

Electronic Supplementary Information for

Donor-Spacer-Acceptor Monodisperse Conjugated Co-Oligomers for Efficient Single-Molecule Photovoltaic Cells Based on Non-Fullerene Acceptor

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General methods.....	S2-5
Experimental section.....	S5-10
¹ H NMR spectrum, MALDI-TOF mass spectrum and POM images of co-oligomers.....	S11-13
Transient absorption spectra characterization.....	S14-15
TEM and SAED of F5T8BTP-C4	S16

General Methods

Instruments. Preparative gel permeation chromatography (PGPC) purification was performed with a JAI LC-9104 recycling preparative high performance liquid chromatography (JAIGEL 2H/3H column assembly), and the eluent was toluene. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AV 400-MHz spectrometer in CDCl_3 with tetramethylsilane (TMS) as an internal standard. Elemental analysis was performed by a Flash EA1112 elemental analysis system. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra (MS) were recorded on a Bruker/AutoflexIII Smartbean MALDI Mass Spectrometer with anthracene-1,8,9-triol as the matrix. Solution cyclic voltammetry (CV) measurements were performed on the CHI660a electrochemical analyzer in anhydrous CH_2Cl_2 solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). A platinum (Pt) electrode with a diameter of 2 mm, a Pt wire and a saturated calomel electrode (SCE) were used as the working, the counter and the reference electrodes, respectively. UV-Vis absorption spectra were recorded on a Shimadzu UV3600 spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a TA Q100 thermal analyzer at a scanning rate of 10 $^\circ\text{C}/\text{min}$ in N_2 . Small angle X-ray scattering (SAXS) was recorded on a Bruker Nanostar instrument operated at 40 kV and 0.65 mA. Powder X-ray diffraction (XRD) was performed on a DMax 2500V X-ray diffractometer.

Transmission electron microscopy (TEM) characterization. To prepare films of the D-S-A co-oligomers for TEM characterization, PEDOT:PSS with a thickness of 40 nm was spin-coated on the pre-cleaned glass slides, and heating at 120 $^\circ\text{C}$ for 30 min. Then co-oligomer layers were spin-coated from chlorobenzene with a concentration of 12 mg/mL, and thermal annealed at 160 $^\circ\text{C}$ for 10 min. At last, the films were floated with water to gilder grids, and all samples were measured at room

temperature. TEM was performed on a JEOL JEM-1011 transmission electron microscope with an acceleration voltage of 100 kV. Selected area electron diffraction (SAED) was taken with camera length of 120 cm and Au (111) diffraction as the external standard.

OPV Devices Fabrication and Measurements. ITO (indium tin oxide) glass plates were cleaned with detergent, ultrasonicated in water and dried at 120 °C for 30 min, and then treated with UV/ozone for 30 min. Poly (3,4-ethylene dioxythiophene):poly (styrene sulphonate) (PEDOT:PSS) with a thickness of ~40 nm was spin-coated on the cleaned ITO at 5000 rpm for 60 s and then baked for 30 min at 120 °C. Then the co-oligomer layer with a thickness of ~70 nm was spin-coated from chlorobenzene solution with a concentration of 12 mg/mL in glovebox. The films were heated at 160 °C for 10 min. Finally, hole blocking-layer *N,N'*-bis(1-ethylpropyl)-3,4,9,10-perylenetetracarboxyl diimide (epPDI, 5 nm), LiF (1 nm) and Al (100 nm) were thermally deposited in a vacuum chamber at a base pressure of less than 5×10^{-4} Pa. The active area of the device is 12 mm². The devices were sealed in the glovebox, and then measured in ambient. An Oriel 150W solar simulator with an AM 1.5G filter was used as a light source to produce an intensity of 100 mW/cm² for the illumination of the photovoltaic cells. The light intensity was calibrated by a calibrated silicon diode with KG-5 visible color filter. Current-voltage (*J-V*) characteristics were obtained with a Keithley 236 source meter. External quantum efficiency (EQE) measurements were performed under short-circuit conditions with a lock-in amplifier (SR830, Stanford Research System) at a chopping frequency of 280 Hz during illumination with a monochromatic light from a Xenon lamp.

Hole-only and electron-only devices fabrication. The device structures for hole-only devices were ITO/PEDOT:PSS (40 nm)/co-oligomer (70 nm)/MoO₃ (6 nm)/Al (100 nm). These devices were fabricated employing the same procedure with the OPV devices expect that MoO₃ (6 nm) was

deposited as a substitute for epPDI/LiF. The device structures for electron-only devices were Al (100 nm)/co-oligomer/Al (100 nm). Al (100 nm) was thermally deposited onto the glass slide in a vacuum chamber. Then the co-oligomer layer with a thickness of ~70 nm was spin-coated from chlorobenzene solution with a concentration of 12 mg/mL in glovebox. After the film heated at 160 °C for 10 min, Al (100 nm) was finally thermally deposited. *J-V* curves were measured under dark with a Keithley 236 source meter in air. The mobilities were determined by fitting the dark current using a model of single-carrier space charge limited current with field-dependent mobility.

