

Supporting Information

Doping-Dependent Energy Transfer from Conjugated Polyelectrolytes to (6,5) Single-Walled Carbon Nanotubes

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Table of Contents

Synthesis of Conjugated Polyelectrolytes and CPDT-BPy	S-3
Selectivity of Conjugated Polymers and Polyelectrolytes towards SWNTs.....	S-9
Comparison of PLE Maps for Polymer-Rich and Polymer-Depleted Dispersions	S-10
Absorption and PLE Maps of Pure PFO and (6,5) SWNT/PFO Hybrids	S-11
Comparison of Quantum Yields for Different (6,5) SWNT Hybrids	S-12
PLE Maps for CoMoCat Dispersions with CPEs.....	S-13
PESA Measurements: Ionization Potentials	S-14
Evolution of PL Spectra for (6,5) SWNT/CPE-S Water-Gated FETs	S-15
REFERENCES	S-16

Synthesis of Conjugated Polyelectrolytes and CPDT-BPy

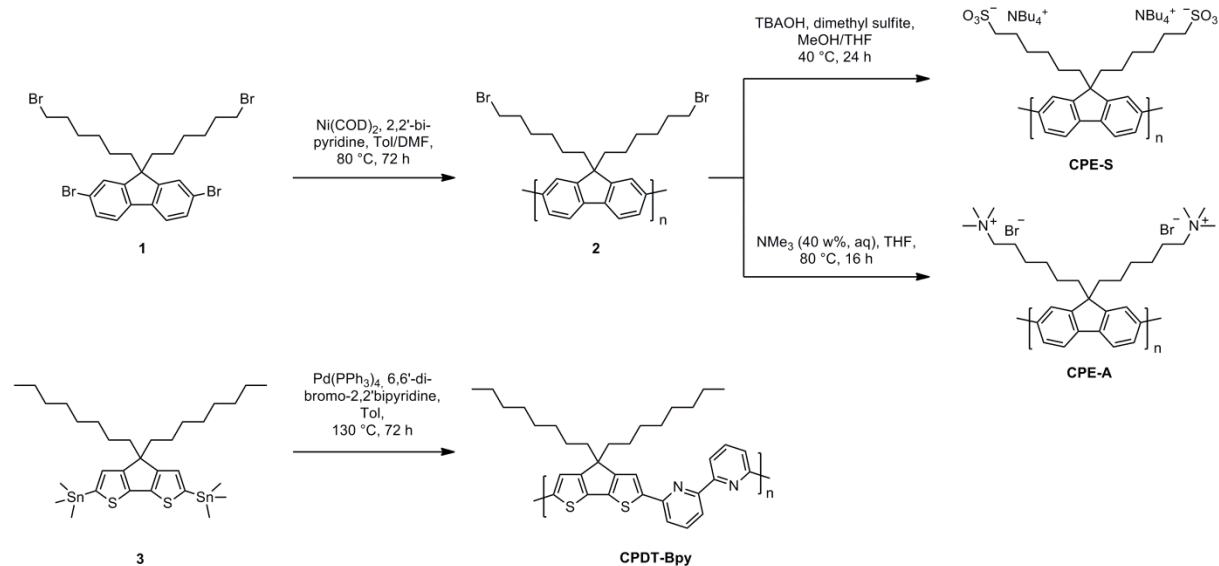


Figure S1. Synthesis scheme for CPE-S, CPE-A and CPDT-BPy.

All chemicals were used as obtained from commercial suppliers. Figure S1 demonstrates the synthesis schemes for the conjugated polyelectrolytes CPE-A (poly[9,9-bis(6-trimethylammoniumhexyl)-9H-fluorene]bromide), CPE-S (poly[9,9-bis(6-sulfonatohexyl)-9H-fluorene] (tetrabutylammonium salt)), and the conjugated polymer CPDT-BPy.

