Supplementary Material (ESI) for Chemical Communications

A New n-Type Low Bandgap Conjugated Polymer P-co-CDT: Synthesis and Excellent Reversible Electrochemical and Electrochromic Properties

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Characterization. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DMX-300 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer.The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard.

Synthesis

Synthesis of compound 2 2,7-dibromoperylene-3,4,9,10-tetracarboxylic acid dianhydride (3.30 g, 6.0 mmol), 60 ml of DMF and 2-ethylhexylamine (3.87g, 30 mmol) were put into a flask and heated to 70^{o}C for 12 hours. The reactant was poured into water and extracted by chloroform for several times. The organic layer was collected, and the solvent was rotary evaporated. The red solid was purified by silica gel column chromatography, using Hexane:dichloromethane (1:1, v/v) as the eluent. A red solid of compound 2 was obtained after the purification (3.34 g, yield 72%).

^{1}H NMR (300 MHz, $CDCl_3$): 9.49 (d, 2H), 8.94 (s, 2H), 8.67 (d, 2H), 4.1 (m, 4H), 2.1-1.8 (m, 2H), 1.6-1.1 (m, 16H), 1.1-0.8 (m, 12H).

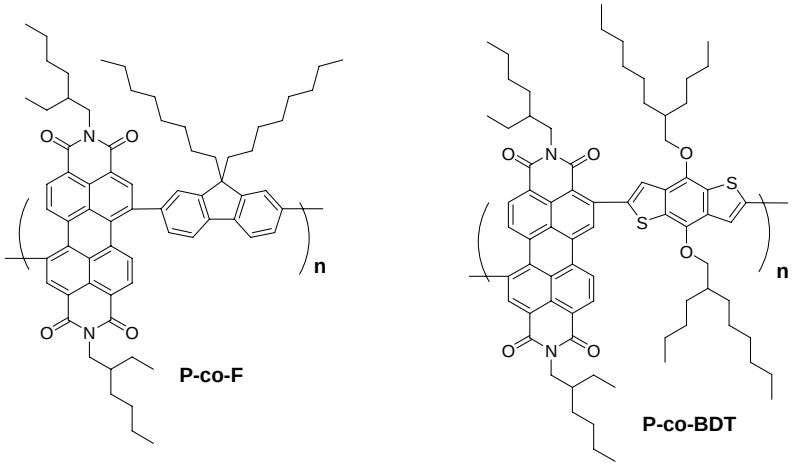
^{13}C NMR ($CDCl_3$): 163.2, 162.7, 138.2, 133.0, 132.8, 130.1, 129.3, 128.5, 126.9, 123.1, 122.7, 120.8, 44.5, 38.0, 30.7, 28.9, 24.1, 23.1, 14.1, 10.8.

Polymerization of P-co-CDT Compound 2 (1mmol), 3 (1mmol) and 50mg of $Pd(PPh_3)_4$ were put into a flask with 60 ml of toluene. The mixture was purged with argon gas for 30 min, and then the reactant was heated to reflux for 24 hours. Then, the reactant was poured into 200 ml of methanol, and the polymer was precipitated, filtered and washed in a Soxlet extractor by using acetone and chloroform successively. Then, the polymer was purified by the method in Ref. 11 and obtained as a dark powder (yield 53%).

Fabrication of polymer solar cell devices. polymer solar cell devices with the structure of ITO/PEDOT-PSS/P-co-CDT: poly[(4,4’-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole-2,6-diyl-alt-2,1,3-benzothiadiazole-4,7-diyl) (1:1, w/w) /Ca/Al were fabricated under conditions as follows: After spin-coating a 30 nm layer of poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) onto a pre-cleaned indium-tin oxide (ITO) coated glass substrates, the polymer/PCBM blend solution was spin-coated. Typical concentration of the blend solution used in this study for spin-coating active layer was 10mg/ml, and dichlorobenezene was used as solvent. The thickness of the active layer was ~80 nm. The devices were completed by evaporating Ca/Al metal electrodes with area of 12.5 mm^2 defined by masks.

Molecular structures of P-co-BDT and P-co-CDT and preliminary CV results of P-doping/dedoping process of them

Scheme s1. Molecular structures of P-co-F and P-co-BDT



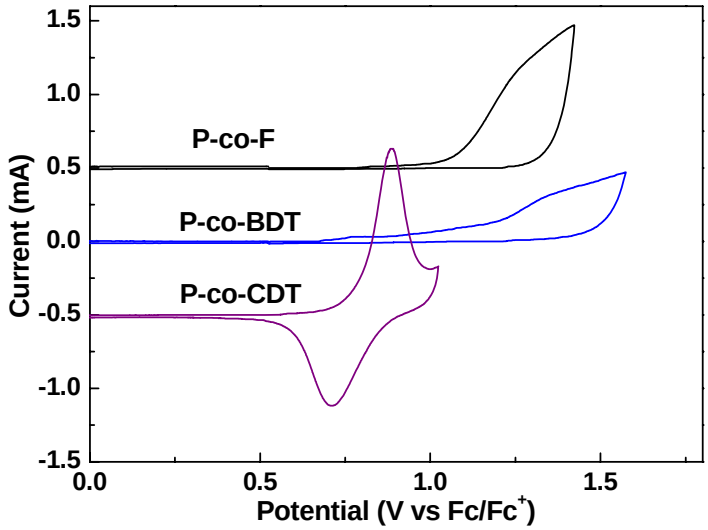


Figure s1. CV plots of P-co-F, P-co-BDT and P-co-CDT