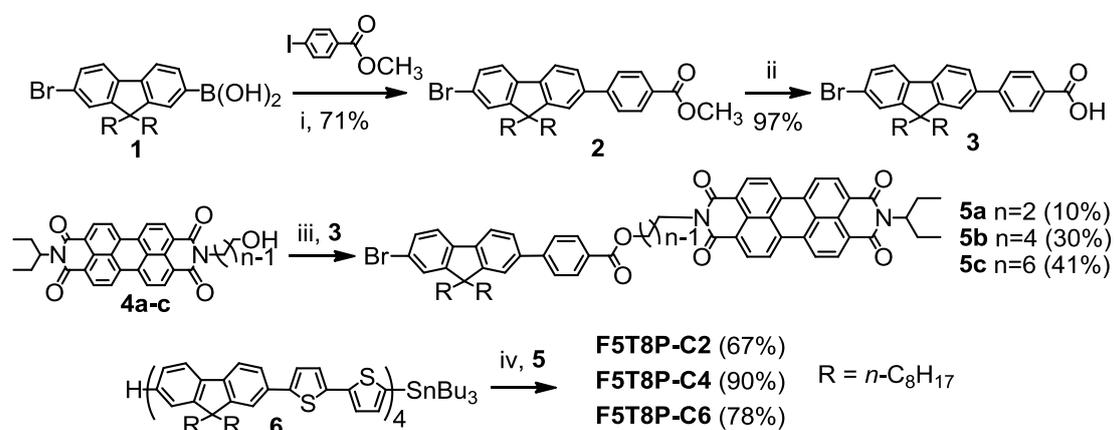
Femtosecond transient absorption spectroscopy. The output of a Ti:Sapphire laser (Tsunami, Spectra Physics) pumped by an Nd:YVO laser (Millennia, Spectra Physics) was amplified in a regenerative amplifier (RGA, Spitfire, Spectra Physics). The output of the amplifier of 1.5-mJ pulse energy, 100 fs pulse width, at 800 nm wavelength with a repetition rate of 250 Hz was split into two parts. One part of the RGA output (800 nm) was then used to generate a white light continuum as probe beam by focusing the beam into a 2 mm water cell. The other part was either used to pump OPA to generate excitation pulse at 610 nm or sent to a 1 mm thick BBO to get the double frequency of 400 nm excitation pulse, which was then sent to a delay line and modulated by a synchronized optical chopper (Newport Model 75160) with a frequency of 125 Hz as the pump beam to excite the sample. Time-resolved transient absorption spectra were recorded with a highly sensitive spectrometer (Avantes AvaSpec-2048 × 14). The dynamics traces were obtained by controlling the relative delay between the pump and the probe pulses with a stepper-motor-driven optical delay line (Newport M-ILS250CC). The group velocity dispersion of the whole experimental system was compensated by a chirp program. The intensities of the pump pulses were measured with a laser power meter (Sanwa LP1). The film of the co-oligomer was spin-coated onto the glass slide from chlorobenzene solution

with a concentration of 12 mg/mL, and thermal annealed at 160 °C for 10 min. Then the film was covered with another glass slide, and sealed with glue for test.

Experimental Section

Materials. Tetrahydrofuran (THF) and Toluene were distilled over sodium/benzophenone. Chloroform was distilled over CaCl₂. Other reagents were used without further purification. Compound **1**, **4a-c**, and **6** were synthesized according to the procedures reported in the literatures.¹⁻³

Scheme 1. The synthetic route of **F5T8P-C2**, **F5T8P-C4** and **F5T8P-C6** (R = *n*-C₈H₁₇).



Condition and reagents: (i) Pd(PPh₃)₄, Na₂CO₃, THF/H₂O, 70 °C; (ii) (1) NaOH, THF/H₂O, reflux; (2) HCl; (ii) 1-Hydroxybenzotriazole (HOBT), 4-Dimethylaminopyridine (DMAP), N,N'-Dicyclohexylcarbodiimide (DCC), CHCl₃, room temperature; (iv) Pd₂(dba)₃, P(o-tolyl)₃, toluene, 105 °C.

Methyl 4-(7-bromo-9,9-dioctyl-fluorene-2-yl)benzoate (2) In absent of light, a mixture of methyl 4-iodobenzoate (3.59 g, 13.70 mmol), 7-bromo-9,9-dioctyl-fluorene-2-yl-boronic acid (**1**, 5.86 g, 11.41 mmol), Pd(PPh₃)₄ (127 mg, 0.11 mmol), THF (100 mL) and Na₂CO₃ aqueous solution (2M, 50 mL) was stirred at 70 °C for 24 hours. The mixture was cooled to room temperature and extracted with petrol ether for three times, then washed with brine and dried over anhydrous MgSO₄. After filtered,

the solvent was evaporated. The crude product was purified with column chromatography on silica gel with petrol ether and dichloromethane (4:1) as eluent to give a white solid (4.87 g, 71%). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.13 (d, $J = 8.1$ Hz, 2H), 7.73 (t, $J = 8.5$ Hz, 3H), 7.58 (m, 3 H), 7.48-7.46 (m, 2H), 3.96 (s, 3H), 2.05-1.92 (m, 4H), 1.26-0.99 (m, 20H), 0.81 (t, $J = 7.1$ Hz, 6H), 0.72-0.58 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 167.0, 153.3, 151.2, 145.9, 140.2, 139.5, 139.2, 130.1, 128.8, 127.1, 126.4, 126.2, 121.6, 121.4, 121.2, 120.2, 55.6, 52.1, 40.2, 31.7, 29.9, 23.7, 22.6, 14.0. Elemental analysis (%) calculated for $\text{C}_{37}\text{H}_{47}\text{BrO}_2$ (602.3): C 73.62, H 7.85, found: C 73.64, H 7.84. MS (MALDI-TOF, reflection mode): m/z : 602.3 $[M]^+$.

4-(7-bromo-9,9-dioctyl-fluorene-2-yl)benzoic acid (3) KOH (0.52 g, 9.24 mmol) dissolved in 4 mL H_2O was added dropwise into the THF (40 mL) solution of methyl 4-(7-bromo-9,9-dioctyl-fluorene-2-yl)benzoate (**2**, 1.86 g, 3.08 mmol), then refluxed for 12 hours. The mixture was poured into the dilute HCl (2M), and stirred for 1 hour. The product was obtained white solid (1.75 g, 97%) after filtered. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.20 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 8.5$ Hz, 3H), 7.65-7.53 (m, 3H), 7.51-7.46 (m, 2H), 2.05-1.92 (m, 4H), 1.26-0.99 (m, 20H), 0.81 (t, $J = 7.1$ Hz, 6H), 0.72-0.58 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 172.0, 153.3, 151.3, 146.9, 140.4, 139.5, 139.1, 130.8, 130.1, 127.9, 127.2, 126.5, 126.3, 121.6, 121.5, 121.3, 120.2, 55.6, 40.2, 31.8, 29.9, 29.2, 23.7, 22.6, 14.0. Elemental analysis (%) calculated for $\text{C}_{36}\text{H}_{45}\text{BrO}_2$ (588.2): C 73.33, H 7.69, found: C 73.25, H 7.70. MS (MALDI-TOF, reflection mode): m/z : 588.2 $[M]^+$.