Column chromatography was carried out with Geduran Si60 silica gel from Merck. NMR spectra were recorded on Bruker Avance 400 or Avance III 600 machines, APCI-MS-spectra were recorded on a Bruker Daltronik micrOTOF. Molecular weight distributions were determined by size exclusion chromatography (SEC) with a PSS SDV pre-column and two PSS SDV linear M columns in series with THF or Chloroform as eluent. SEC of CPE-S and CPE-A were determined for the prepolymer PF6Br (**2**).

2,7-Dibromo-9,9-bis(6-bromohexyl)-9*H*-fluorene (1)

Under inert conditions 15.0 g (46.3 mmol, 1.0 equiv.) 2,7-dibromo-9*H*-fluorene and 4.5 g (14.0 mmol, 0.3 equiv.) tetrabutylammonium bromide were added to a three-necked flask. After addition of 30 g of 50 % w/w aqueous sodium hydroxide solution and 70 mL (462 mmol, 10 equiv.) 1,6-dibromohexane the resulting mixture was stirred 3 h at 80 °C. The mixture was diluted with 100 mL water and extracted with diethyl ether. The organics were washed with brine, dried over MgSO₄ and the crude product was purified via column chromatography with *n*-hexane as eluent. After recrystallization from ethanol the product was obtained as colorless crystals (15.6 g, 23.9 mmol, 52 %).

¹H-NMR (400 MHz, CDCl₃, 300 K) δ 7.55 (d, J = 8.0 Hz, 2 H), 7.52 – 7.44 (m, 4 H), 3.31 (t, J = 6.8 Hz, 4 H), 1.99 – 1.91 (m, 4 H), 1.69 (quint, J = 7.4 Hz, 4 H), 1.29 – 1.18 (m, 4 H), 1.17 – 1.06 (m, 4 H), 0.68 – 0.56 (m, 4 H)

MS (APCI): m/z : 649.9 (M⁺)

Poly[9,9-bis(6-bromohexyl)-9*H*-fluorene] PF₆Br (2)

In a glovebox, a Schlenk tube was filled with 1.185 g (4.31 mmol, 2.8 equiv.) Ni(COD)₂ and 0.673 g (4.31 mol, 2.8 equiv.) 2,2'-bipyridine. After the addition of 30 mL toluene, 10 mL dimethyl formamide and 0.5 mL (4.31 mmol, 2.8 equiv.) cyclooctadiene the solution was stirred 45 min at 80 °C. Then a solution of 1.00 g (1.54 mmol, 1.0 equiv.) 2,7-dibromo-9,9-bis(6-bromohexyl)-9*H*-fluorene in 10 mL toluene was added and the mixture was stirred for additional 72 h at 80 °C. The solution was diluted with chloroform and washed three times with 2 M aqueous hydrochloric acid,

once with saturated aqueous sodium carbonate solution, three times with saturated aqueous EDTA solution and once with brine. The solvents were removed under reduced pressure and the crude polymer was purified by precipitation into methanol and subsequent Soxhlet extractions with methanol, acetone, ethyl acetate and chloroform. The product was isolated as a beige solid in the ethyl acetate and chloroform fractions with an overall yield of 372 mg (49 %).

¹H-NMR (600 MHz, C₂D₂Cl₄, 300 K) δ 7.85 – 7.52 (m, 4H), 7.23 – 6.94 (m, 2H), 3.49 – 3.17 (m, 4H), 2.27 – 1.91 (m, 4H), 1.77 – 1.47 (m, 4H), 1.34 – 0.71 (m, 12H)

SEC (CHCl₃)

EtOAc-fraction: M_n: 7,800 g/mol; M_w: 13,500 g/mol; PDI: 1.75

CHCl₃-fraction: M_n: 12,700 g/mol; M_w: 37,000 g/mol; PDI: 2.96

Poly[9,9-bis(6-sulfonatohexyl)-9*H*-fluorene] (tetrabutylammonium salt) (CPE-S)

In a Schlenk tube 80 mg (0.162 mmol) polyfluorene **PF6Br** were dissolved in 30 mL THF. A mixture of 4.5 mL 1 M tetrabutylammonium hydroxide in methanol and 0.5 mL dimethyl sulfite was added and the resulting polymer solution was stirred 24 h at 40 °C. The polyelectrolyte solution was purified by dialysis against methanol (3 days, molecular weight cutoff (MWCO) of the dialysis membrane: 3,500 g/mol). The synthesis yielded 156 mg (0.159 mmol, 98 %) product as a beige solid.

