

Electronic Supplementary Information

PBDTTPD for plastic solar cells via Pd(PPh₃)₄-catalyzed Direct (Hetero)Arylation Polymerization

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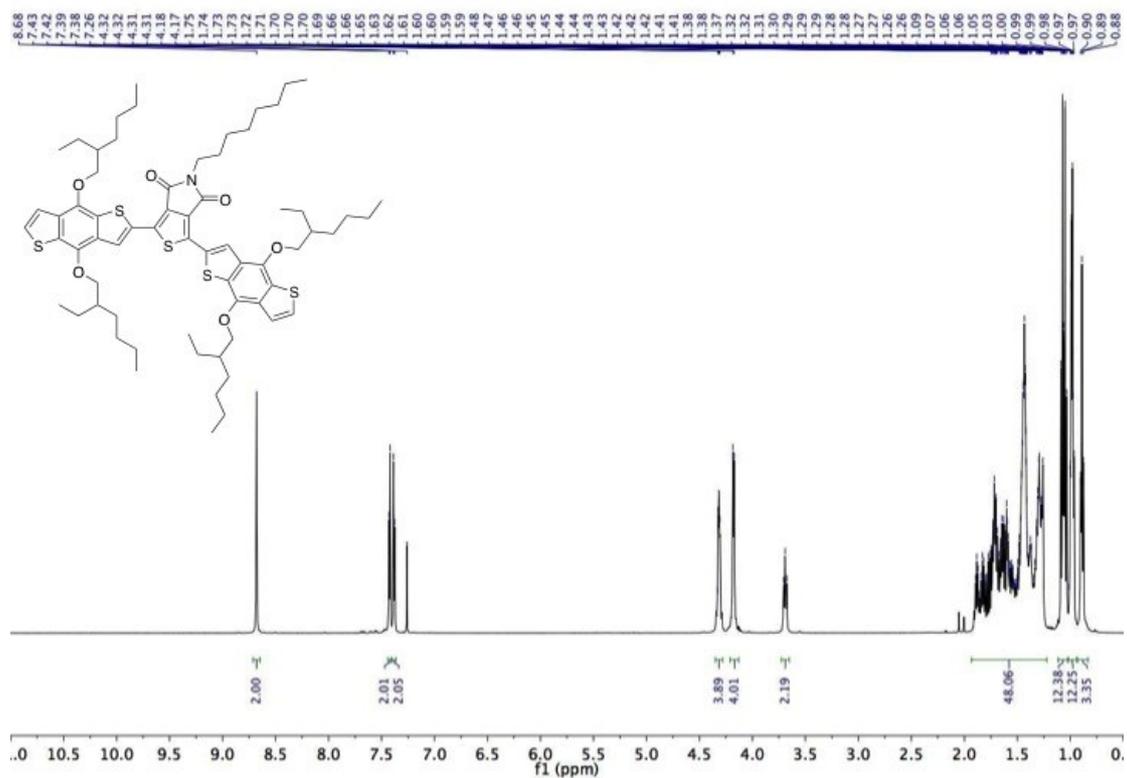


Figure S1. ¹H NMR (CDCl₃, 500 MHz) spectrum of 1,3-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione

