.18$ with DCM/MeOH 20:1). ¹H NMR (400 MHz, CDCl₃): 8.11-8.02 (m, 1H), 7.44-7.28 (m, 3H), 7.20-6.99 (m, 8H), 6.74 (br s, 2H), 6.25 (br s, 1H), 5.51-5.35 (m, 2H), 4.71-4.61 (m, 1H), 4.50 (t, ³*J* (H,H) = 5.2 Hz, 1H), 4.33-4.21 (m, 2H), 4.13-4.01 (m, 2H), 3.68-3.49 (m, 32H), 3.45 (s, 6H), 3.36 (m, 6H), 2.45-2.37 (m, 1H), 1.82-1.73 (m, 3H), 1.03-0.91 (m, 6H); MS (MALDI, DCTB): 2042 (100, [M+H]⁺).

Compound 10. Following the general procedure A, **10** (10 mg, 49%) was obtained from **T**₄-**A** and **9** as a brown solid (R_f = 0.16 with DCM/MeOH 20:1). ¹H NMR (400 MHz, CDCl₃): 8.18-8.01 (m, 1H), 7.46-7.32 (m, 2H), 7.24-6.90 (m, 9H), 6.77 (br s, 2H), 6.26 (br s, 1H), 5.52-5.30 (m, 2H), 4.72-4.60 (m, 1H), 4.50 (t, ³*J* (H,H) = 5.6 Hz, 1H), 4.36-4.21 (m, 2H), 4.05 (d, ³*J* (H,H) = 5.6 Hz, 2H), 3.70-3.45 (m, 32H), 3.45 (s, 6H), 3.36 (m, 6H), 2.45-2.37 (m, 1H), 1.83-1.73 (m, 3H), 0.95 (d, ³*J* (H,H) = 5.6 Hz, 6H); MS (MALDI, DCTB): 2029 (100, [M+H]⁺).

Compound T₄-6 (general procedure B). To a solution of **10a** (21 mg, 12 μ mol) in DCM (1.0 mL) was added TFA (0.4 mL). Then immediately the mixture was concentrated *in vacuo*. After several times of redissolving in DCM and evaporation, the product was washed with DCM/Hexane. The product was obtained in quantitative yield as a brown solid and used for the stack exchange without further purification. ¹H NMR (300 MHz, CD₂Cl₂): 9.75-9.71 (m, 1H), 8.15-7.99 (m, 1H), 7.74-7.33 (m, 6H), 7.24-6.97 (m, 5H), 6.91-6.76 (m, 1H), 5.47-5.36 (m, 2H), 5.19-5.08 (m, 2H), 4.67-4.44 (m, 2H), 4.37-4.12 (m, 5H), 3.76-3.43 (m, 22H), 3.36-3.23 (m, 6H), 1.95-1.78 (m, 3H), 1.00-0.87 (m, 6H); MS (MALDI, DCTB): 1958 (13, [M+H₂O]⁺), 1941 (100, [M+H]⁺), 1929 (52, [M-CH₃]⁺).

Compound T₄-7. Following the general procedure B, **T₄-7** was obtained from **10b** in quantitative yield as a brown solid and used for the stack exchange without further purification. ¹H NMR (300 MHz, CD₂Cl₂): 9.78-9.68 (m, 1H), 8.17-8.02 (m, 1H), 7.82-7.35 (m, 6H), 7.30-6.75 (m, 6H), 5.55-5.38 (m, 2H), 5.24-5.06 (m, 2H), 4.73-4.43 (m, 3H), 4.39-4.09 (m, 4H), 3.84-3.40 (m, 22H), 3.39-3.29 (m, 6H), 1.88-1.56 (m, 3H), 1.06-0.84 (m, 6H); MS (MALDI, DCTB): 1970 (10, $[M+H_2O]^+$), 1953 (100, $[M+H]^+$), 1938 (69, $[M-CH_3]^+$).

Compound T₄-5. Following the general procedure A, **T₄-5** was obtained from **10c** in quantitative yield as a brown solid and used for the stack exchange without further purification. ¹H NMR (300 MHz, CD₂Cl₂): 9.79-9.67 (m, 1H), 8.19-7.99 (m, 1H), 7.72-7.33 (m, 4H), 7.24-6.76 (m, 7H), 5.66-5.43 (m, 2H), 4.71-4.53 (m, 1H), 4.42-4.19 (m, 2H), 4.17-3.96 (m, 2H), 3.73-3.40 (m, 32H), 3.36-3.26 (m, 6H), 2.48-2.33 (m, 1H), 1.93-1.74 (m, 3H), 1.06-0.83 (m, 6H); MS (MALDI, DCTB): 1953 (42, $[M+Na]^+$), 1930 (100, $[M+H]^+$), 1915 (44, $[M-CH_3]^+$).

