

Supporting Information

Supramolecular Complexes of Single Walled Carbon Nanotubes with Conjugated Polymers

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Experimental Section

General: Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc. (Houston, TX). All reagents and solvents were purchased from commercial suppliers and used as received. UV-Visible spectra were measured by using a Cary 50 UV-visible spectrophotometer. Ultrasonication was carried out in a Banson Ultrasonics B1510, and B2500 bath sonicator. Beckman Allegra^[TM] X-22R Benchtop centrifuge was used for centrifugation. Filtration was performed through a 450 nm-pore Teflon membrane (Millipore). Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) analyses by using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector,a Waters 2475 Multilfluorescence detector, and four Polymer Labs PL gel individual pore-size columns. Polystyrene standards were used for calibration, and THF was used as the eluent at a flow rate of 1.0 mL min⁻¹. Raman spectra from all samples were collected with a Renishaw Ramanscope at excitation laser wavelengths of 785 nm. NMR spectra were measured on Bruker Avance 200 spectrometers. Fluorescence spectra were measured using a Jobin-Yvon SPEX Fluorolog 3.22

equipped with a 450 W Xe lamp, double-excitation and double-emission monochromators, and a digital photon-counting photomultiplier. Slit widths were set to 2 nm band-pass on both excitation and emission. Correction for variations in lamp intensity over time and λ was achieved using a reference silicon photodiode.

Synthesis

(1) Poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,7-(9,9-didodecylfluorene)] (PF)

A 250 mL flask equipped with a magnetic stir bar charged with toluene (36 mL), aqueous potassium carbonate (24 mL, 2 M), 9,9-didodecyl-2,7-dibromofluorene (1.3212g, 2mmol), and 9,9-dioctylfluorene-2,7-bis(trimethylene) borate (1.1168g, 2 mmol), then the mixture was bubbled with N₂ for 15 min, degassed via three freeze- pump-thaw cycles, and the flask was then back-filled with Ar. A catalytic amount of Pd(PPh₃)₄ (1.0 mol %) was added, and the resulting mixture was stirred at 85 °C under Ar for 48 h. After cooling to room temperature the solution poured into 500 ml mixture of methanol and de-ionized water (10:1), and filtered. Then the solid dissolved in small amount of THF and re-precipitated into methanol (500 ml), washed with methanol, water and acetone (300 mL each) respectively. After dried in vacuum for 20 h at 50 °C, a greenish yellow solid was obtained in 84 % yield. ¹H NMR (CDCl₃, 200 MHz): δ 7.85 (br, 8 H), 7.65 (br, 4 H), 2.09 (br, 8 H), 1.13 (br, 56 H), 0.73 (br, 20 H). UV-Vis (THF): $\lambda_{\text{max}} = 380$ nm; UV-Vis (film): PL (THF): $\lambda_{\text{em}} = 416, 440$ nm. GPC: M_n = 9 kg/ mol, M_w/M_n = 1.6.

(2) Poly[(2,7-(9,9-dioctylfluorene)-*alt*-2,5-(3-dodecylthiophene)] (PFT)

A 250 mL flask equipped with a magnetic stir bar charged with DMF (40 mL), Cs₂CO₃ (7.5g, 23 mmol), and 9,9-dioctylfluorene-2,7-bis(trimethylene)borate (1.117g, 2 mmol). 2,5-dibromo-3-

dodecyl-thiophene (0.820 g, 2 mmol) in 10 mL of toluene was added, then the mixture was bubbled with N₂ for 15 min, degassed via three freeze- pump-thaw cycles, and the flask was then back-filled with Ar. A catalytic amount Pd(PPh₃)₄ (1.0 mol %) was added, and the resulting mixture was stirred at 100 °C under Ar for 24 h. After cooling to room temperature, the solvent was evaporated, and the residue was dissolved in a minimum amount of THF and then precipitated into methanol (500 ml). The precipitate was filtered, and the solid was washed with methanol, water and acetone, (300 mL each) respectively. After drying under vacuum for 20 h at 50°C, a greenish yellow solid was obtained in 91 % yield. ¹H NMR (CDCl₃, 200 MHz): δ 7.75-7.47 (m, 6 H), 7.32 (s, 1 H), 2.75 (br, 2 H), 2.04 (br, 4 H), 1.72 (br, 2 H), 1.26-0.81 (m, 49 H). UV-Vis (THF): λ_{max} = 405 nm; PL (THF): λ_{em} = 458, 488 nm. GPC: M_n = 15kg/mol, M_w/M_n = 2.7.

