Supporting Information

Effect of Side-Chain Length on Regioregular Poly[3-(4-*n*-alkyl)phenylthiophene]/PCBM and ICBA Polymer Solar Cells

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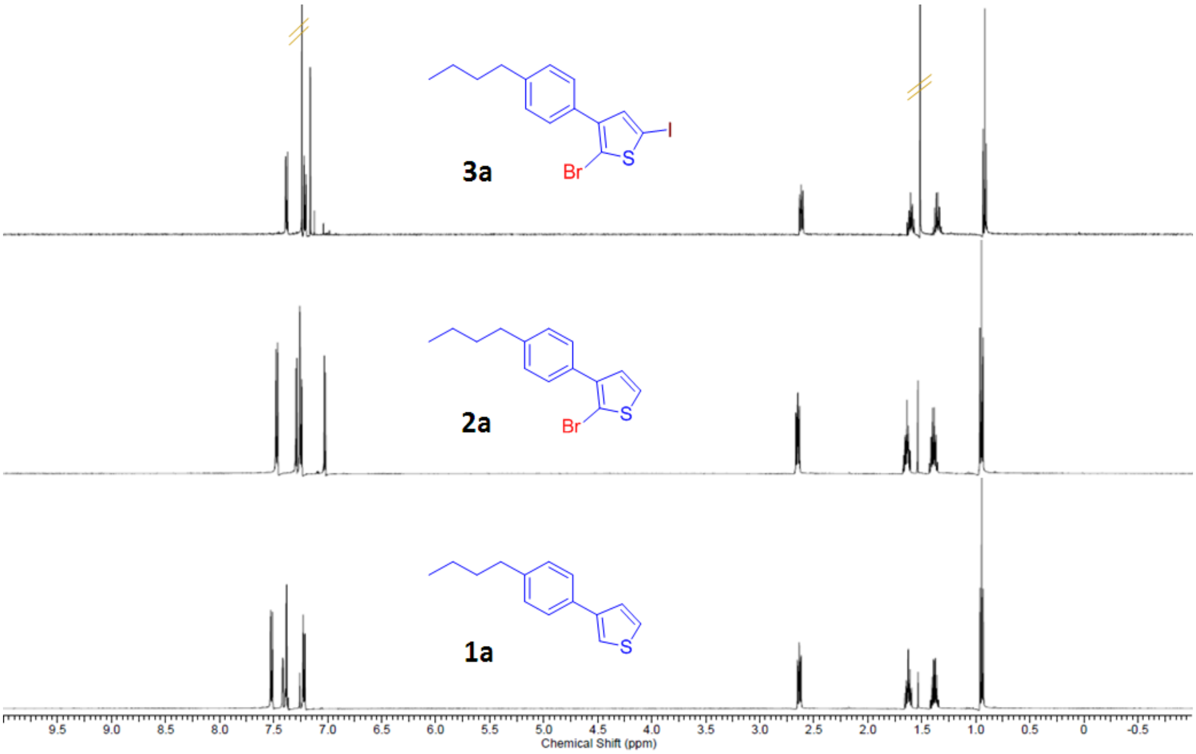
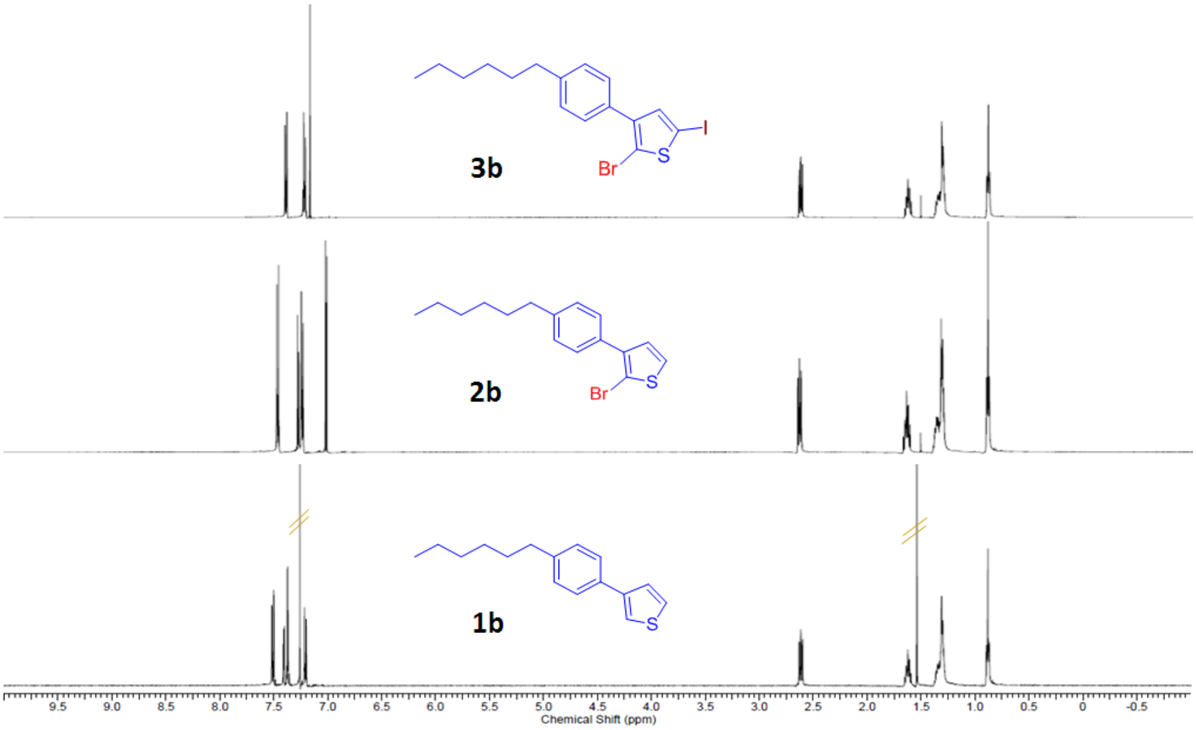
◈ Synthesis and Characterization of Polymers