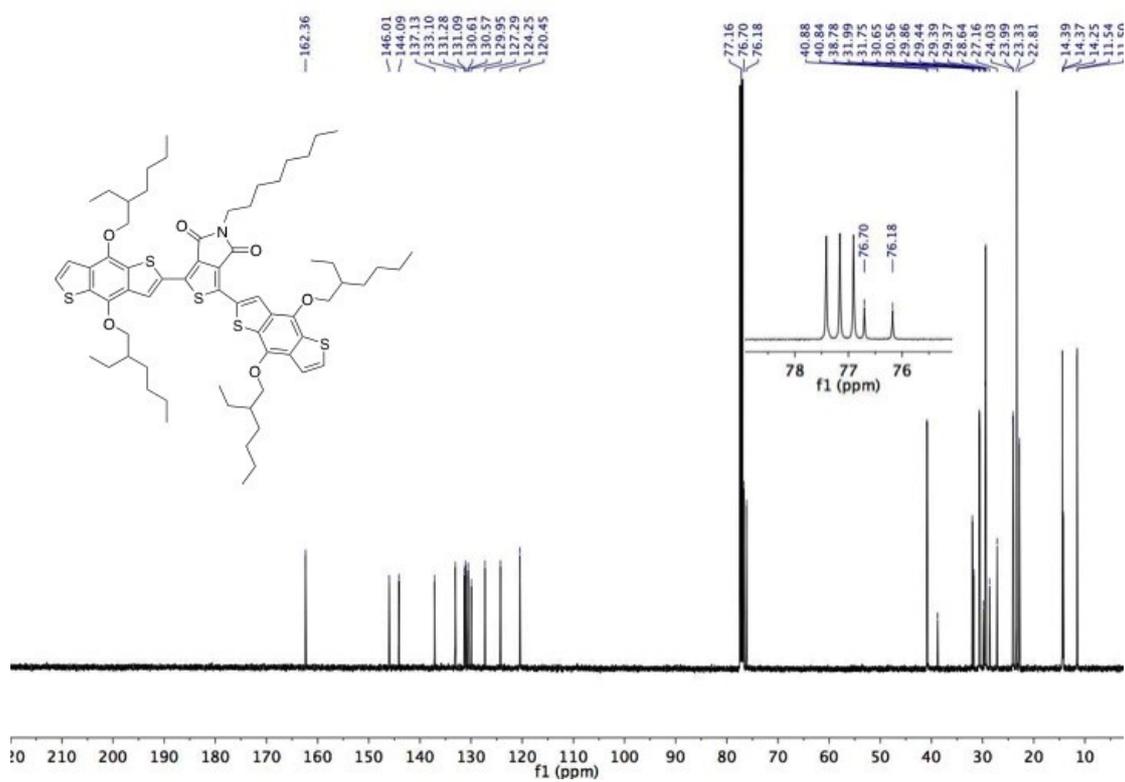


Figure S2. ¹³C NMR spectrum (CDCl₃, 100 MHz) of 1,3-bis(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophen-2-yl)-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione

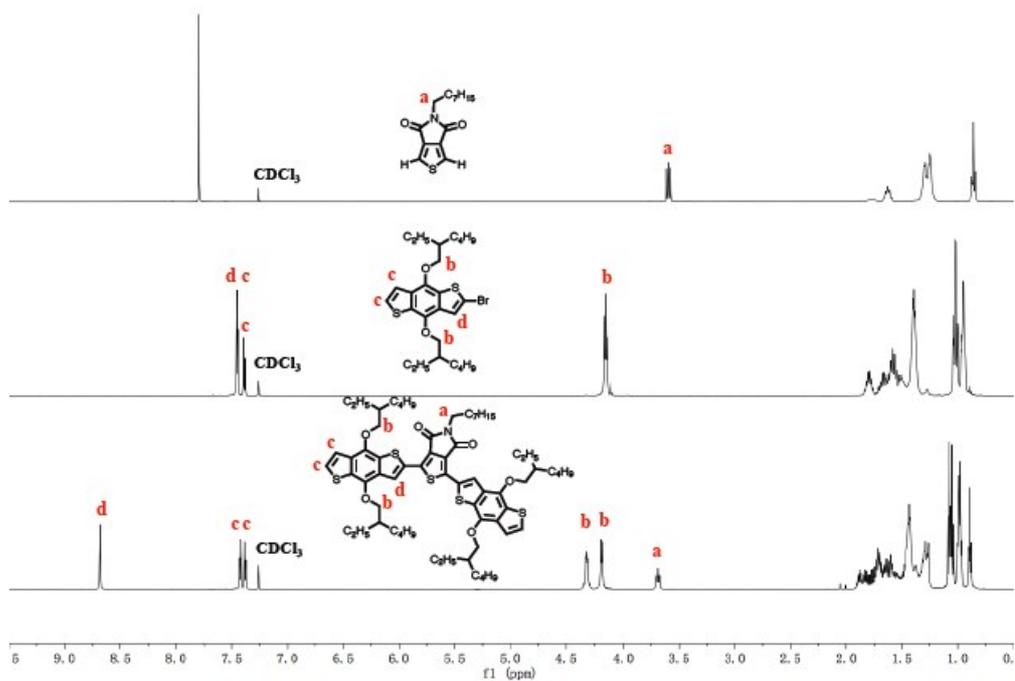


Figure S3. ¹H-NMR spectra (500 MHz, CDCl₃) of 1, 2 and 3 involved in the model direct arylation reaction