¹H-NMR (600 MHz, DMSO-d₆, 353 K) δ 8.05 – 7.66 (m, 4 H), 7.32 – 6.94 (m, 2 H), 3.25 – 3.16 (m, 16 H), 2.33 (s, 4 H), 1.70 – 1.58 (m, 16 H), 1.39 – 1.32 (m, 16 H), 1.30 – 1.01 (m, 16 H), 0.99 – 0.93 (m, 24 H)

Poly[9,9-bis(6-trimethylammoniumhexyl)-9H-fluorene]bromide (CPE-A)

In a Schlenk tube 100 mg (0.203 mmol) **PF6Br** were stirred in 8.5 mL THF and 1 mL of a 40 % w/w solution of trimethylamine in water over night at 80°C. After dialysis against methanol (3 d, MWCO: 3,500 g/mol) 117 mg (0.192 mmol, 94 %) product were obtained as a beige solid.

¹H-NMR (600 MHz, MeOD, 300 K) δ 8.05 – 6.92 (m, 6 H), 3.18 (s, 4 H), 3.03 (s, 18 H), 2.37 – 1.96 (m, 8 H), 1.61 – 0.76 (m, 12 H)

2,6-Bis(trimethylstannyl)-4,4-dioctyl-4H-cyclopenta[1,2-b:5,4-b']dithiophene (3)

2,6-Bis(trimethylstannyl)-4,4-dioctyl-4H-cyclopenta[1,2-b:5,4-b']dithiophene was obtained using literature procedures¹⁻².

¹H NMR (600 MHz, CDCl₃, 300 K) δ 7.03 (s, 2H), 1.91 – 1.85 (m, 4H), 1.40 – 1.29 (m, 7H), 1.29 – 1.18 (m, 15H), 1.17 – 1.07 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 6H), 0.51 – 0.40 (m, 18H).

¹³C NMR (151 MHz, CDCl₃, 300 K) δ 160.4, 142.3, 136.9, 129.4, 52.2, 37.6, 31.8, 30.0, 29.7, 29.3, 29.2, 24.6, 22.7, 14.1, -8.1.

Poly[(cyclopentadithiophene-2,7-diyl)-alt-(6,6'-[2,2'-bipyridine])] (CPDT-BPy)

The polymer was prepared according to a procedure reported in the literature with minor modification³: A mixture of 6,6'-dibromo-2,2'-bipyridine (0.241 g, 0.766 mmol, 1.0 equiv.) and **3** (0.558 g, 0.766 mmol, 1.0 equiv.) was dissolved in 17 mL toluene under an argon atmosphere. Tetrakis(triphenylphosphino)palladium(0) (0.044 g, 0.038 mmol, 0.05 equiv.) dissolved in 10 mL toluene) was added. The mixture was heated to 130°C and stirred at this temperature for 3 days. The product was cooled and washed with a saturated solution of EDTA, water, and brine. The product was filtered through a plug of celite and the solvent was evaporated under vacuum. The residue was re-dissolved in chloroform and precipitated into cold methanol. After successive Soxhlet extraction of the precipitate with methanol, acetone, ethylacetate and chloroform, the chloroform fraction was concentrated under reduced pressure. The residue was reprecipitated into cold methanol and collected by filtration. After drying in high vacuum, the product CPDT-BPy was obtained as a brown solid (266 mg, 63 %).