Compound 5a A solution of 4-(7-bromo-9,9-dioctyl-fluorene-2-yl)benzoic acid (**3**, 0.50 g, 0.85 mmol), **4a** (0.36 g, 0.71 mmol), 1-hydroxybenzotriazole (HOBt, 96 mg, 0.71 mmol), 4-dimethylaminopyridine (DMAP, 87 mg, 0.71 mmol), and N,N' -dicyclohexylcarbodiimide (DCC, 0.15 g, 0.71 mmol) in anhydrous CHCl_3 (30 mL) was stirred at room temperature for 3 days. The mixtures

was extracted with CHCl_3 for three times. The organic layer was washed with brine and dried over MgSO_4 . Evaporation of the solvent and then purified with column chromatography on silica gel with chloroform and acetone (100:1) as eluent to give a red solid (76 mg, 10%). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.74-8.53 (m, 8H), 8.12 (d, $J = 8.3$ Hz, 2H), 7.75-7.67 (m, 3H), 7.58 (d, $J = 8.7$ Hz, 2H), 7.55 (s, 1H), 7.50-7.42 (m, 2H), 5.11-5.03 (m, 1H), 4.73 (s, 4 H), 2.34-2.20 (m, 2H), 2.05-1.88 (m, 6H), 1.25-0.99 (m, 20 H), 0.94 (t, $J = 7.4$ Hz, 6H), 0.79 (t, $J = 7.1$ Hz, 6H), 0.71-0.58 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 166.4, 163.2, 153.3, 151.2, 145.9, 140.2, 139.5, 139.2, 134.6, 134.0, 131.3, 130.3, 130.1, 129.4, 129.3, 128.7, 127.0, 126.4, 126.3, 126.2, 126.1, 123.0, 122.8, 121.5, 121.4, 121.2, 120.2, 62.4, 57.8, 55.6, 40.2, 39.3, 31.7, 29.9, 29.1, 25.0, 23.7, 22.6, 14.0, 11.4. Elemental analysis (%) calculated for $\text{C}_{67}\text{H}_{67}\text{BrN}_2\text{O}_6$ (1074.4): C 74.78, H 6.28, N 2.60, found: C 74.69, H 6.30, N 2.56. MS (MALDI-TOF, reflection mode): m/z : 1074.4 [M] $^+$.

Compound 5b Similar procedure for preparation of **5a** was followed to obtain a red solid (0.17 g, 30%). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.74-8.53 (m, 8H), 8.13 (d, $J = 8.3$ Hz, 2H), 7.71 (dd, $J = 10.9, 8.2$ Hz, 3H), 7.58 (d, $J = 8.7$ Hz, 2H), 7.54 (s, 1H), 7.50-7.42 (m, 2H), 5.11-5.03 (m, 1H), 4.44 (t, $J = 6.5$ Hz, 2 H), 4.33 (t, $J = 7.6$ Hz, 2H), 2.33-2.21 (m, 2H), 2.04-1.90 (m, 10H), 1.25-0.99 (m, 20 H), 0.94 (t, $J = 7.4$ Hz, 6H), 0.79 (t, $J = 7.1$ Hz, 6H), 0.71-0.58 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) 166.5, 163.1, 153.3, 151.2, 145.8, 140.2, 139.5, 139.3, 134.4, 133.9, 131.1, 130.1, 129.4, 129.1, 129.0, 127.0, 126.4, 126.2, 126.1, 126.0, 122.9, 122.8, 121.6, 121.4, 121.2, 120.2, 64.7, 57.9, 55.6, 40.2, 31.7, 29.9, 29.1, 26.5, 25.1, 24.9, 23.7, 22.6, 14.0, 11.4. Elemental analysis (%) calculated for $\text{C}_{69}\text{H}_{71}\text{BrN}_2\text{O}_6$ (1102.4): C 75.05, H 6.48, N 2.54, found: C 75.07, H 6.45, N 2.55. MS (MALDI-TOF, reflection mode): m/z : 1102.4 [M] $^+$.

Compound 5c Similar procedure for preparation of **5a** was followed to obtain a red solid (0.19 g,

41%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.74-8.53 (m, 8H), 8.13 (d, *J* = 8.3 Hz, 2H), 7.71 (dd, *J* = 10.9, 8.2 Hz, 3H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.54 (s, 1H), 7.50-7.42 (m, 2H), 5.11-5.03 (m, 1H), 4.44 (t, *J* = 6.5 Hz, 2 H), 4.33 (t, *J* = 7.6 Hz, 2H), 2.33-2.21 (m, 2H), 2.04-1.90 (m, 10H), 1.62-1.60 (m, 4H), 1.25-0.99 (m, 20 H), 0.94 (t, *J* = 7.4 Hz, 6H), 0.79 (t, *J* = 7.1 Hz, 6H), 0.71-0.58 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 166.5, 163.1, 153.3, 151.2, 145.8, 140.2, 139.5, 139.3, 134.3, 134.0, 131.1, 130.1, 129.4, 129.1, 127.0, 126.4, 126.2, 126.1, 123.0, 122.9, 122.8, 121.6, 121.4, 121.2, 120.2, 65.0, 57.8, 55.6, 40.5, 40.2, 31.7, 29.1, 28.0, 25.8, 25.0, 23.7, 22.6, 14.0, 11.4. Elemental analysis (%) calculated for C₇₁H₇₅BrN₂O₆ (1130.5): C 75.31, H 6.68, N 2.47, found: C 75.19, H 6.65, N 2.46. MS (MALDI-TOF, reflection mode): *m/z*: 1130.5 [*M*]⁺.

