Supplementary data

Fluoro-Functionalization of Vinylene Units in a Polyarylenevinylene for Polymer Solar Cells: Impact of Fluorination on Morphological and Optical Properties and on Photovoltaic Performances.

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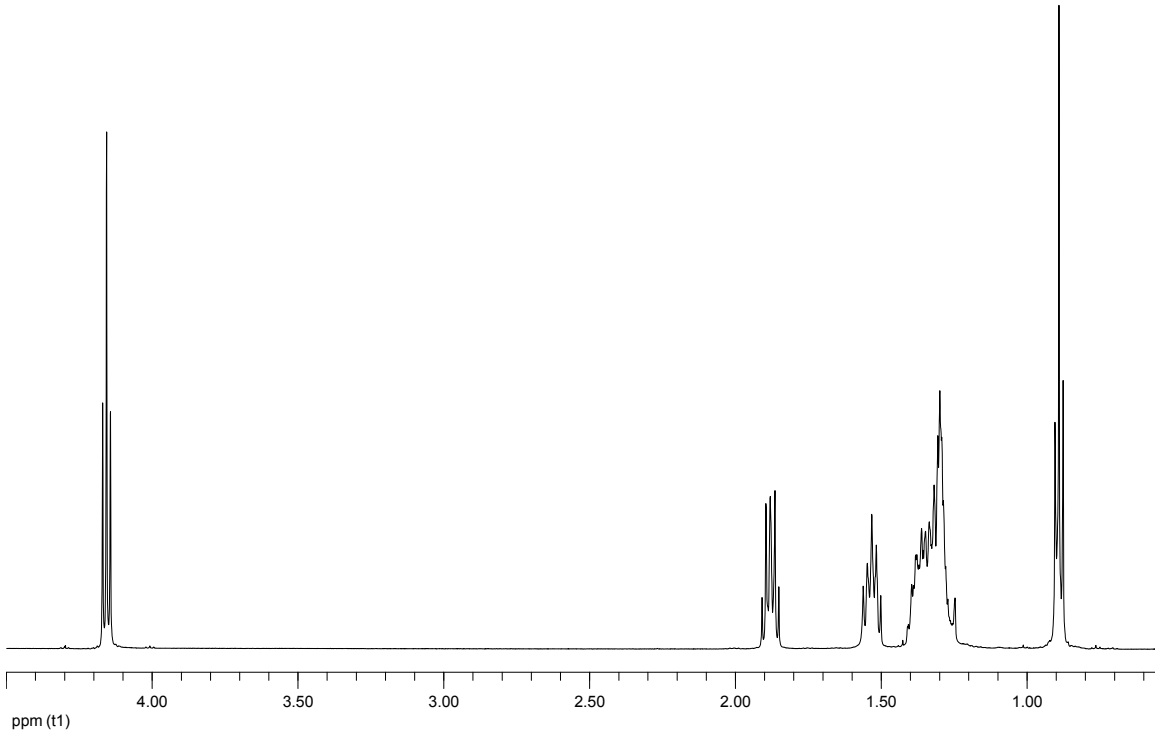

Figure S1.[1]H NMR spectrum of 4,7-dibromo-5,6-di-octyloxy-2,1,3-benzothiadiazole **4**.