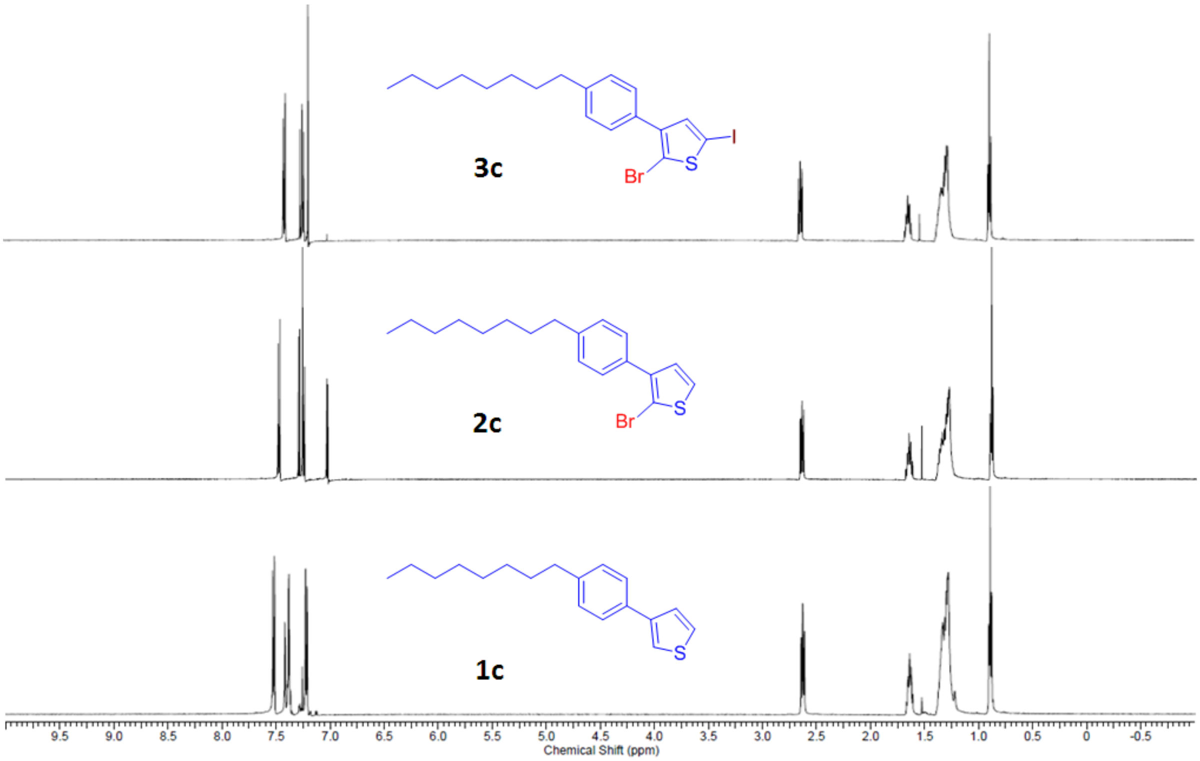
General: All commercially available reagents were used without further purification unless otherwise indicated. 4-*n*-Alkylbromobenzenes (hexyl, octyl, and decyl) were purchased from TCI Chemical Co., Ltd., and 4-butylbromobenzene was pursed from Aldrich Chemical Co., Ltd. Isopropylmagnesium chloride (2.0 M in THF) was purchased from Aldrich Chemical Co., Ltd. Tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$], 1,2-bis(diphenylphosphinoethane)nickel(II) chloride [$Ni(dppp)Cl_2$], 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos) were purchased from Aldrich Chemical Co., Ltd. and stored in a vacuum atmosphere glovebox under nitrogen. The organic solvents (THF, $CHCl_3$, *etc.*) were used as anhydrous solvents. Butyl alcohol solvent was dried overnight over activated 3 Å molecular sieves prior to use. All ^1H NMR spectra were recorded at 500 MHz, using $CDCl_3$ as a solvent, unless otherwise stated. The chemical shifts of all ^1H NMR spectra are referenced to the residual signal of $CDCl_3$ (δ 7.26 ppm) by Bruker 500 MHz NMR instrument. All coupling constants, *J*, are reported in Hertz (Hz). The progress of monomer reaction was checked by thin-layer chromatography (TLC) analysis using Merck silica gel 60 F_{254} precoated plates (0.25 mm) with a fluorescent indicator and visualized with UV light (254 and 365 nm) or by iodine-vapor staining. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). The GPC measurements were performed on a Waters RI system equipped with a UV detector, a differential refractometer detector, and an Ultrastyragel linear column at 35 °C using THF (HPLC grade) as the eluent. The molecular weight (M_n) and the polydispersity index (PDI) were calculated using monodisperse polystyrene standards.