F5T8P-C2 In absence of light, a solution of **6** (0.16 g, 0.063 mmol), **5a** (62 mg, 0.057 mmol) and Pd₂(dba)₃ (10.0 mg, 0.01 mmol), P(*o*-tolyl)₃ (12.0 mg, 0.04 mmol) in anhydrous toluene (10 mL) was stirred at 105 °C under argon for 24 hours. The mixtures was cooled to room temperature and then extracted with chloroform. The organic layer was washed with brine and dried over MgSO₄. Evaporation of the solvent and then purified with column chromatography on silica gel with chloroform as eluent to give a red solid (0.12 g, 67%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.73-8.51 (m, 8H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.76-7.68 (m, 12 H), 7.61-7.57 (m, 18H), 7.35-7.31 (m, 11H), 7.24-7.19 (m, 8H), 5.11-5.04 (m, 1H), 4.73 (s, 4H), 2.33-2.22 (m, 2H), 2.17-1.90 (m, 22H), 1.26-1.00 (m, 100H), 0.94 (t, *J* = 7.4 Hz, 6H), 0.85-0.55 (m, 50H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 166.4, 163.5, 152.0, 151.8, 151.6, 150.9, 146.0, 144.0, 143.8, 140.9, 140.8, 140.6, 140.4, 140.2, 138.9, 136.6, 136.4, 134.9, 134.3, 133.2, 133.0, 132.8, 131.6, 130.3, 129.6, 128.6, 127.2, 127.0, 126.8, 126.6, 126.4, 124.7, 124.5, 123.7, 123.6, 123.2, 123.0, 122.9, 121.5, 120.4, 120.2, 120.1, 119.8, 62.4, 57.8, 55.4, 55.2, 40.4, 39.2, 31.8, 30.0, 29.2, 25.0, 23.8, 22.6, 14.1, 13.7, 11.4. Elemental analysis (%) calculated for

$C_{215}H_{244}N_2O_6S_8$ (3205.7): C 80.48, H 7.66, N 0.87, found: C 80.29, H 7.65, N 0.85. MS (MALDI-TOF, reflection mode, m/z): calculated for $C_{215}H_{244}N_2O_6S_8$ 3205.6615, found: 3205.6502.

F5T8P-C4 Similar procedure for preparation of **F5T8P-C2** was followed to obtain a dark-red solid (0.34 g, 90%). 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.73-8.51 (m, 8H), 8.09 (d, $J = 8.2$ Hz, 2H), 7.76-7.68 (m, 12 H), 7.61-7.57 (m, 18H), 7.35-7.31 (m, 11H), 7.24-7.19 (m, 8H), 5.11-5.03 (m, 1H), 4.44 (t, $J = 6.5$ Hz, 2 H), 4.33 (t, $J = 7.6$ Hz, 2H), 2.33-2.21 (m, 2H), 2.17-1.90 (m, 26H), 1.26-1.00 (m, 100H), 0.94 (t, $J = 7.4$ Hz, 6H), 0.85-0.55 (m, 50H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 166.5, 163.4, 152.0, 151.8, 151.6, 150.9, 146.0, 144.0, 143.8, 140.9, 140.8, 140.6, 140.4, 140.2, 138.9, 136.6, 136.4, 134.8, 134.4, 133.2, 133.0, 132.8, 131.5, 130.2, 129.6, 129.4, 128.9, 127.2, 127.0, 126.9, 126.5, 126.4, 124.7, 124.5, 123.7, 123.6, 123.1, 123.0, 122.9, 121.6, 120.4, 120.2, 120.1, 119.8, 119.7, 64.7, 57.8, 55.3, 55.2, 40.4, 40.2, 31.8, 30.0, 29.2, 27.3, 26.6, 25.1, 23.8, 22.6, 14.1, 13.7, 11.4. Elemental analysis (%) calculated for $C_{217}H_{248}N_2O_6S_8$ (3233.7): C 80.52, H 7.72, N 0.87, found: C 80.31, H 7.70, N 0.85. MS (MALDI-TOF, reflection mode, m/z): calculated for $C_{217}H_{248}N_2O_6S_8$ 3233.6928, found: 3233.6803.

F5T8P-C6 Similar procedure for preparation of **F5T8P-C2** was followed to obtain a dark-red solid (0.24 g, 78%). 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.73-8.51 (m, 8H), 8.09 (d, $J = 8.2$ Hz, 2H), 7.76-7.68 (m, 12 H), 7.61-7.57 (m, 18H), 7.35-7.31 (m, 11H), 7.24-7.19 (m, 8H), 5.11-5.03 (m, 1H), 4.37 (t, $J = 6.5$ Hz, 2 H), 4.24 (t, $J = 7.6$ Hz, 2H), 2.33-2.21 (m, 2H), 2.04-1.90 (m, 26H), 1.62-1.60 (m, 4H), 1.26-1.00 (m, 100H), 0.94 (t, $J = 7.4$ Hz, 6H), 0.85-0.55 (m, 50H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 166.6, 163.4, 152.0, 151.8, 151.6, 150.9, 145.9, 144.0, 143.8, 140.9, 140.8, 140.6, 140.4, 140.2, 138.9, 136.6, 136.4, 134.7, 134.4, 133.1, 133.0, 132.8, 131.4, 130.1, 129.6, 129.4, 129.1, 127.2, 127.0, 126.8, 126.5, 126.4, 124.7, 124.5, 123.7, 123.6, 123.3, 123.1, 123.0, 122.9, 121.6, 120.4, 120.2, 120.1,

119.8, 119.7, 65.0, 57.8, 55.4, 55.2, 40.4, 40.2, 31.8, 30.0, 29.2, 28.7, 28.0, 27.3, 26.8, 25.9, 25.0, 23.8, 22.6, 14.1, 13.7, 11.4. Elemental analysis (%) calculated for $C_{219}H_{252}N_2O_6S_8$ (3261.7): C 80.56, H 7.78, N 0.86, found: C 80.42, H 7.74, N 0.82. MS (MALDI-TOF, reflection mode, m/z): calculated for $C_{219}H_{252}N_2O_6S_8$ 3261.7241, found: 3261.7156.