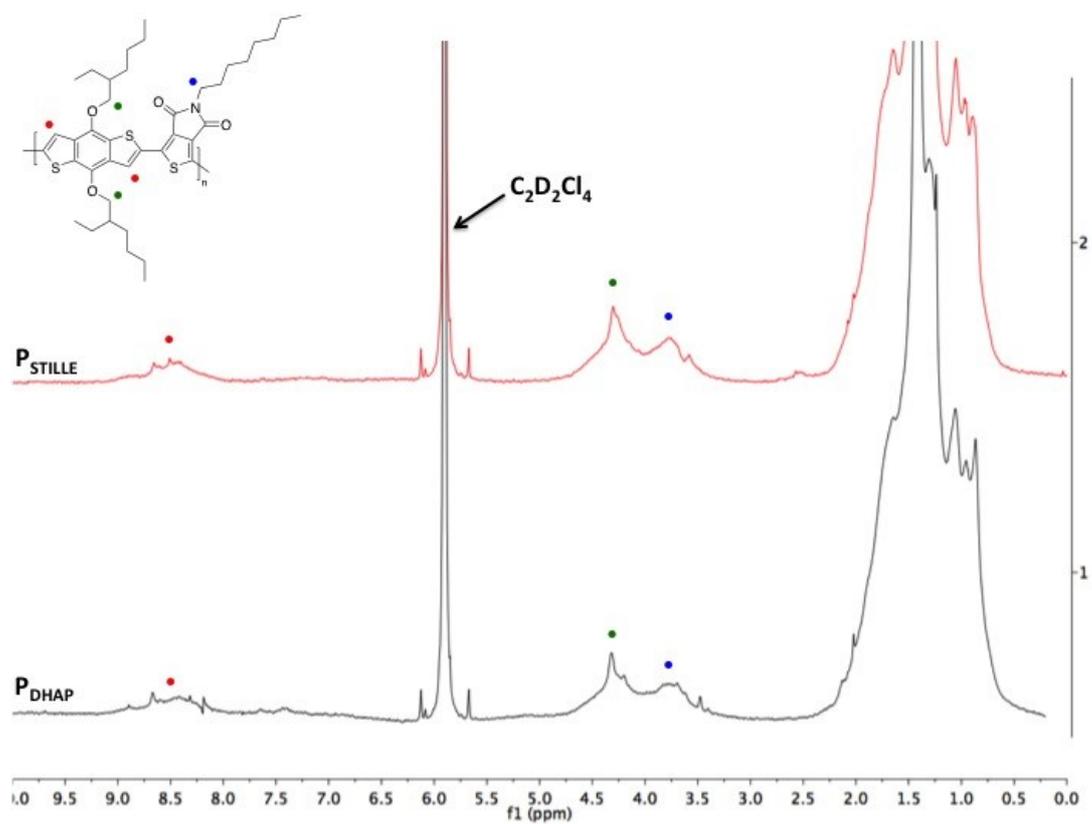


Figure S4. High temperature ¹H NMR spectra (C₂D₂Cl₄, 500 MHz, 90°C) of P_{DHAP} and P_{STILLE} polymers