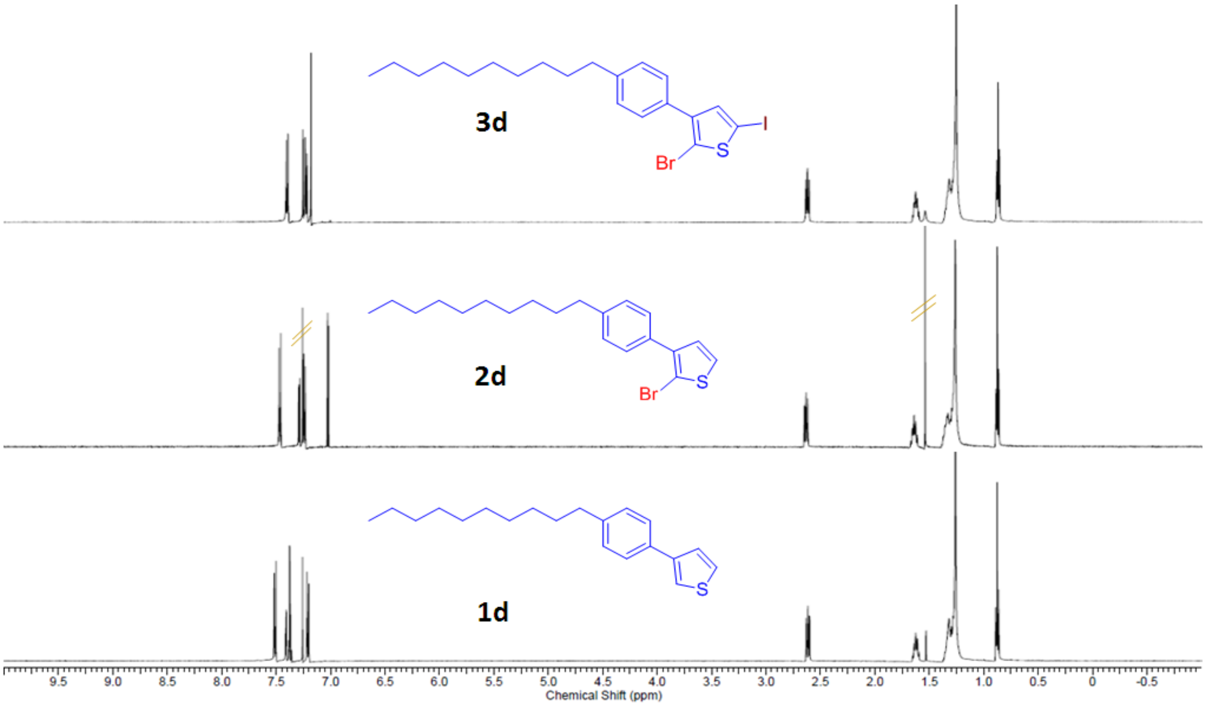
Scheme S1. ^{1}H NMR data for **PBPT** precursor **1a**, **2a**, and **3a**