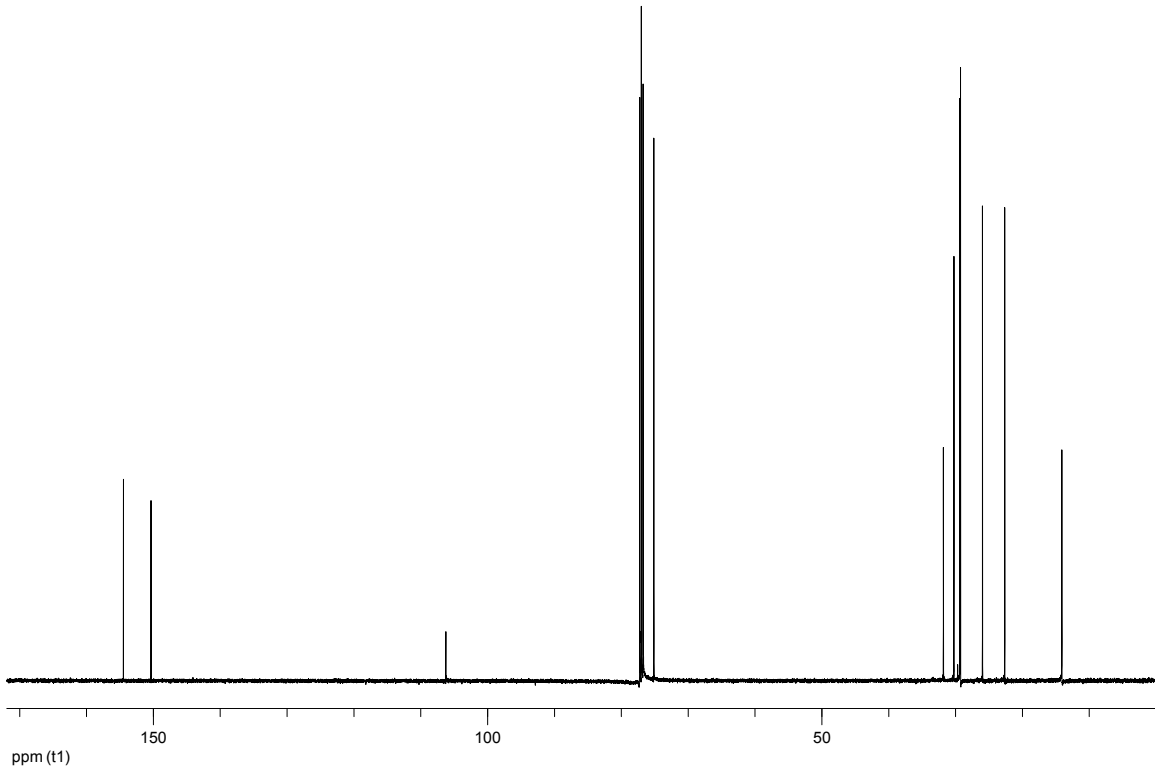

Figure S2. [13]C NMR spectrum of 4,7-dibromo-5,6-di-octyloxy-2,1,3-benzothiadiazole **4**.