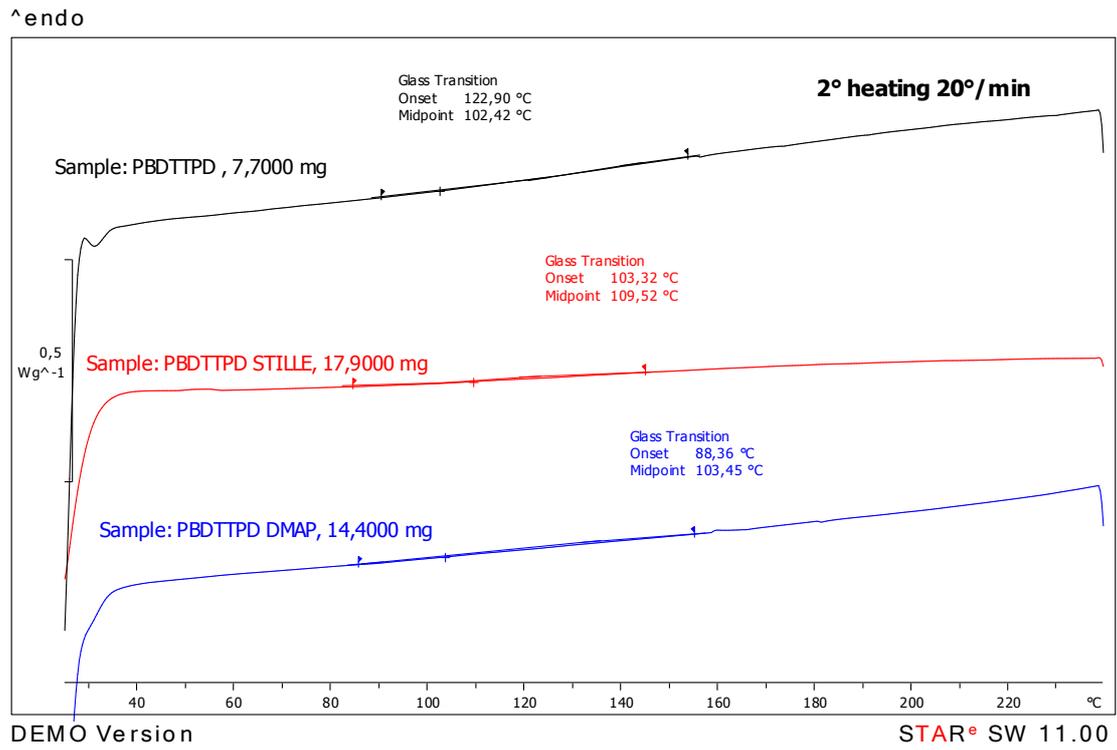


Figure S5. DSC thermograms of P_{COMM} (blackcurve), P_{STILLE} (red curve) and P_{DHAP} (blue profile)