(3) Poly(3-dodecylthiophene) (PT)

A suspension of anhydrous FeCl₃ (2.59 g, 16 mmol) in 100 mL of freshly distilled CHCl₃ was stirred for 15 min, a dark green solution with some residue FeCl₃ was obtained, and 3-dodecyl thiophene (1g, 4mmol) solution in 50 ml freshly distilled CHCl₃ was added dropwise over a period of 60 min. The mixture was stirred for 15 h at room temperature, and then added slowly to 600 ml MeOH. The resulting black precipitate was dissolved in 100 ml CHCl₃ and 5 ml of concentrated aqueous ammonia and stirred for 15 min at room temperature. Some insoluble materials was filtered, the organic phase was washed with water 3 times. Then the concentrated solution was precipitated in methanol, washed with methanol, acetone, and then dried in vacuum at 50 °C for 24 h. Dark red solid was obtained in 61 % yield. ¹H- NMR (CDCl₃, 200 MHz): δ = 7.00 pm(b,1H), δ = 2.80 pm(b, 2H), δ = 1.66-0.87 pm(m, b, 10H). UV-Vis (THF): λ_{max} = 435 nm; PL (THF): λ_{em} = 564 nm GPC: M_n = 48kg/ mol, M_w/M_n = 1.5

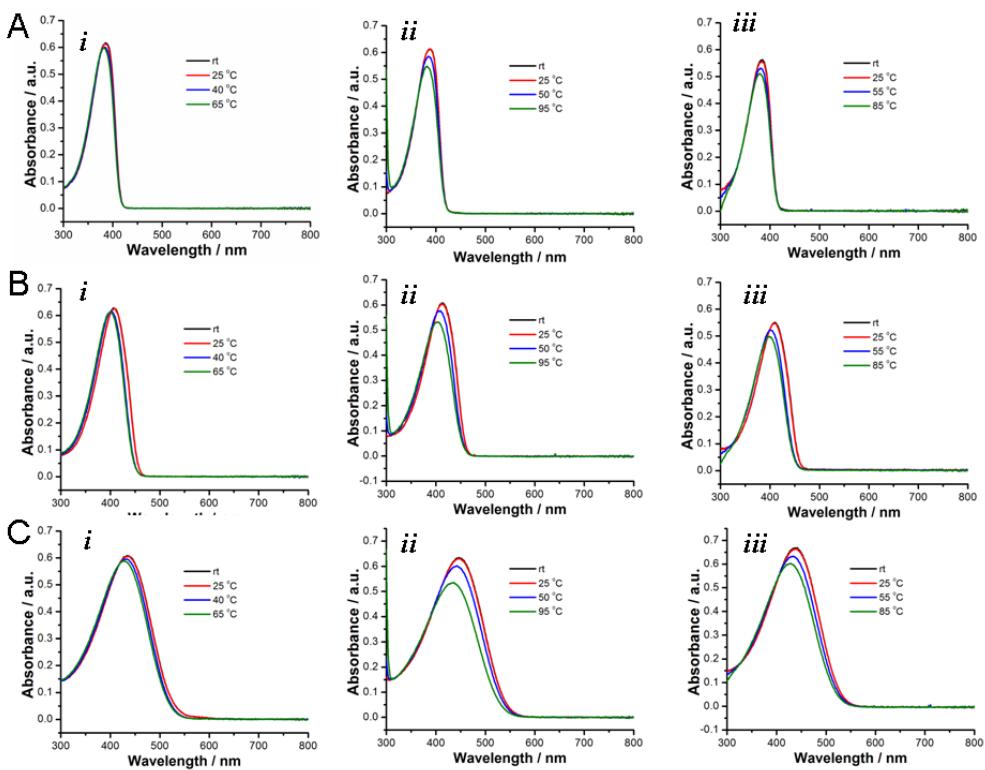


Figure S1. UV-Vis absorption data of the polymer in THF, dichlorobenzene, and toluene

at variable temperature. PF (A), PFT (B), and PT (C) complexes in THF(*i*), dichlorobenzene(*ii*) and toluene(*iii*).