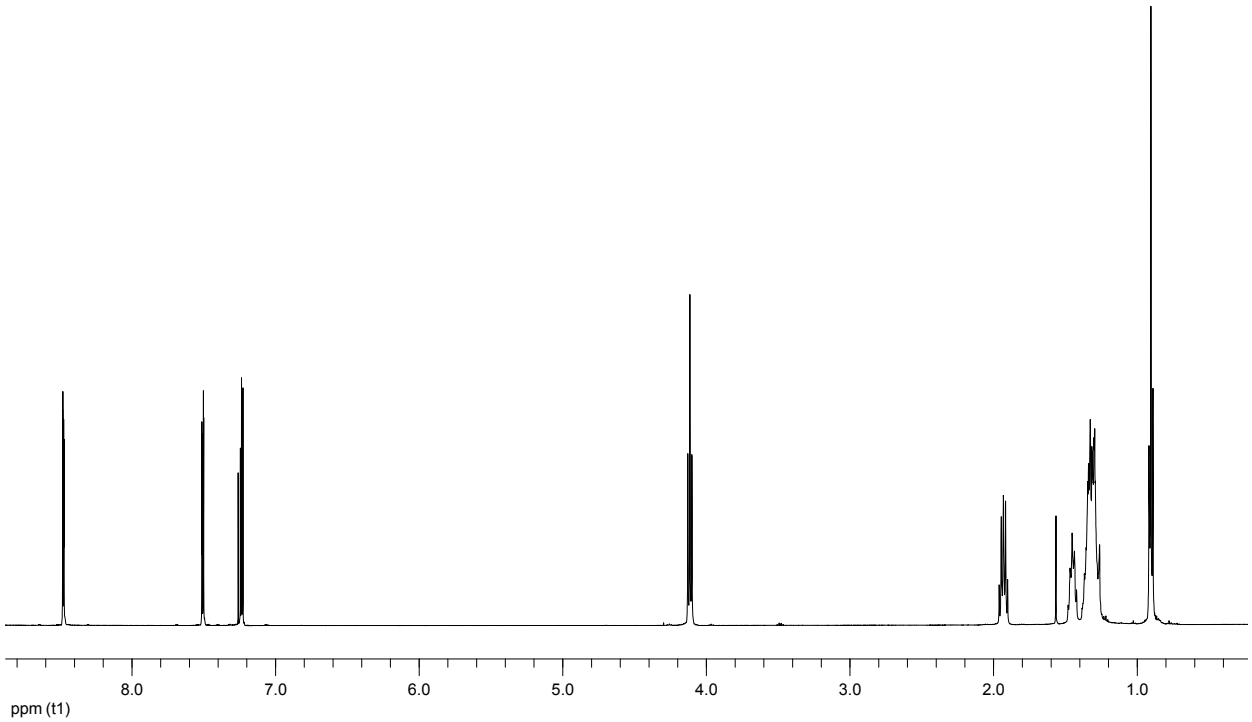

Figure S3. ^{1}H NMR spectrum of 5,6-di-octyloxy-4,7-di-2'-thienyl-2,1,3-benzothiadiazole **5**.

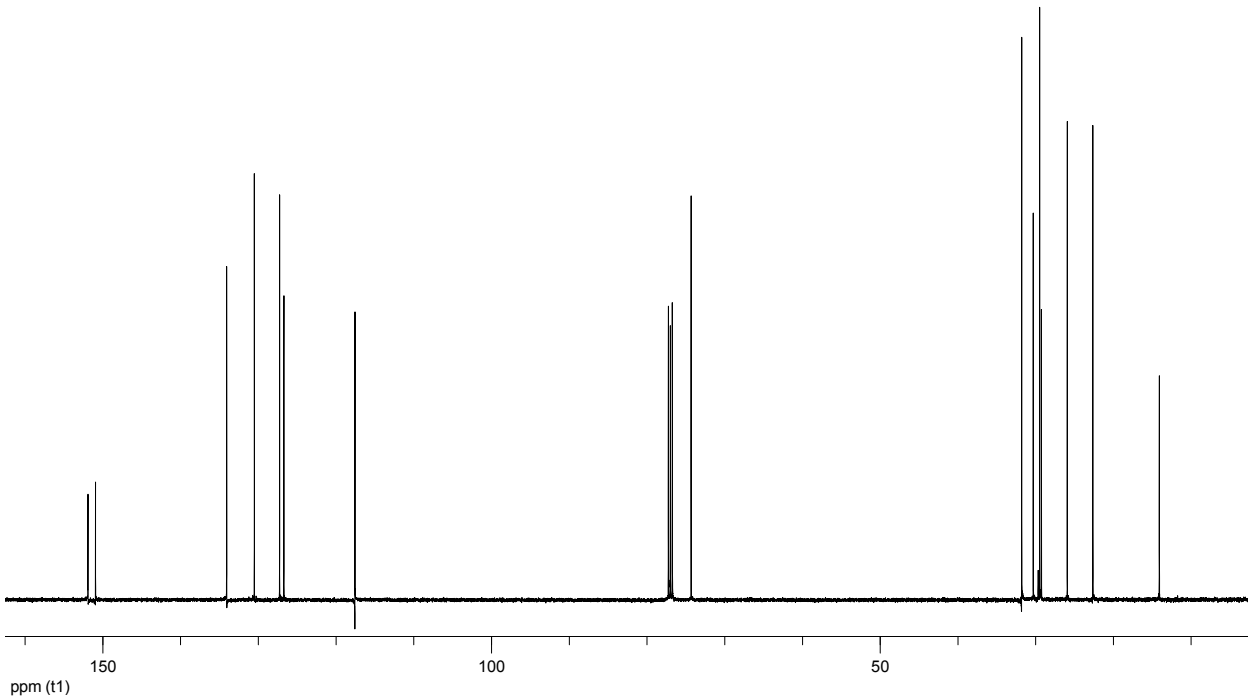

Figure S4. ^{13}C NMR spectrum of 5,6-di-octyloxy-4,7-di-2'-thienyl-2,1,3-benzothiadiazole **5**.