Compound T₄-8. Following the general procedure A, **T₄-8** was obtained from **10d** in quantitative yield as a brown solid and used for the stack exchange without further purification. ¹H NMR (300 MHz, CDCl₃): 9.83-9.72 (m, 1H), 8.14-8.00 (m, 1H), 7.53-7.36 (m, 2H), 7.20-6.71 (m, 9H), 5.54-5.35 (m, 2H), 4.77-4.59 (m, 1H), 4.43-4.24 (m, 2H), 4.15-4.00 (m, 2H), 3.77-3.46 (m, 32H), 3.40-3.27 (m, 6H), 2.47-2.33 (m, 1H), 1.79-1.67 (m, 3H), 1.03-0.87 (m, 6H); MS (MALDI, DCTB): 2019 (100, $[M+Na]^+$), 1996 (8, $[M+H]^+$).

Compound T₄-9. Following the general procedure A, **T₄-9** was obtained from **10** in quantitative yield as a brown solid and used for the stack exchange without further purification. ¹H NMR (300 MHz, CDCl₃): 9.82-9.74 (m, 1H), 8.12-7.95 (m, 1H), 7.56-7.37 (m, 2H), 7.19-6.72 (m, 9H), 5.51-5.25 (m, 2H), 4.73-4.60 (m, 1H), 4.43-4.23 (m, 2H), 4.15-3.98 (m, 2H), 3.72-3.46 (m, 32H), 3.39-3.29 (m, 6H), 2.50-2.31 (m, 1H), 1.82-1.64 (m, 3H), 1.04-0.87 (m, 6H); MS (MALDI, DCTB): 2004 (100, $[M+Na]^+$).

2.2. Electrochemistry

The reduction potentials of the fullerenes **5-9** were determined using differential pulse voltammograms (DPV, scan rate 100 mV/s) vs Fc⁺/Fc in DCM (supporting electrolyte: 100 mM Bu₄NPF₆, working electrode: glassy carbon electrode, counter electrode: Pt wire, reference electrode: Ag wire in a 10 mM AgNO₃/0.1 M Bu₄NPF₆ in acetonitrile solution, Supporting Figure S1). LUMO energies *vs* vacuum were calculated from reduction peak in DPV using the Supporting equation (S1).^{S5} The optical band gap E_g^{opt} was calculated from the onset of the lowest energy band using the Supporting equation (S2). HOMO energy levels were estimated from difference between E_{LUMO} and E_g^{opt} (S3).

$$E_{\rm LUMO} = -5.1 \text{ eV} - E_{\rm DPV} \text{ vs} (\text{Fc}^+/\text{Fc})$$
(S1)

$$E_{\rm g}^{\rm opt} = 1240 \,/ \,\lambda_{\rm max}^{\rm onset} \,(\rm nm) \tag{S2}$$

$$E_{\rm HOMO} = E_{\rm LUMO} - E_{\rm g}^{\rm opt}$$
(S3)

2.3. Stack Exchange

The SOSIP electrode based on photosystem ITO-**NDI-Benzaldehyde** (ITO-**NDI-B**) was prepared according to the reported procedures.^{S6} The obtained electrode was treated with aqueous NH₂OH (1 M) for 24 h at 40 °C, leading to the photosystem ITO-**NDI**. This prepared electrode was dipped in a solution of corresponding dyads in DMSO and acetic acid (9:1, 10 mM) and shaken for 24 h at 40 °C. The desired ITO-**NDI-T4-Fullerene** (ITO-**NDI-F**) photosystem was obtained when no more changes in UV-vis absorption spectra were observed (Supporting Scheme S3 and Figures S2-3). The yield of stack exchange was roughly estimated from the molar ratio *R* obtained from the absorbances of the film after stack exchange at 390 nm and 450 nm by using following equations:

 $A'_{\text{at 390 nm}} = \varepsilon'_{\text{NDI}}[\text{NDI}] + \varepsilon'_{\text{dyad}}[\text{dyad}]$

$$A''_{\text{at 450 nm}} = \varepsilon''_{\text{NDI}}[\text{NDI}] + \varepsilon''_{\text{dyad}}[\text{dyad}]$$

where *A*' and *A*'' are the absorbances at 390 nm and 450 nm, ε'_{NDI} and ε''_{NDI} are the molar absorption coefficients of NDI at 390 nm and 450 nm, and ε'_{dyad} and ε''_{dyad} are the molar absorption coefficients of the corresponding dyad at 390 nm and 450 nm, respectively. Quantitative yield was assumed for a 2:1 ratio (*R* = 2.0).