References

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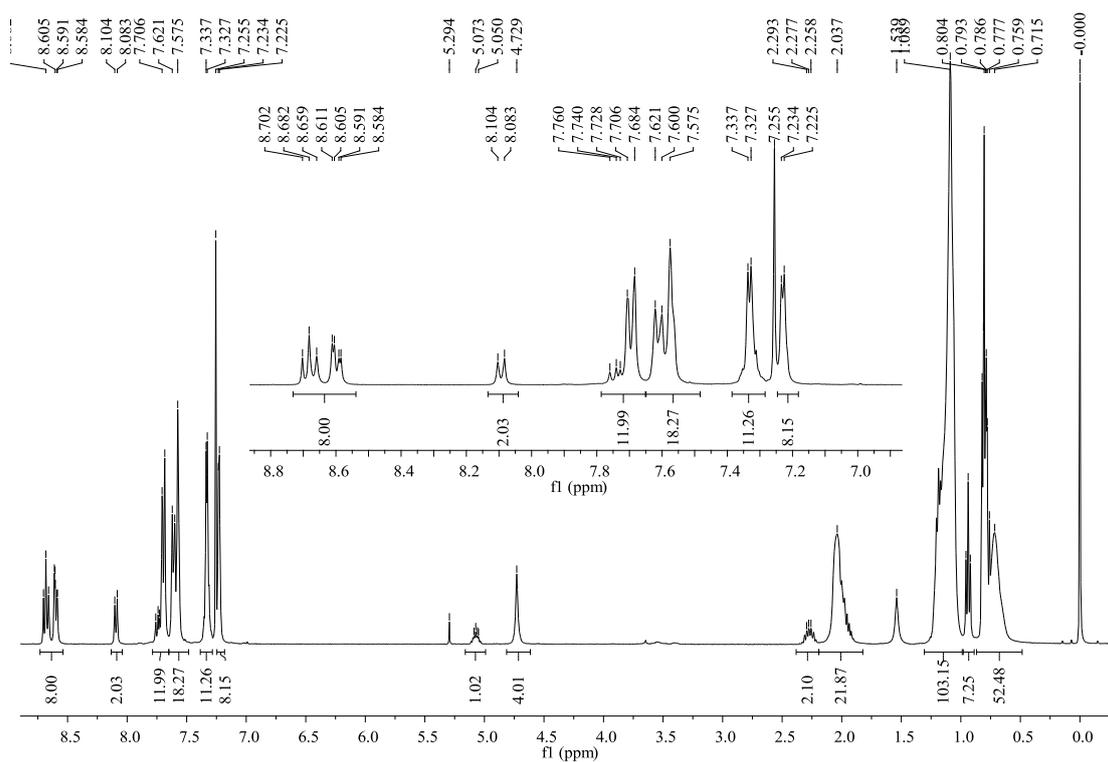


Figure S1. The ^1H NMR spectrum of F5T8P-C2.

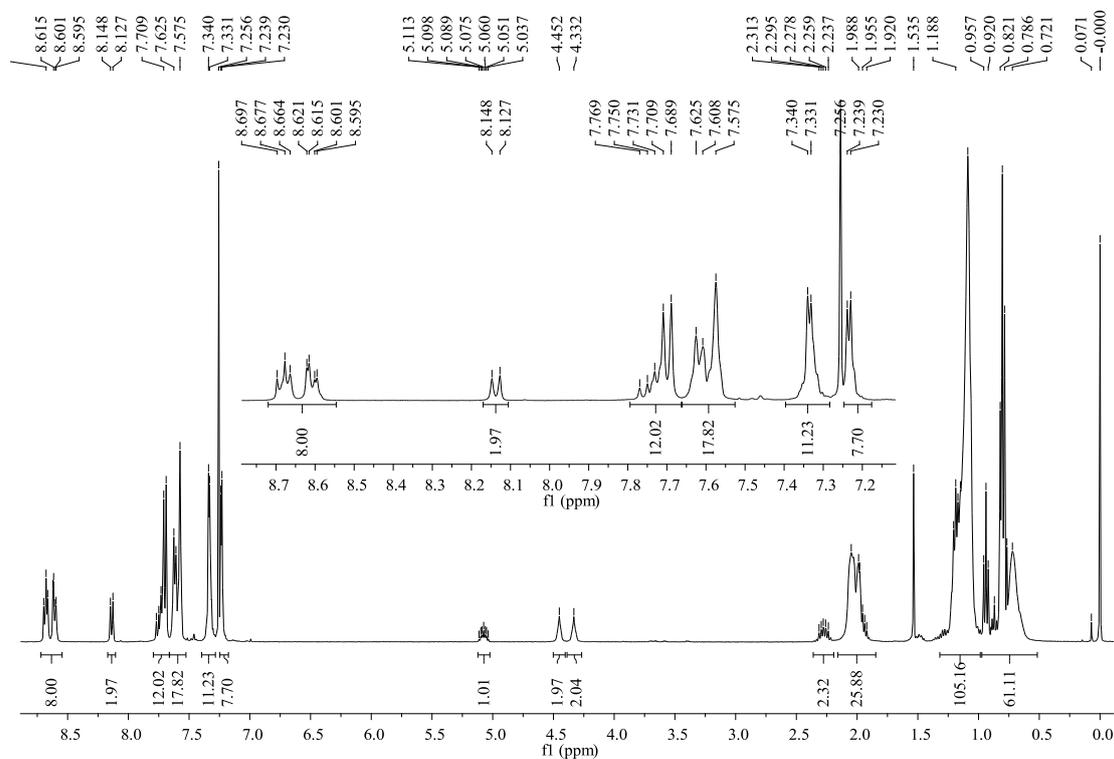


Figure S2. The ^1H NMR spectrum of F5T8P-C4.