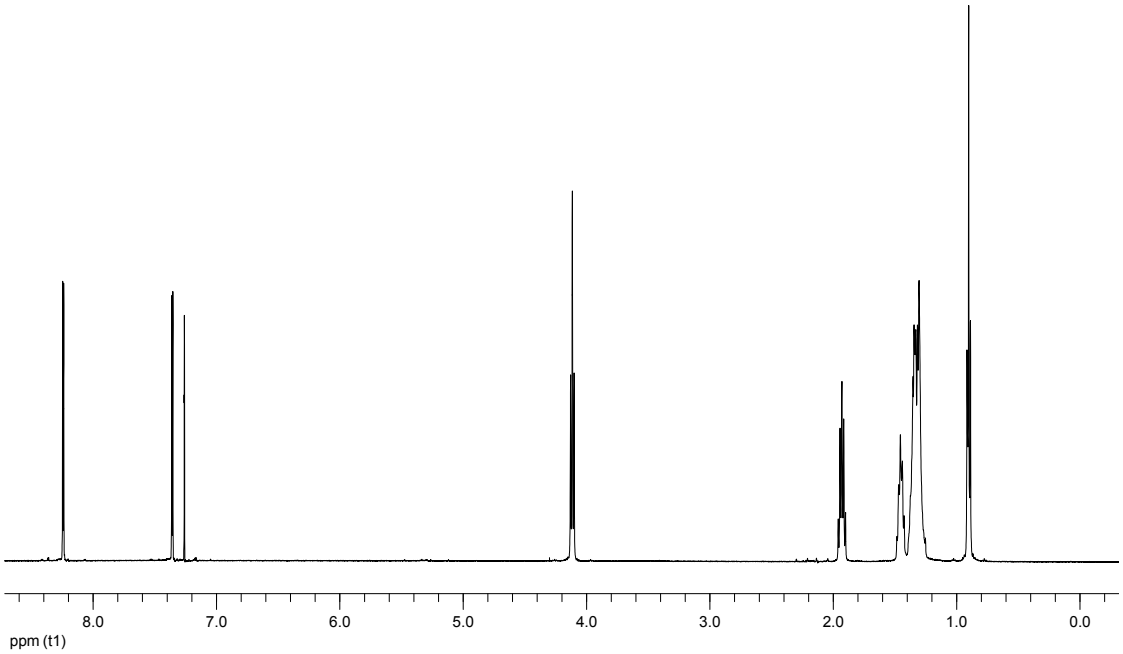

Figure S5. ^{1}H NMR spectrum of 4,7-di-(5'-iodothiophen-2'-yl)-5,6-di-octyloxy-2,1,3-benzothiadiazole **M3**.