¹H NMR (600 MHz, C₂D₂Cl₄, 300 K) δ 8.46 (d, J = 7.4 Hz, 2H), 7.90 – 7.85 (m, J = 6.2 Hz, 2H), 7.70 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 8.4 Hz, 2H), 2.06 – 1.95 (m, 4H), 1.31 – 1.18 (m, 24H), 0.86 (t, J = 6.9 Hz, 6H).

SEC (THF)

CHCl₃-fraction: M_n: 11,000 g/mol; M_w: 19,300 g/mol; PDI: 1.75

Preparation of CoMoCAT Dispersions

Different conjugated polymer (CP) and conjugated polyelectrolyte (CPE) solutions were prepared in toluene and methanol, respectively, at a concentration of 1.0 mg/mL. CoMoCAT dispersions were prepared as described previously⁴⁻⁶ with minor modifications. Briefly, 0.75 mg/mL CoMoCAT raw material (CHASM Advanced Materials, Lot # SG65i-L58) was dispersed in 1 mg/mL CP or CPE solution in a sonication bath (Branson 2510) for 1 hour, keeping the bath temperature around 25 °C. The dispersion was centrifuged at 60,000 g for 45 minutes (Beckman Coulter Avanti J26XP centrifuge) to separate the non-exfoliated material. The supernatant was then filtered through a 0.1 µm pore sized polytetrafluoroethylene membrane filter (Merck Omnipore, JVWP, pore size 0.1 µm, diameter 25 mm) to remove the excess free polymer and the filter cake was re-dispersed in 1 mL of neat solvent by sonication for 30 min.

Selectivity of Conjugated Polymers and Polyelectrolytes towards SWNTs

The conjugated polymer PFO-BPy disperses (6,5) SWNTs highly selectively among the other chiralities in the CoMoCAT raw material.⁷⁻⁸ On the other hand, when a conjugated polymer CPDT-BPy with a different backbone or one of the conjugated polyelectrolytes were employed, the selectivity decreased drastically, resulting in polychiral dispersions (see Figure S2). The dispersions also included metallic nanotubes, making them inadequate for semiconductor device applications. In order to eliminate the metallic nanotubes and to focus on an interaction between one species of SWNT and different polymers, the (6,5) SWNTs were pre-selected with PFO-BPy and the wrapping polymer was exchanged afterwards.