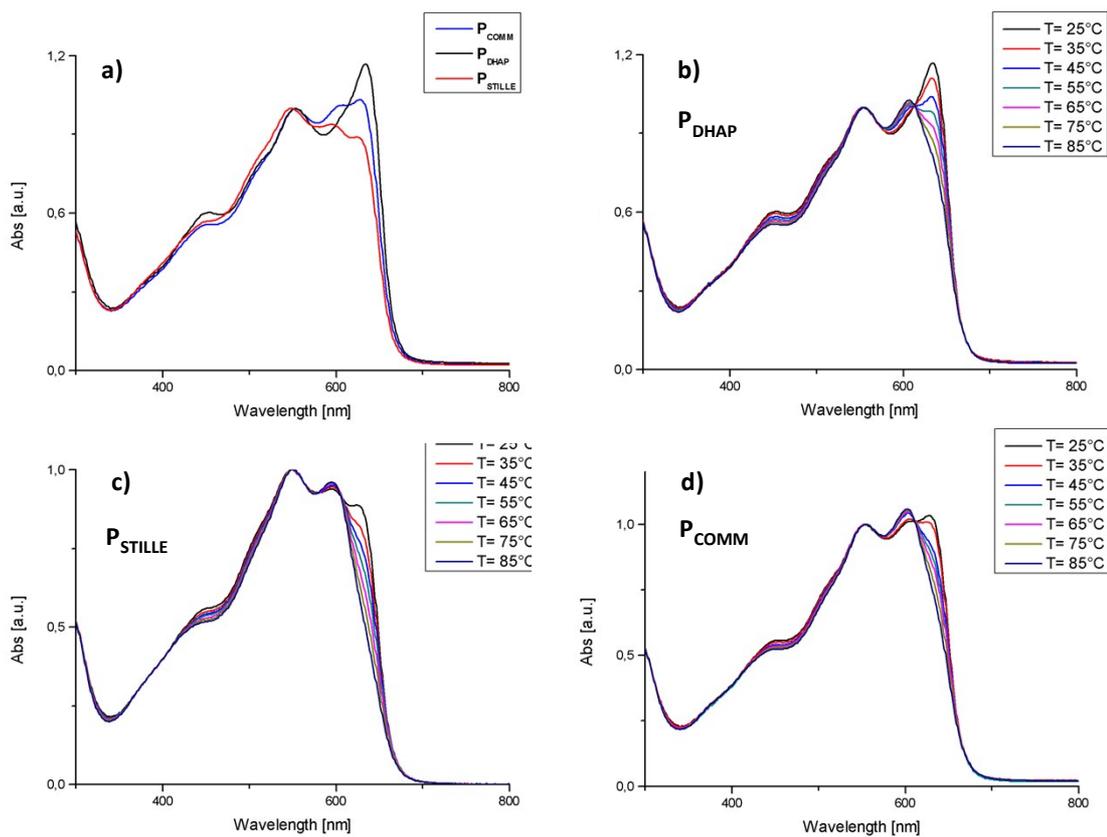


Figure S6. Normalized UV-Vis absorption spectra of P_{DHAP} , P_{STILLE} and P_{COMM} in chlorobenzene solution (0.2 mg/mL) a) Comparison of the absorption spectra at 25°C b) c) d) Temperature-dependent UV-Vis spectra of P_{DHAP} , P_{STILLE} and P_{COMM} , respectively, in the range 25°C–85°C.

Table S1. ICP-MS analyses of P_{COMM}, P_{DHAP} and P_{STILLE}. All samples were completely digested under microwave conditions prior to analysis.

	P _{COMM} (mg/Kg)	P _{DHAP} (mg/Kg)	P _{STILLE} (mg/Kg)
Na	<100	<100	<100
K	<100	<100	<100
Pd	7060±40	870±10	420±10
Sn	6100±100	/	1410±10

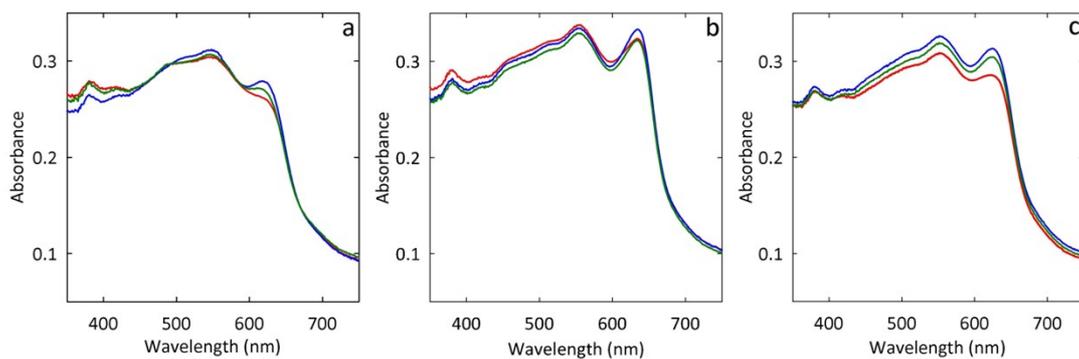


Figure S7. Absorbance spectra of the active layers based on PC₇₁BM blended with P_{STILLE} (a), P_{DHAP} (b), P_{COMM} (c). Red curves are related to different deposition conditions: from pure Chlorobenzene (red), from Chlorobenzene with 4% w/w of 1-chloronaphthalene (blue) and Chlorobenzene with 4% w/w of 1-chloronaphthalene treated with ethanol after deposition (green).