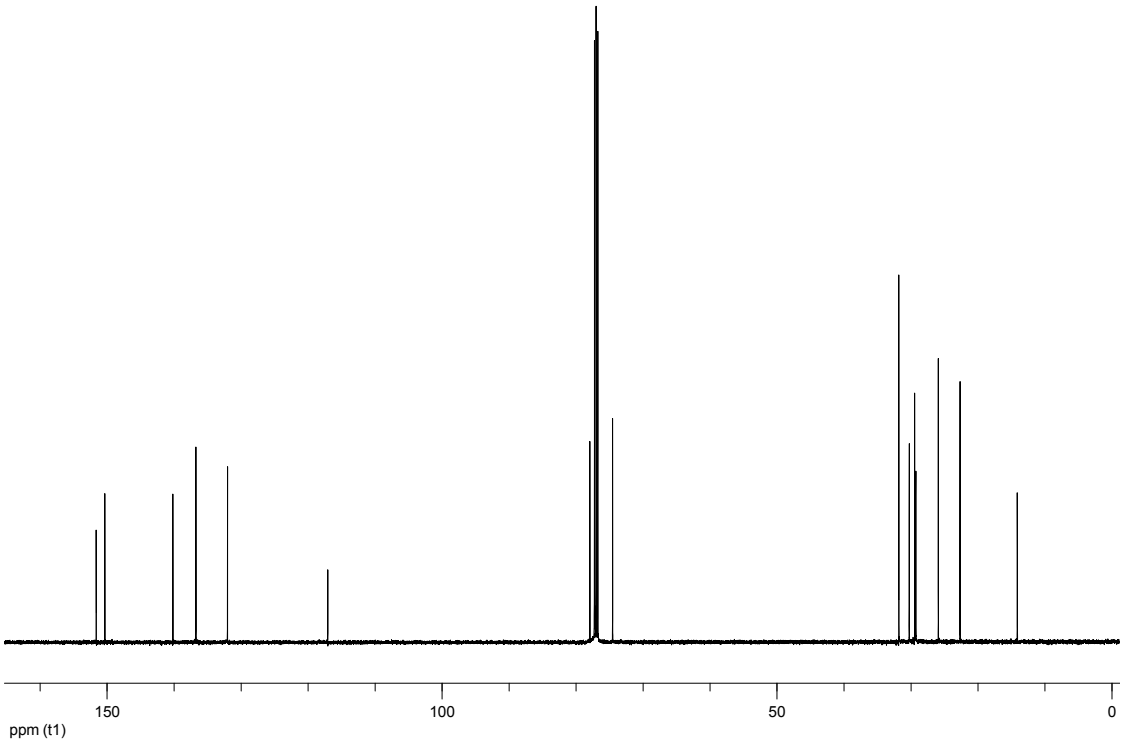

Figure S6. ^{13}C NMR spectrum 4,7-di-(5'-iodothiophen-2'-yl)-5,6-di-octyloxy-2,1,3-benzothiadiazole **M3**.

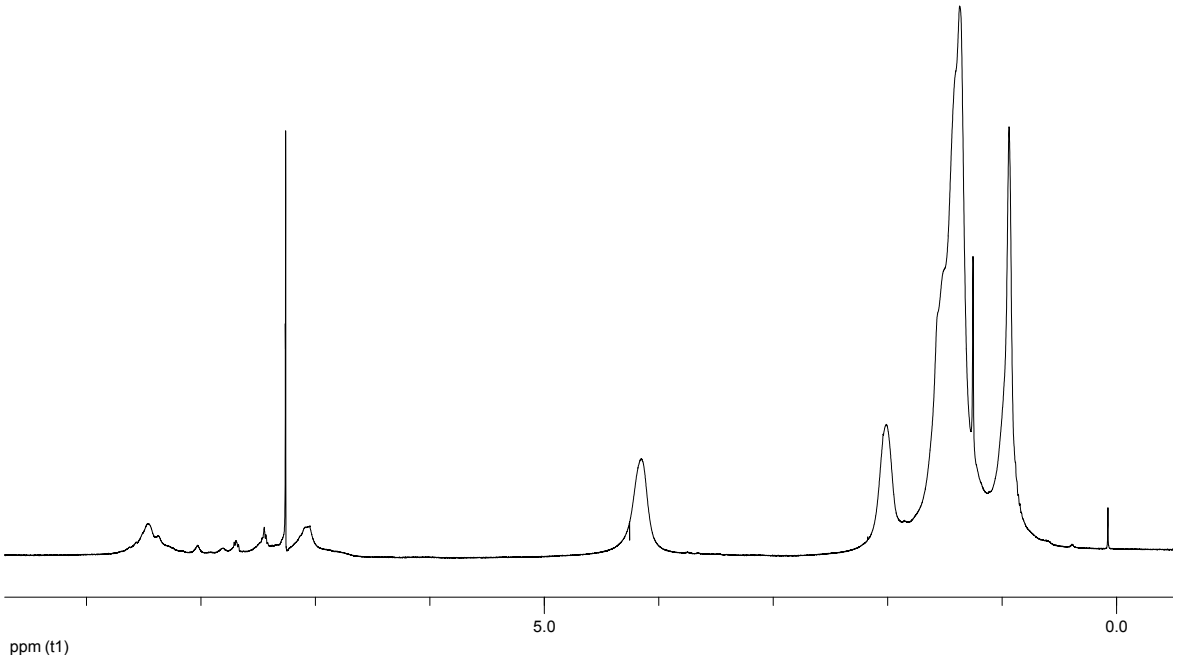

Figure S7. ^{1}H NMR spectrum of Poly[5,5-(5',6'-di-octyloxy-4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)-alt-1'',2''-difluorovinylene] **PDTBTFV**.