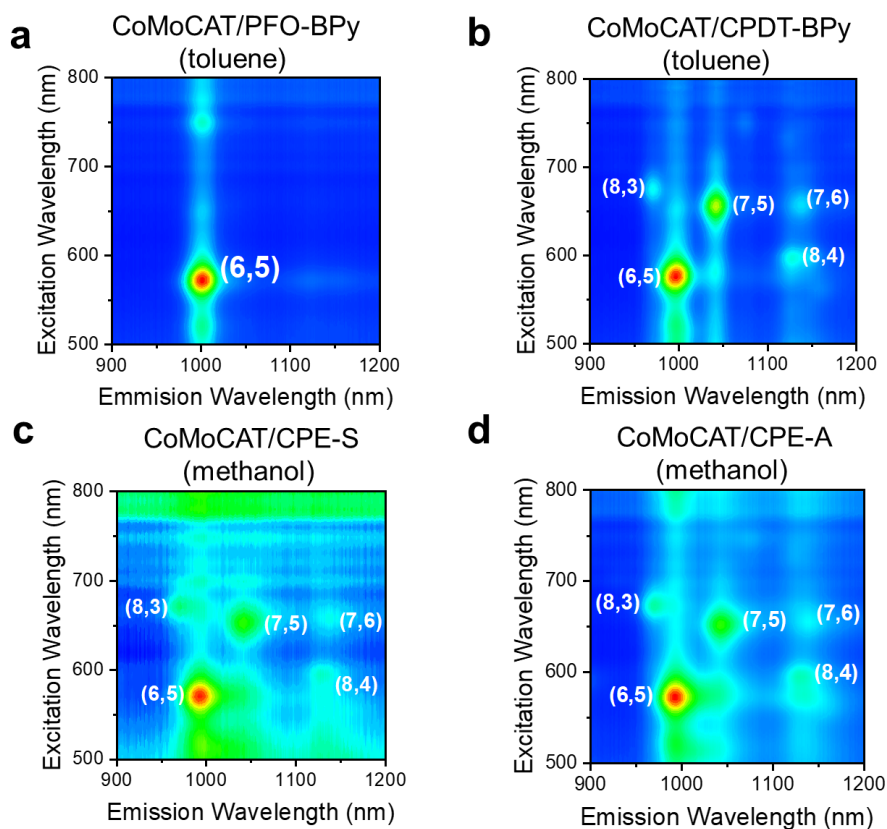


Figure S2. PLE maps of CoMoCAT raw material dispersions with (a) PFO-BPy, (b) CDPT-BPy, (c) anionic CPE-S and (d) cationic CPE-A in toluene.

Comparison of PLE Maps for Polymer-Rich and Polymer-Depleted Dispersions

For the investigation of energy transfer in a SWNT/polymer hybrid, an efficient removal of the free polymer is crucial. In a polymer rich dispersion, the incident light might be attenuated by the absorption of the excess free polymer. This leads to a distortion of the excitation spectra as shown in Figure S3a, where the polymer excitation at 360 nm (Figure S3b) seems to be red-shifted to 380 nm. Hence it is highly important to remove free polymer as much as possible before recording PLE maps. PLE maps.

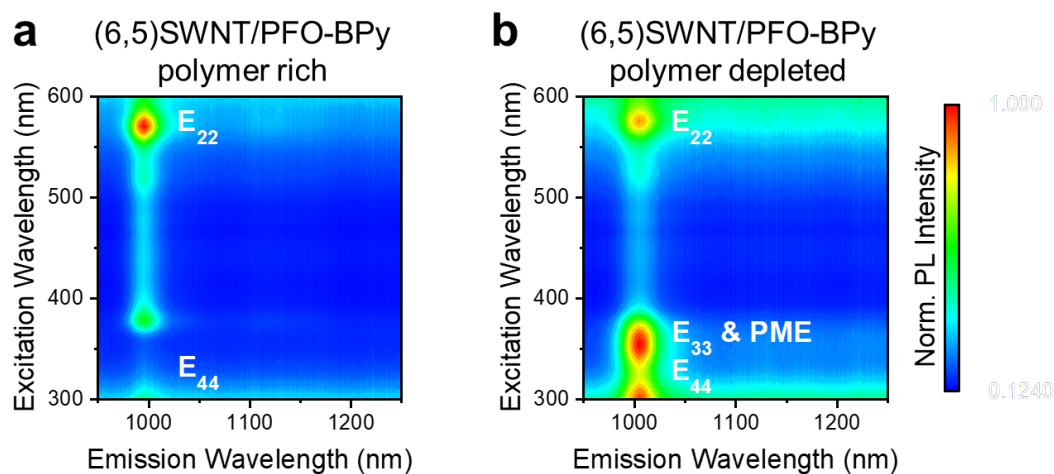


Figure S3. PLE maps of (6,5) SWNT/PFO-BPy within the excitation wavelength range of the PFO-BPy for a polymer-rich dispersion showing strong absorption (a) and PLE map for a polymer-depleted dispersion (b) without strong absorption by the PFO-BPy.

Absorption and PLE Maps of Pure PFO and (6,5) SWNT/PFO Hybrids

Polymer exchange of the original (6,5) SWNT/PFO-BPy dispersion was carried out with the conjugated polymer PFO, which is known to selectively disperse (7,6), (8,6) and mainly (7,5) SWNTs.^{4,9} PFO has the same backbone as the two conjugated polyelectrolytes used in this study, therefore a dispersion with (6,5) SWNTs was prepared and analyzed in a similar manner. Figure S4a shows E₂₂, E₃₃ and E₄₄ absorbance of the (6,5) SWNTs as well as the PFO absorbance at 387 nm. Similarly, all excitonic transitions of (6,5) SWNTs and the polymer mediated excitation (PME) can be identified in the PLE map (Figure S4b), which indicates a direct energy transfer from PFO to (6,5) SWNTs.