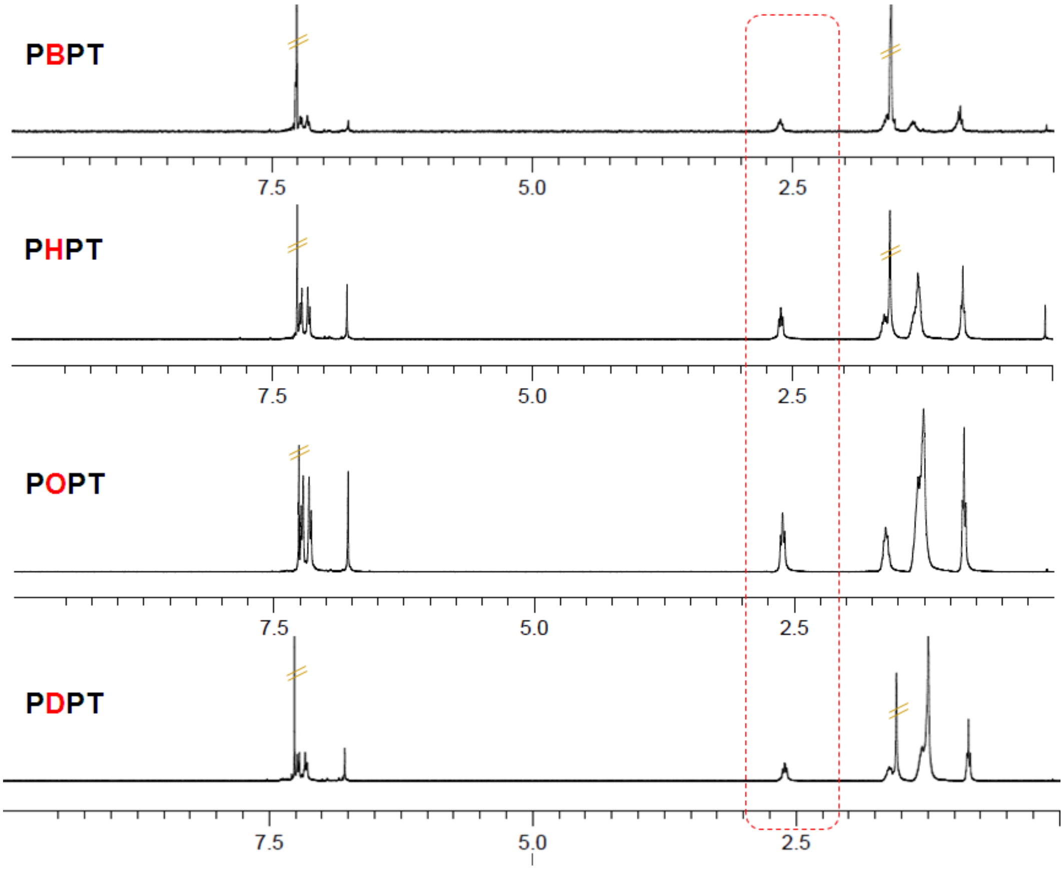
Scheme S2. ^{1}H NMR data for **PHPT** precursor **1b**, **2b**, and **3b**