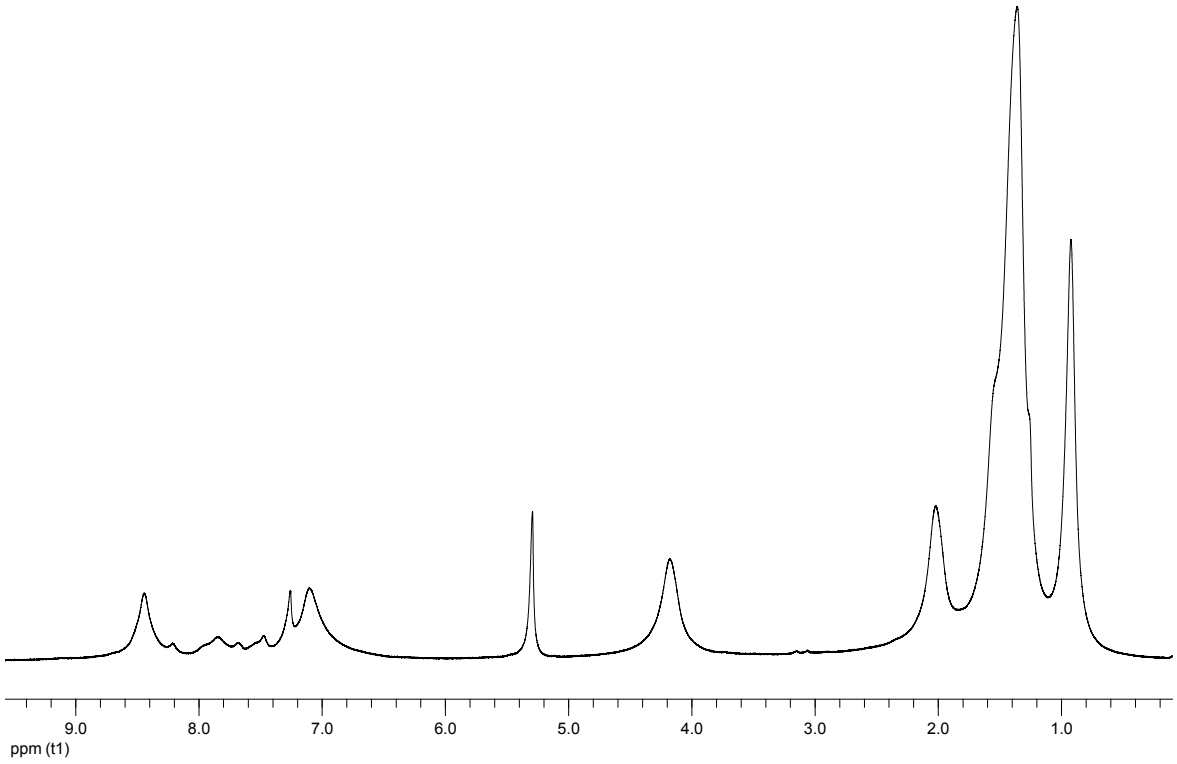

Figure S8. ^{1}H NMR spectrum Poly[5,5-(5',6'-di-octyloxy-4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)-alt-1'',2''-vinylene] **PDTBTV**.

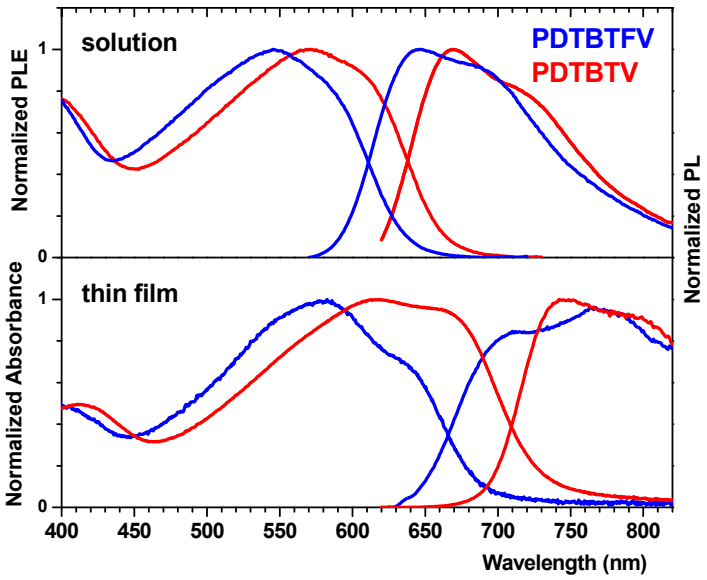

Figure S9. Absorbance and photoluminescence spectra of **PDTBTFV** and **PDTBTV** in solution and thin film.