2.4. Photosystem Characterization

Photocurrent measurements. The final triad photosystems 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 Ar gas) aqueous solution of TEOA (50 mM) and Na₂SO₄ (0.1 M) and irradiated with a solar simulator (area of irradiation: $a \sim 0.5 \text{ cm}^2$). Changes in current upon on-off switching of irradiations were measured at 0 V vs Ag/AgCl unless stated. The power of irradiation was 88 mWcm⁻² unless stated otherwise. Bimolecular recombination efficiencies η_{BR} were calculated from the dependence of photocurrent densities (*J*) to the irradiation power (*I*) using the Supporting equations (S4) and (S5).^{S7}

$$J \propto I^{\alpha} \tag{S4}$$

$$\eta_{\rm BR} = \mathbf{a}^{-1} - 1 \tag{S5}$$

Activation energies (E_a , eV) of the system were calculated from the dependence of photocurrent densities (J, A/cm²) to the temperature (T, K) using the Supporting equation S6.^{S8}

$$J(T, I_{light}) = J_{00}(I_{light})e^{\frac{-E_a}{kT}}$$
(S6)

where I_{light} is the irradiation power and k is the Boltzmann constant 8.617 × 10⁻⁵ eV / K. $I_{light} = 88$ mW cm⁻² was used for determining E_a values.

2.5. Time Resolved Fluorescence

Fluorescence dynamics on the nanosecond timescale were measured by a time-correlated single photon counting (TCSPC). Excitation was performed at 395 nm using ~60 ps pulse at 10 MHz produced by a laser diode (picoquant, LDH-P-C-400B). The full width at half-maximum (FWHM) of the instrument response function (IRF) was around 200 ps. Faster fluorescence dynamics were monitored by fluorescence up-conversion (FU) using the same setup as reported.^{S9} Excitation was performed at 400 nm with the frequency-doubled output of a Kerr-lens mode-locked Ti:sapphire laser (Spectra-Physics, Mai Tai). The pump intensity on the sample was around 5 μ Jcm⁻², and the

FWHM of the IRF was ca. 200 fs. The sample solutions in acetonitrile were located in a 1 mm rotating cell and at an absorbance of about 0.05 at the excitation wavelength.

The fluorescence decays are mono-exponential. They can be reproduced with a convolution of the IRF and a mono-exponential decay. For the analysis of the femtosecond FU data, the decay time found from TCSPC was fixed. FU measurements were made at three different wavelengths (480, 510 and 540 nm). A global analysis of the three sets of data was then made. A three-exponential decay had to be used. The results from the analysis are summarized in Table S3. (The origin of τ_3 of all dyads is unclear. It could originate from a residual impurity of T_4 , but such an impurity was not detectable and thus not removable by other spectroscopic and analytical methods. In situ hydrolysis of the bridging oximes is unlikely considering their stability but cannot be fully excluded.)

3. Supporting Schemes and Figures



Supporting Scheme S1. a) 1,2-dicyano[60]fullerene (for **6a**), dicyanomethane[60]fullerene (for **7a**), DBU, I₂, dry PhMe, 15 min, -15 °C, **6a**: 60%, **7a**: 56%; b) TFA, H₂O, DCM, 2 h, rt, **6**: 58%, **7**: 56%; Note: **6a**, **7a**, **6** and **7** are mixtures of regioisomers.



Supporting Scheme S2. a) DIAD, PPh₃, dry DCM, overnight, 0 °C to rt, 50%; b) LiAlH₄, dry THF, 5 h, 0 °C to rt, 87%; c) 2-Cyanoacetic acid, EDC, DMAP, dry DCM, overnight, 0 °C to rt, 55%; d) Dess-Martin periodinane, dry DCM, overnight, rt, 85%; e) C₆₀ (for **5**), dicyanomethane[60]fullerene (for **8**), 1,2-dicyano[60]fullerene (for **9**), DBU, I₂, dry PhMe, 15 min, -15 °C, **5**: 15%, **8**: 9%, **9**: 16%. Note: **8** and **9** are mixtures of regioisomers.