Scheme S3. ^{1}H NMR data for **POPT** precursor **1c**, **2c**, and **3c**



Scheme S4. ^{1}H NMR data for **PDPT** precursor **1d**, **2d**, and **3d**



Scheme S5. ^{1}H NMR data for **PAPTs** include different alkyl (C_nH_{2n+1}) side chains; PBPT (n = 4), PHPT (n = 6), POPT (n = 8), and PDPT (n = 10)

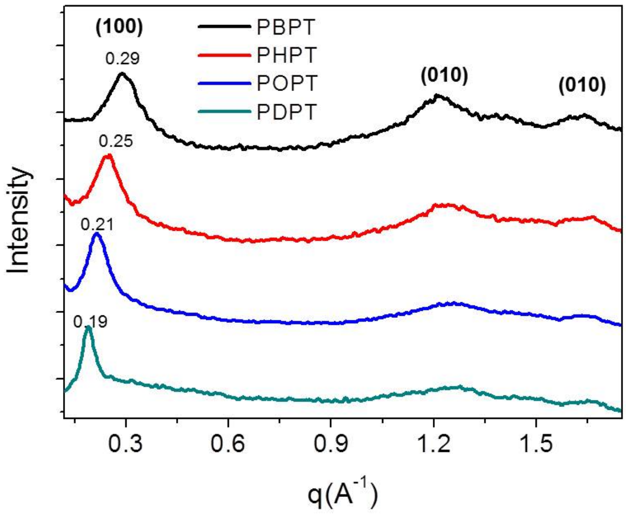
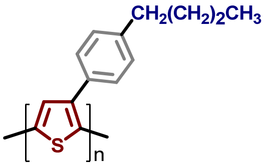
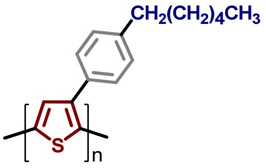


Fig. S1 In-plane X-ray diffraction profiles (q_{xy}) of four different PAPT polymers.

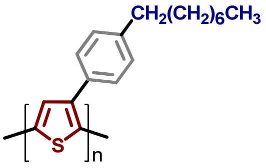
Table S1. Characteristics of PAPT polymers used in our study



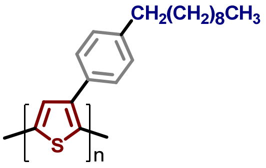
PBPT



PHPT



POPT



PDPT

polymer	M_n (K)[a]	M_w (K)[a]	PDI[a]	D_p[b]	solubility[c]	RR[d]
PBPT	10.3	20.0	1.94	48	poor	99<
PHPT	22.4	44.4	1.98	91	moderate[d]	99<
POPT	22.0	38.3	1.74	81	moderate[d]	99<
PDPT	7.9	14.4	1.82	27	good	99<

[a] M_n, M_w, and PDI of the polymers were determined by GPC in THF using polystyrene standards. [b] Degree of polymerization. [c] Solubility in $CHCl_3$ at room temperature. [d] Calculated from ^1H NMR spectroscopy (see Scheme S1-S4).