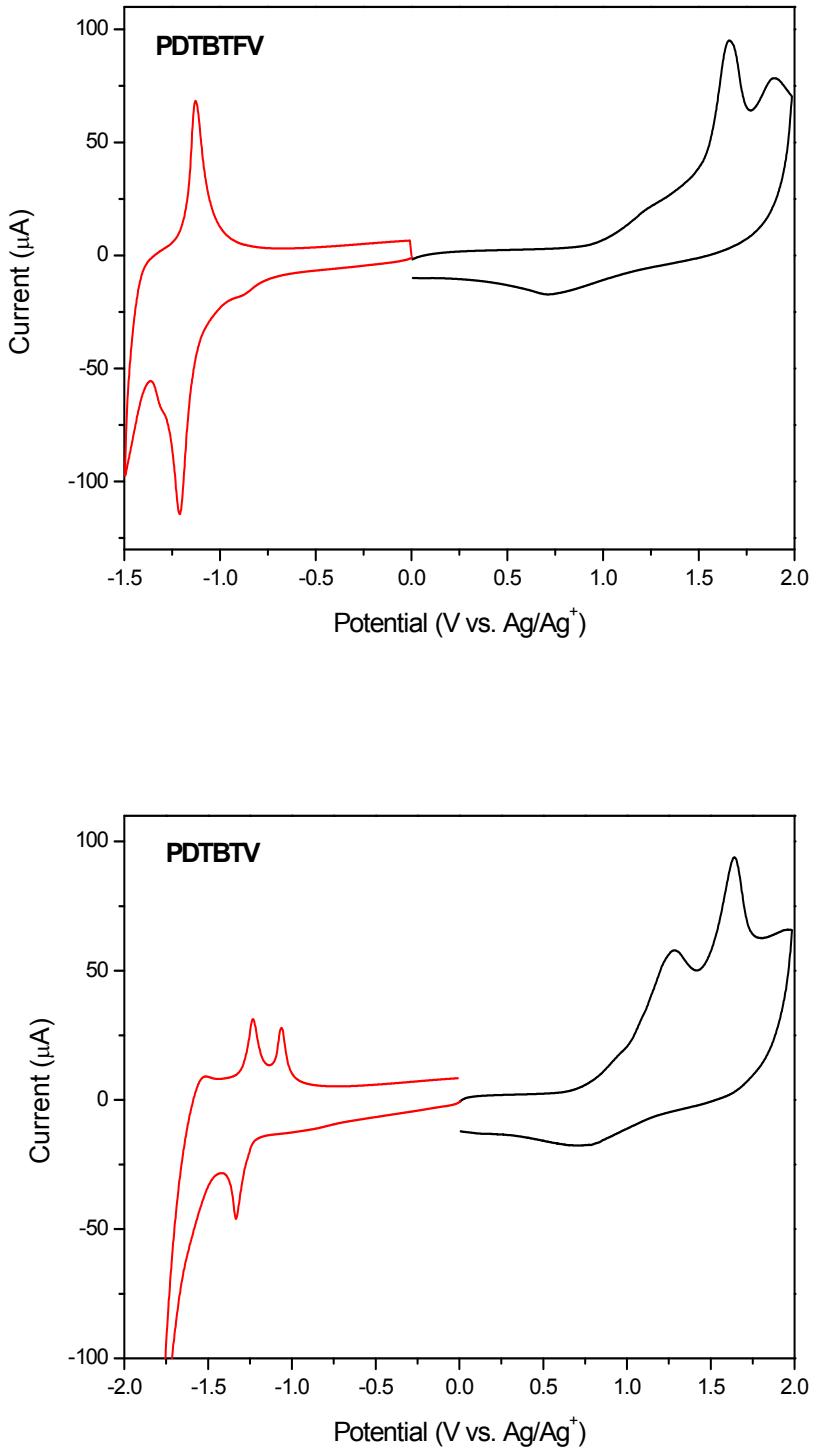

Figure S10. Cyclic Voltammetry of thin films of **PDTBTFV** and **PDTBTV** deposited onto ITO electrode and recorded in acetonitrile solution containing 0.1 M $TBAPF_6$ at a scan rate of 100 mV/s.