Supporting Scheme S3. Synthesis of the dyads (top) and stack exchange scheme with schematic structures for ITO-NDI-B, ITO-NDI-T4-F (bottom). a) 1. *n*-Bu₃SnH, Pd(PPh₃)₂Cl₂, DCM, AcOH;
Corresponding Fullerenes, DCM, 10a: 73%, 10b: 69%, 10c: 78%, 10d: 31%, 10: 49%; b) TFA, DCM, quantitative yields; Note: 10a, 10b, 10d, 10 and T₄-6, T₄-7, T₄-8 and T₄-9 are mixtures of regioisomers; c) NH₂OH; d) AcOH, DMSO.



Supporting Figure S1. a) Original and b) normalized differential pulse voltammograms (DPV) of 6 (black), 7 (blue), 5 (red), 8 (purple) and 9 (green).



Supporting Figure S2. UV-vis absorption spectra of photosystems based on a) ITO-**NDI-T₄-6** and b) ITO-**NDI-T₄-7** before (dash-dot line) and after (solid line) templated stack exchange. TSE yields: ITO-**NDI-T₄-6** (72%), ITO-**NDI-T₄-7** (52%).



Supporting Figure S3. UV-vis absorption spectra of photosystems based on a) ITO-NDI-T₄-5, b) ITO-NDI-T₄-8, and c) ITO-NDI-T₄-9, before (dash-dot line) and after (solid line) templated stack exchange. TSE yields: ITO-NDI-T₄-5 (74%), ITO-NDI-T₄-8 (51%) and ITO-NDI-T₄-9 (58%).



Supporting Figure S4. a) Photocurrent generation and b) I-V curves of electrodes based on NDIoligothiophene-fullerene photosystems ITO-NDI-T₄-6 (black), ITO-NDI-T₄-7 (blue), ITO-NDI-T₄-5 (red), ITO-NDI-T₄-8 (purple) and ITO-NDI-T₄-9 (green).



Supporting Figure S5. a) Dependence of the short-circuit current density (J_{SC}) on the light intensity (I) for photosystems based on ITO-NDI-T₄-6 (black), ITO-NDI-T₄-7 (blue), ITO-NDI-T₄-5 (red), ITO-NDI-T₄-8 (purple), ITO-NDI-T₄-9 (green) and b) Temperature dependence of photocurrent (J_{SC}) for photosystems ITO-NDI-T₄-6 (black), ITO-NDI-T₄-7 (blue) and ITO-NDI-T₄-5 (red).



Supporting Figure S6. ¹H (top) and ¹³C NMR (bottom) spectra of 6 in CDCl₃.



Supporting Figure S7. ¹H (top) and ¹³C NMR (bottom) spectra of 7 in CDCl₃.



Supporting Figure S8. ¹H (top) and ¹³C NMR (bottom) spectra of 5 in CDCl₃.



Supporting Figure S9. ¹H (top) and ¹³C NMR (bottom) spectra of 8 in CDCl₃.



Supporting Figure S10. ¹H (top) and ¹³C NMR (bottom) spectra of 9 in CDCl₃.



Supporting Figure S11. MALDI MS of 6 (top) and 7 (bottom).



Supporting Figure S12. MALDI MS of **5** (top), **8** (center) and **9** (bottom).



Supporting Figure S13. MALDI MS of T_4-6 (top) and T_4-7 (bottom).



Supporting Figure S14. MALDI MS of T_4 -5 (top), T_4 -8 (center) and T_4 -9 (bottom).

4. Supporting Tables

| | 1 | 4 | 5 | 6 | 7 | 8 | 9 |
|--|-------|-------|-------|-------|-------|-------|-------|
| <i>E</i> _{red} (mV vs Fc ⁺ / Fc) ^a | -1230 | -1050 | -998 | -974 | -952 | -891 | -885 |
| LUMO (eV) ^b | -3.87 | -4.05 | -4.10 | -4.13 | -4.15 | -4.21 | -4.22 |
| HOMO (eV) ^c | -6.17 | -6.35 | -6.39 | -6.43 | -6.46 | -6.51 | -6.52 |

Table S1. The reduction potentials and LUMO, HOMO energy levels of the fullerenes 5-9,compared to 1 and 4.