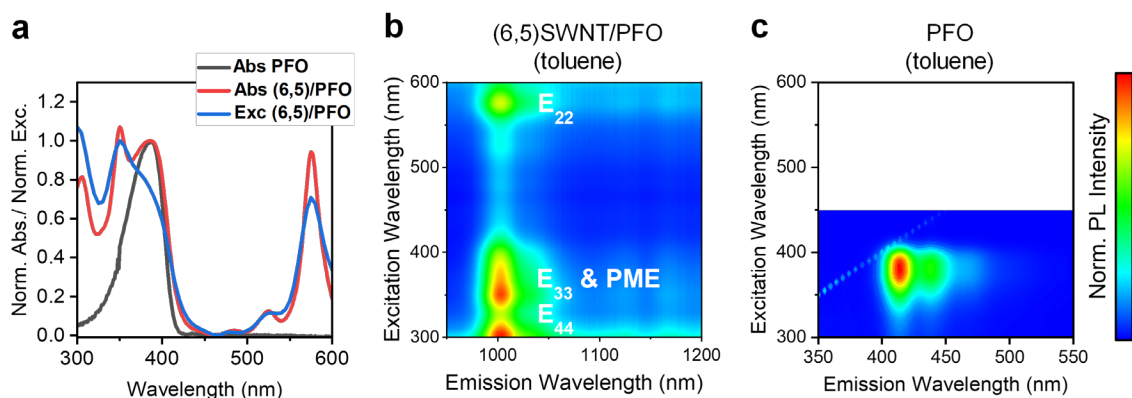


Figure S4. (a) Normalized absorbance and excitation spectra of the PFO and (6,5) SWNT/PFO hybrids in toluene. (b, c) PLE maps of (6,5) SWNT/PFO and PFO, respectively.

Comparison of Quantum Yields for Different (6,5) SWNT Hybrids

Dispersions of (6,5) SWNTs with PFO in toluene, and CPE-A and CPE-S in methanol were prepared at similar E_{11} optical densities (OD). The corresponding PL intensities (I) were divided by the absorbance at E_{11} in order to compare quantum yields (QY) for the dispersions. (6,5) SWNT/PFO in toluene was chosen as the reference and all the values were normalized to it, also considering the refractive indices (n) of toluene and methanol:

$$QY = 1 \cdot \frac{I}{I_{PFO}} \cdot \frac{OD_{PFO}}{OD} \cdot \frac{n_{Methanol}^2}{n_{Toluene}^2}$$

As shown in **Table S1**, the (6,5) SWNT/CPE-A dispersion shows a slight PL enhancement whereas (6,5) SWNT/CPE-S indicates substantial PL quenching in comparison to (6,5) SWNT/PFO. This suggests that not only energy transfer but also the emission yield of the SWNTs were affected by the choice of CPE. The quenched nanotube photoluminescence and the hindered energy transfer in the (6,5) SWNT/CPE-S dispersion might arise from partial p-doping of the nanotubes in air. The doping is assumed to be fairly low, as the emission is not fully quenched and can be restored by adding a mild reducing agent (β -mercaptoethanol, BME), which also substantially increases the PL quantum yield of the dispersion.

Table S1. Photoluminescence intensities divided by the absorbance at E_{11} for the dispersions of (6,5) SWNTs with the different polymers (depleted). All values are normalized to the reference sample (6,5) SWNT/PFO.