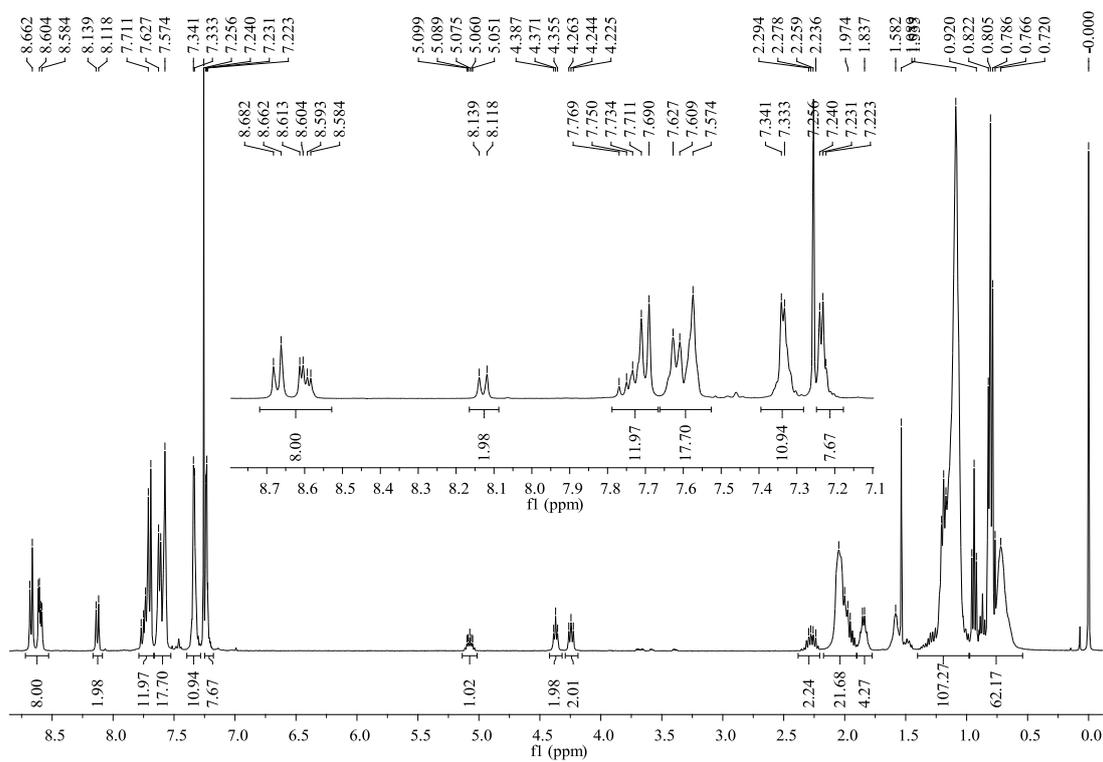


Figure S3. The ^1H NMR spectrum of **F5T8P-C6**.

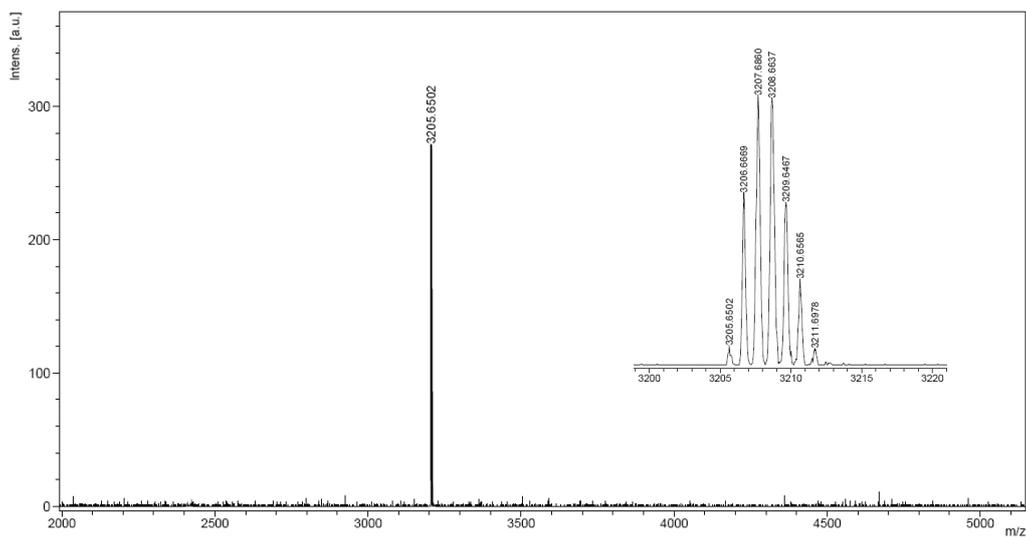


Figure S4. MALDI-TOF mass spectrum of **F5T8P-C2**.

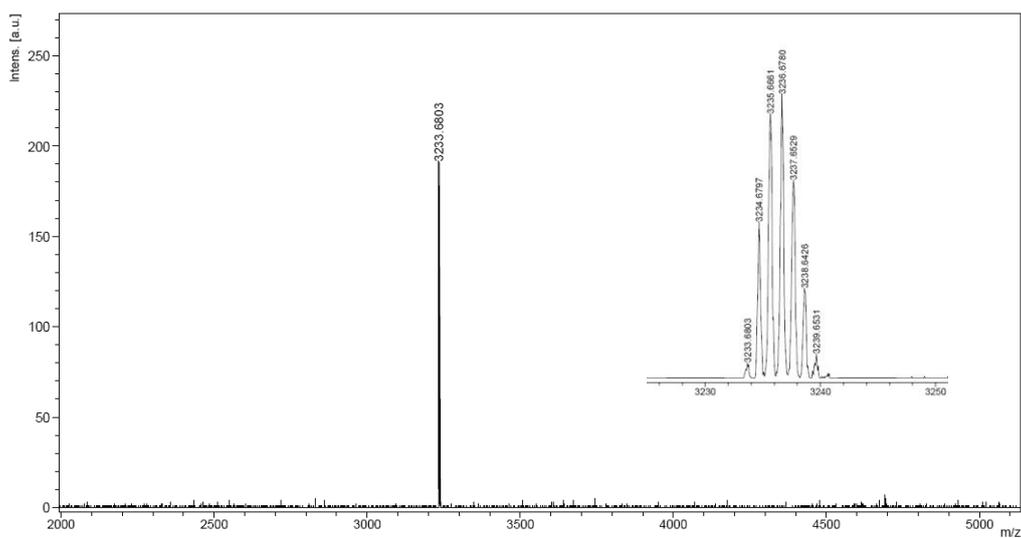


Figure S5. MALDI-TOF mass spectrum of F5T8P-C4.