^aObtained from DPV reduction potential. ^bCalculated from reduction potential in DPV using the equation S1. ^cEstimated from the gradual onset of their absorption and LUMO energy level.

| Photosystem | Δ LUMO (eV) ^b | Δ HOMO (eV) ^c | TSE (%) ^d | J _{sc} (µAcm ⁻²) ^e | $V_{\rm oc}$ (V) ^f | $\eta_{ m BR} \ (\%)^{ m g}$ | $E_{\rm a}$ (meV) ^h |
|--|-----------------------------|-----------------------------|-------------------------|--|----------------------------------|------------------------------|--------------------------------|
| 1 ITO- NDI-T₄-1 ^a | -0.67 | -0.27 | 67 | 2.2 | 0.24 | 97 | _ |
| 2 ITO- NDI-T₄-4 ^a | -0.85 | -0.45 | 62 | 12 | 0.27 | 58 | - |
| 3 ITO-NDI-T ₄ -5 | -0.89 | -0.49 | 74 | 8.1 | 0.32 | 64 | 258 |
| 4 ITO- NDI-T₄-6 | -0.93 | -0.53 | 72 | 5.2 | 0.30 | 51 | 243 |
| 5 ITO- NDI-T ₄ -7 | -0.96 | -0.56 | 52 | 5.3 | 0.31 | 43 | 196 |
| 6 ITO-NDI-T ₄ -8 | -1.01 | -0.61 | 52 | 6 | 0.27 | 46 | - |
| 7 ITO-NDI-T ₄ -9 | -1.02 | -0.62 | 58 | 5 | 0.26 | 35 | - |
| | | | | | | | |

Table S2. Characteristics of triple channel photosystems.

^aSee ref. S1. ^bEnergy difference to the LUMO of T_4 (from DPV, compare Figure 1 and Supporting Figure S1). ^cEnergy difference from the HOMO of T_4 . ^dYield for templated stack exchange, estimated from absorption spectra, see Supporting Figure S2 and S3. ^eShort-circuit photocurrent density generated by irradiation with white light (solar simulator, W = 88 mWcm⁻², 50 mM TEOA, 0.1 M Na₂SO₄, Pt counter electrode, Ag/AgCl reference electrode). ^fOpen-circuit voltage. ^gBimolecular charge recombination efficiencies were determined from the dependence of the photocurrent generation on the intensity of irradiation. ^hActivation energy E_a from the dependence of J_{SC} on temperature (Supporting Figure S5).

| Dyads | λ [nm] | a ₁ | $	au_1$ [ps] | a ₂ | $	au_2$ [ps] | a ₃ | $	au_3{}^a$ [ps] |
|-------------------|-------------------|----------------------|--------------|----------------------|--------------|----------------------|------------------|
| T ₄ -1 | 480 510 540 | 0.40 0.33 0.36 | 2.2 | 0.35 0.43 0.39 | 30.0 | 0.25 0.24 0.25 | 540 |
| T ₄ -4 | 480 510 540 | 0.24 0.19 0.16 | 1.4 | 0.12 0.20 0.17 | 16.9 | 0.64 0.62 0.67 | 545 |
| T ₄ -9 | 480 510 540 | 0.26 0.22 0.21 | 1.4 | 0.08 0.23 0.11 | 17.2 | 0.66 0.54 0.68 | 535 |

Table S3. Best-fit parameters of FU data for dyads T_4 -1, T_4 -4 and T_4 -9.

^aTaken from TCSPC measurements.

5. Supporting References

- S1 A. Bolag, J. López-Andarias, S. Lascano, S. Soleimanpour, C. Atienza, N. Sakai, N. Martín and S. Matile, *Angew. Chem. Int. Ed.*, 2014, 53, 4890-4895.
- S2 M. Keshavarz-K, B. Knight, G. Srdanov and F. Wudl, *J. Am. Chem. Soc.*, 1995, **117**, 11371-11372.
- S3 T.-H. Zhang, P. Lu, F. Wang and G.-W. Wang, Org. Biomol. Chem., 2003, 1, 4403-4407.
- S. Zhu, J. Zhang, G. Vegesna, F.-T. Luo, S. A. Green and H. Liu, *Org. Lett.*, 2011, 13, 438-441.
- S5 C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, 23, 2367-2371.
- S6 N. Sakai and S. Matile, J. Am. Chem. Soc., 2011, 133, 18542-18545.
- S7 L. J. A. Koster, M. Kemerink, M. M. Wienk, K. Maturová and R. A. J. Janssen, *Adv. Mater.*, 2011, 23, 1670-1674.
- S8 I. Riedel, J. Parisi, V. Dyakonov, L. Lusten, D. Vanderzande and J. C. Hummelen, Adv. Funct. Mater., 2004, 14, 38-44.
- S9 G. Duvanel, J. Grilj, H. Chaumeil, P. Jacques and E. Vauthey, *Photochem. Photobiol. Sci.*, 2010, 9, 908-915.