Hybrids of (6,5) SWNTs with	PFO	CPE-A	CPE-S	CPE-S + BME
PL intensity/ Absorbance at E_{11} Norm. to PFO/ (6,5) SWNT	1.00	1.10	0.34	0.49

PLE Maps for CoMoCat Dispersions with CPEs

Energy transfer in dispersions of CoMoCAT raw material with the conjugated polyelectrolytes CPE-A and CPE-S in methanol was investigated as described for the (6,5) SWNT/polymer hybrids. Semiconducting SWNTs (main species (6,5), (7,5) and (8,4)) wrapped with the cationic CPE-A showed E_{11} emission at different wavelengths (995 nm, 1042 nm and 1139 nm) for excitation of the CPE at ~ 360 nm, indicating energy transfer. In contrast to that, the CoMoCAT dispersion with the anionic CPE-S, exhibited no E_{11} emission for the same excitation wavelength. However, after addition of 2 % β -mercaptoethanol (BME) to the dispersion the energy transfer and emission from E_{11} was restored (see Figure S5).

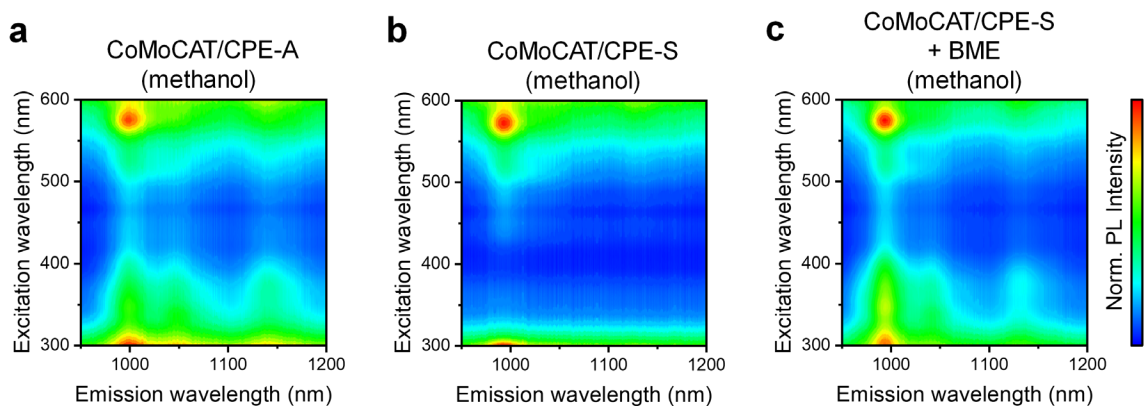


Figure S5. PLE maps of (a) CoMoCAT/CPE-A, (b) CoMoCAT/CPE-S and (c) CoMoCAT/CPE-S with 2 % β -mercaptoethanol.