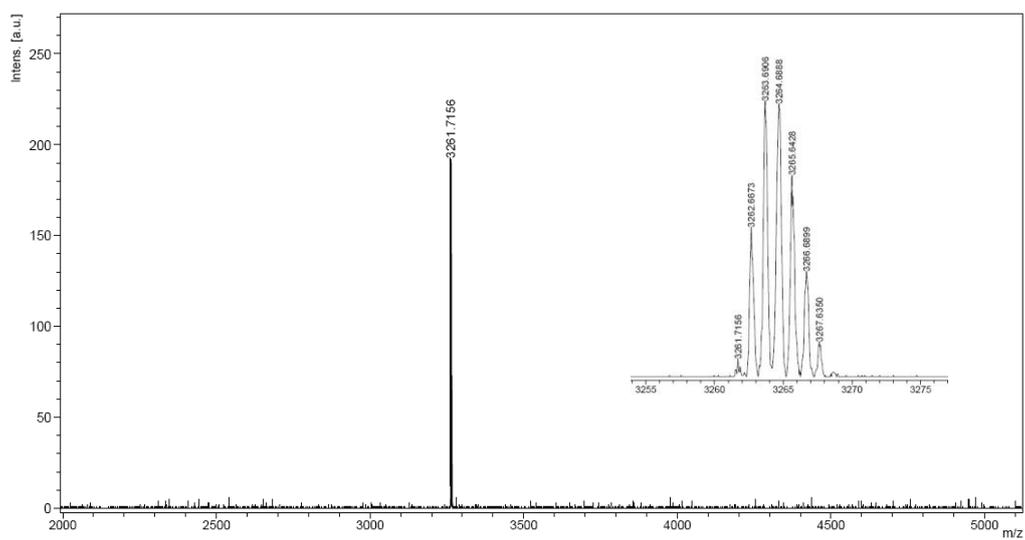


Figure S6. MALDI-TOF mass spectrum of F5T8P-C6.

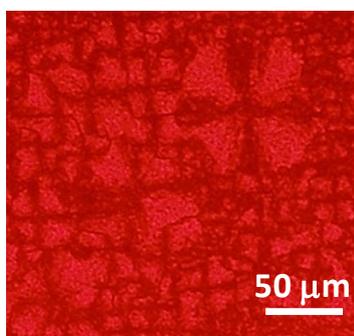


Figure S7. Optical microscopic image of F5T8P-C2 under crossed polarizer at 250 °C.

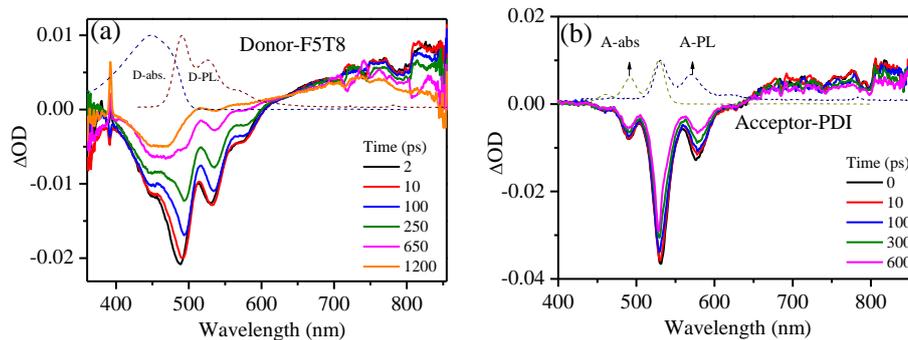


Figure S8. The transient absorption spectra of the donor **F5T8** (a) and the acceptor **PDI** (b) in solution with a concentration of 10^{-5} mol/L. The dotted line is the steady state absorption (abs) and photoluminescence (PL).

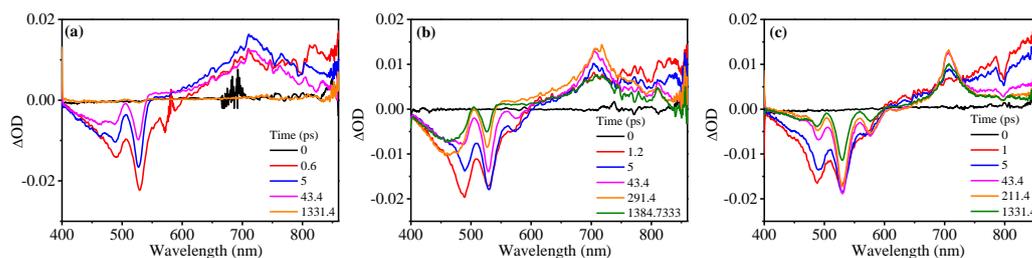


Figure S9. The transient absorption spectra of **F5T8-epP** (a), **F5T8P-C2** (b) and **F5T8P-C6** (c) in $CHCl_3$ with a concentration of 10^{-5} mol/L.

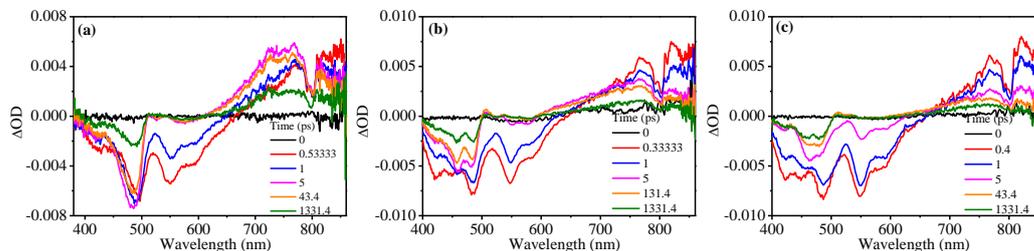


Figure S10. The transient absorption spectra of **F5T8-epP** (a), **F5T8P-C2** (b) and **F5T8P-C6** (c) films with a thickness of ~ 70 nm.