Table S1. Fitting parameters derived from the ellipsometric analysis of spectra of both fluorinated (**PDTBTFV**) and non-fluorinated (**PDTBTV**) polymer films (the samples refer to spectra in Fig. 10). n_∞ is the high frequency refractive index,ω_j, γ_j and f_j are the frequency, width and amplitude of the j-th.

Polymer	n_∞	f_I	ω_I	γ_I	f_{II}	ω_{II}	γ_{II}	fI_{II}	ω_{III}	γ_{III}	f_{IV}	ω_{IV}	γ_{IV}	f_V	ω_V	γ_V
PDTBTFV	1.49 ± 0.01	0.053 ± 0.013	2.25 ± 0.01	0.39 ± 0.01	0.002 ± 0.002	3.14 ± 0.02	0.253 ± 0.061	0.004 ± 0.002	3.60 ± 0.08	0.45 ± 0.09	0.002 ± 0.001	4.68 ± 0.05	0.40 ± 0.12	0.028 ± 0.005	6.10 ± 0.01	1.39 ± 0.12
PDTBTV	1.47 ± 0.03	1.40 ± 0.059	2.05 ± 0.02	0.27 ± 0.01	0.002 ± 0.002	3.10 ± 0.04	0.209 ± 0.008	0.004 ± 0.001	3.72 ± 0.20	0.49 ± 0.06	0.0002 ± 0.0001	4.67 ± 0.20	0.23 ± 0.08	0.002 ± 0.001	6.10 ± 0.10	0.60 ± 0.02

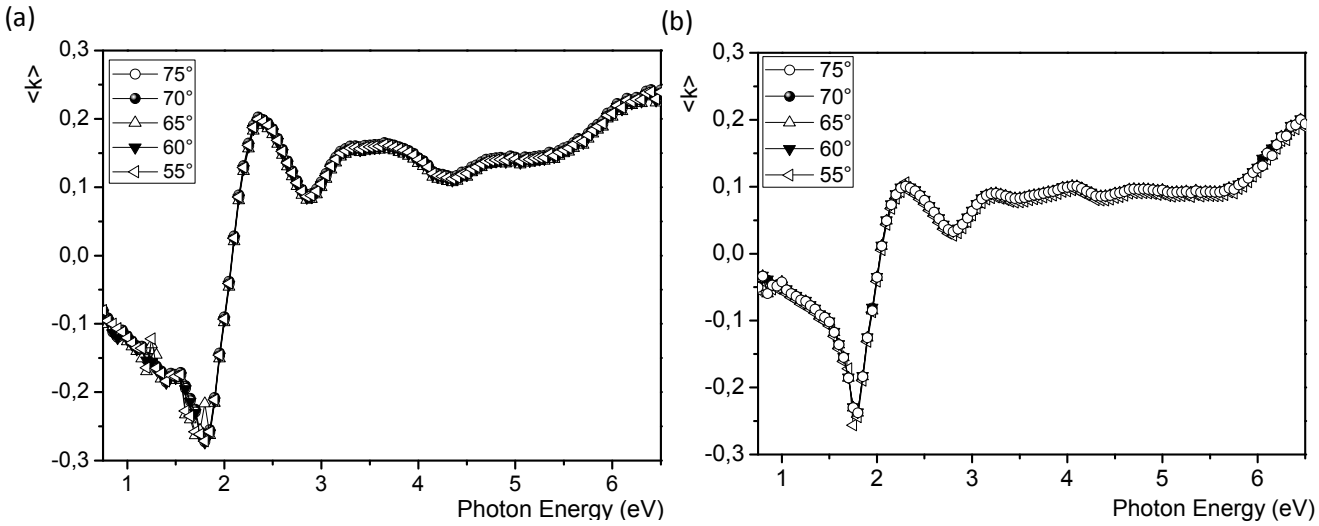

Figure S11. Experimental ellipsometric spectra, acquired at various angles of incidence in the range 55°-75°, of the pseudoextinction coefficient for (a) the fluorinated, **PDTBTFV**, and (b) non fluorinated, **PDTBTV**, films of similar thickness of approximately 15 nm.