PESA Measurements: Ionization Potentials

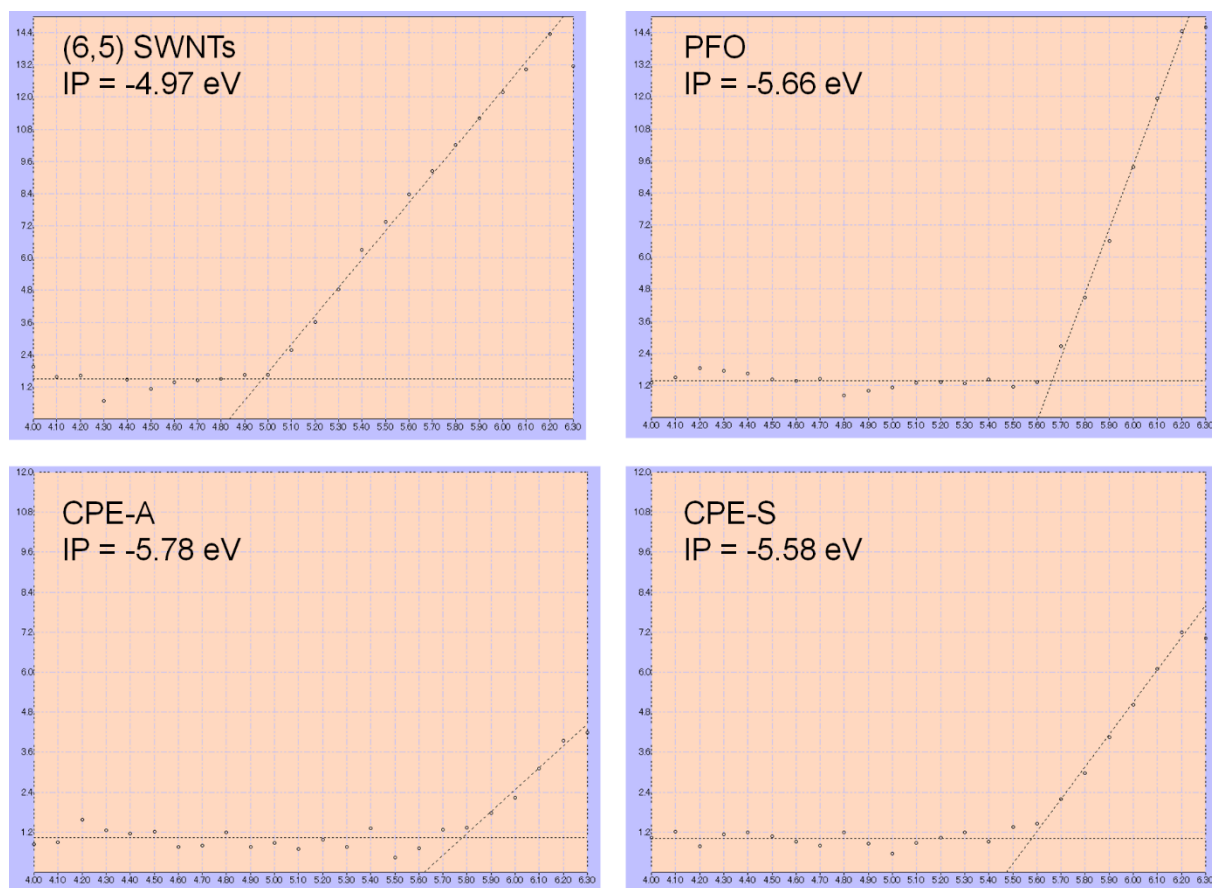


Figure S6. PESA measurements of thin films of (6,5) SWNTs and different polymers on ITO substrates, including extracted ionization potentials.

Evolution of PL Spectra for (6,5) SWNT/CPE-S Water-Gated FETs

PL spectra obtained from the channel region of water-gated FETs with a network of (6,5) SWNT/CPE-S hybrids were acquired for different gate voltages as shown in Figure S7. When sweeping the gate voltage from +1.0 V to -1.0 V the PL intensity and the spectral composition changed dramatically. Accumulation of holes (negative gate voltages) resulted in a blue-shift of up to 7 nm of E_{11} emission peak and an increase of trion emission at 1170 nm.

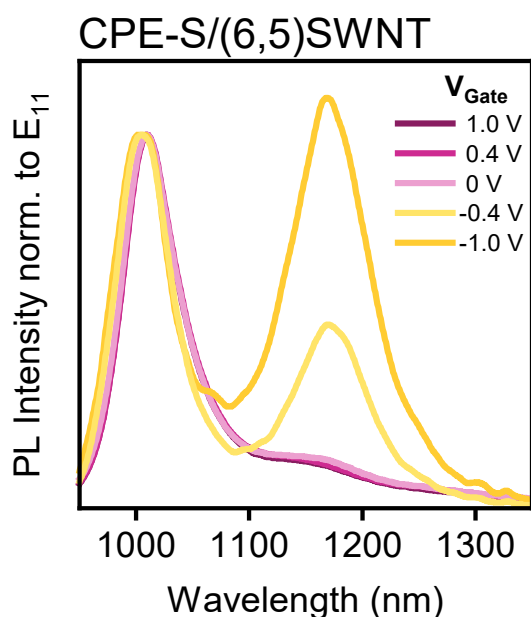


Figure S7. Gate-voltage dependent PL spectra recorded from the channel of a water-gated FET with a thin film of (6,5) SWNT/CPE-S hybrid normalized to the E_{11} emission peak.

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