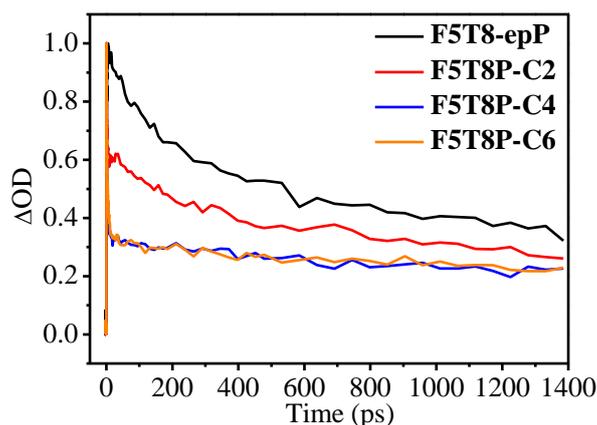


Figure S11. The primary comparison of the CT state dynamics of the four co-oligomers.

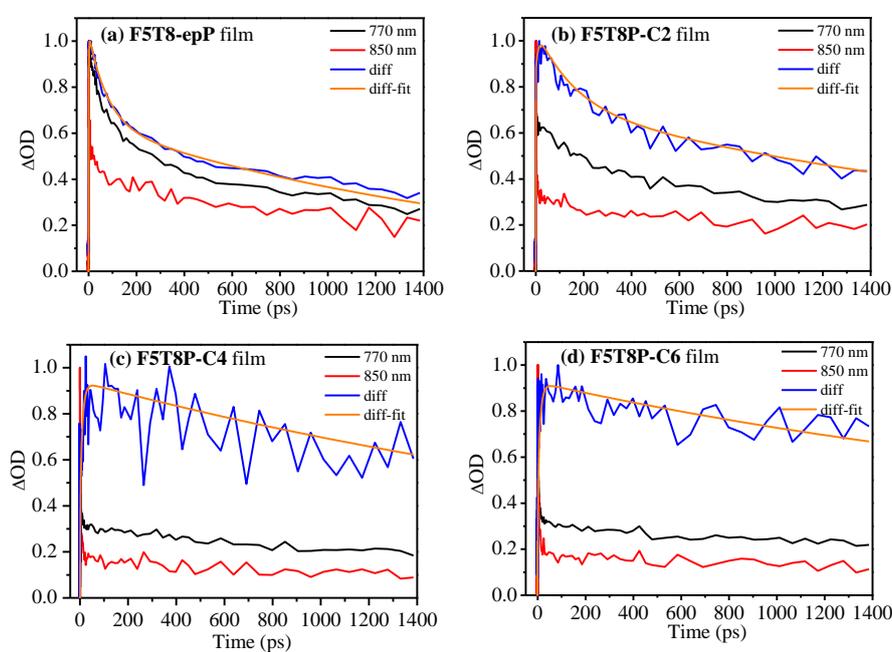


Figure S12. Spectral calculation for getting a relatively pure CT state of **F5T8-epP** (a), **F5T8P-C2** (b), **F5T8P-C4** (c) and **F5T8P-C6** (d). The dynamics of 850 nm (red line), which is mainly composed of the exciton state, is subtracted from the dynamics of 770 nm (black line), which is composed of the CT state and the exciton state with the CT state taking a higher portion. Diff (blue line) is the difference (subtracted result) of 770nm and 850 nm. The diff-fit (orange line) is the fitting line of the difference curve.

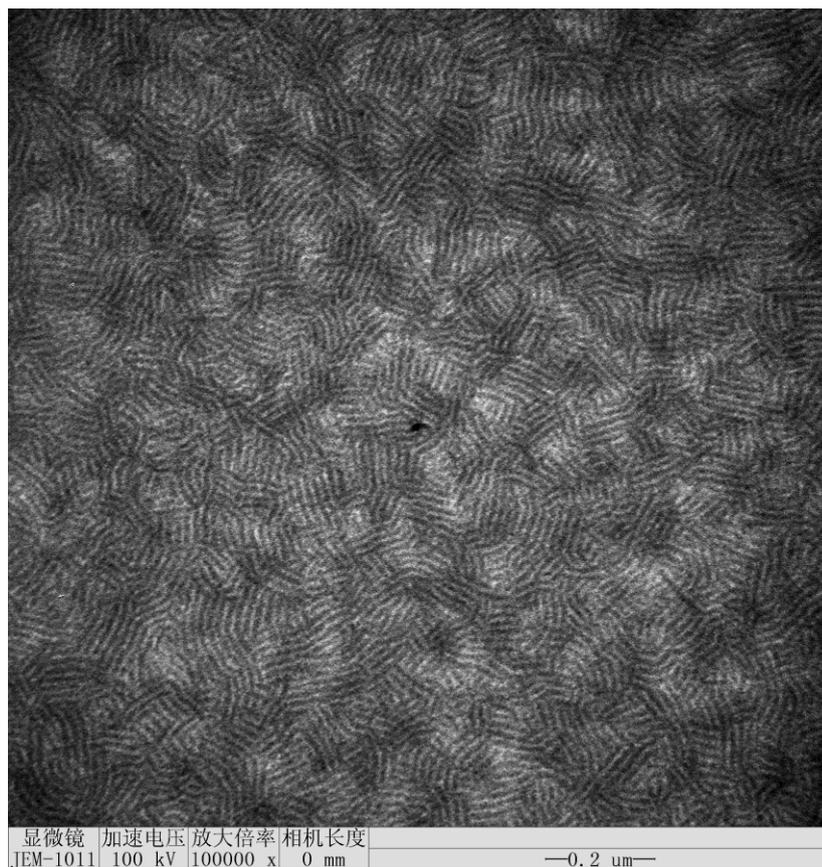


Figure S13. The TEM image of **F5T8BTP-C4** thin film with a thickness of ~ 70 nm. The film was thermal annealed at 170 °C for 10 min, and the measurements were done at room temperature.

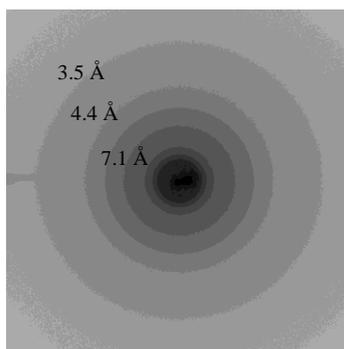


Figure S14. The SAED pattern of **F5T8BTP-C4** thin film with a thickness of ~ 70 nm. The film was thermal annealed at 170 °C for 10 min, and the measurements were done at room temperature.