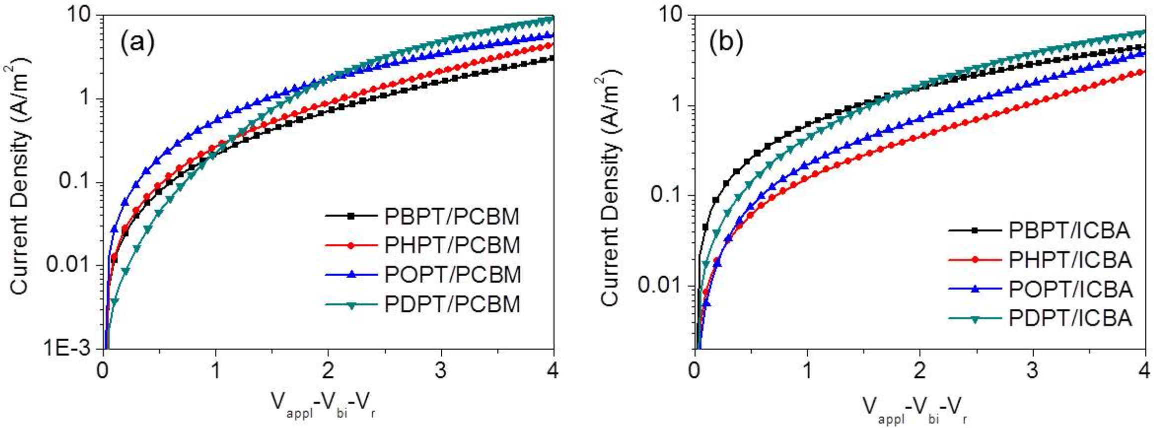


Fig. S2 Measured space-charge-limited *J*–*V* characteristics of the (a) PAPT:PCBM and (b) PAPT:ICBA blend devices under dark conditions using optimized device conditions for hole-only devices.

Table S2. Calculated SCLC hole mobility values of PAPT:PCBM and PAPT:ICBA films under optimized device conditions.

PAPT:PCBM	mobility ($cm^2V^{-1}s^{-1}$)	PAPT:ICBA	mobility ($cm^2V^{-1}s^{-1}$)
PBPT	4.57×10^{-4}	PBPT	1.90×10^{-4}
PHPT	4.29×10^{-4}	PHPT	1.43×10^{-4}
POPT	2.98×10^{-4}	POPT	1.27×10^{-4}
PDPT	1.85×10^{-4}	PDPT	1.70×10^{-4}

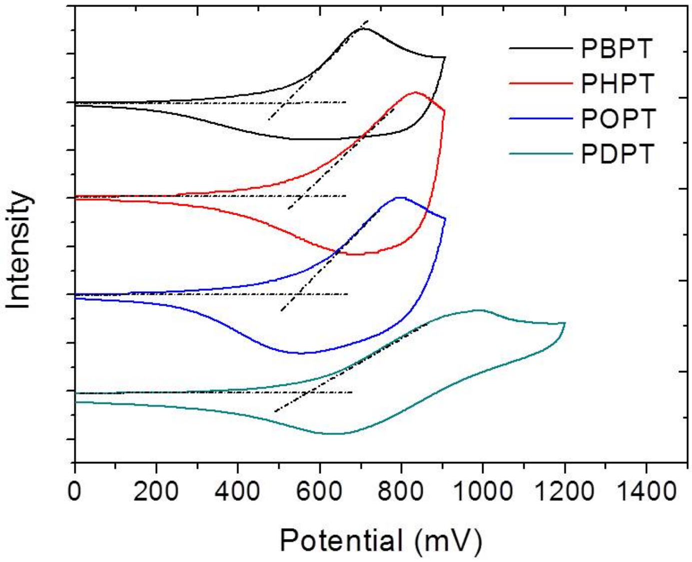


Fig. S3 Cyclic voltammetry (CV) curves for PBPT, PHPT, POPT and PDPT.

Table S2. Optical and electrochemical properties of polymers used in our study

polymer	λ_{max}/nm	λ_{onset}[a]/nm	E_g[b]/eV	HOMO[c]/eV
PBPT	596	703	1.76	-5.32
PHPT	600	702	1.77	-5.35
POPT	597	702	1.77	-5.34
PDPT	585	700	1.77	-5.36

[a] Onset point from film absorption spectra. [b] Optical bandgap. [c] Obtained from CV.

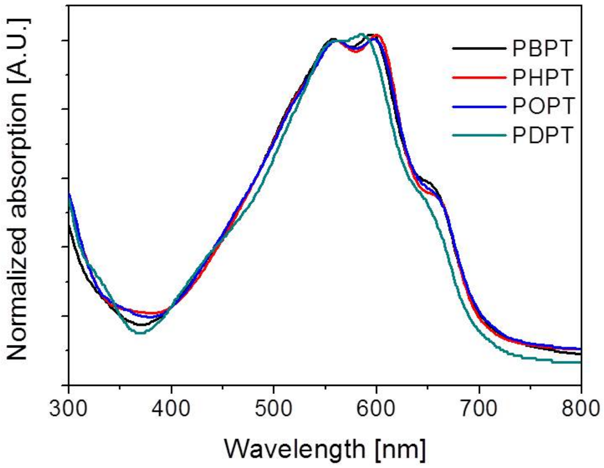


Figure S4. UV-vis absorption spectra of thin films of PBPT, PHPT, POPT and PDPT.