Supplementary Information

Effect of molecular structure on the photochemical stability of acceptor and donor polymers used in organic solar cells

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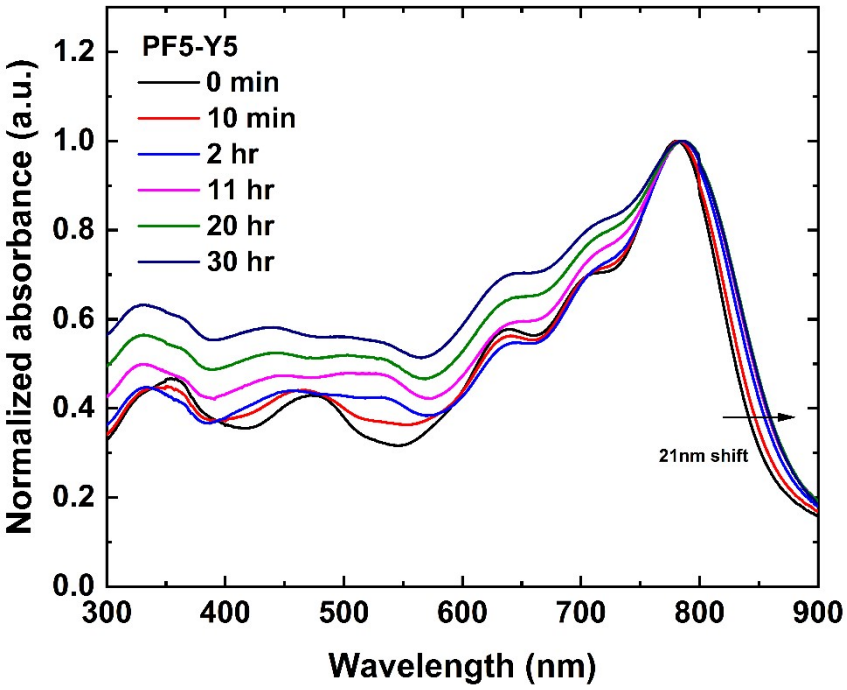


Figure S1: Normalized absorption spectra of PF5-Y5 exposed in ambient air for 0 min, 10 min, 2 hr, 11 hr, 20 hr, and 30 hr under AM 1.5 (one-sun-equivalent illumination).

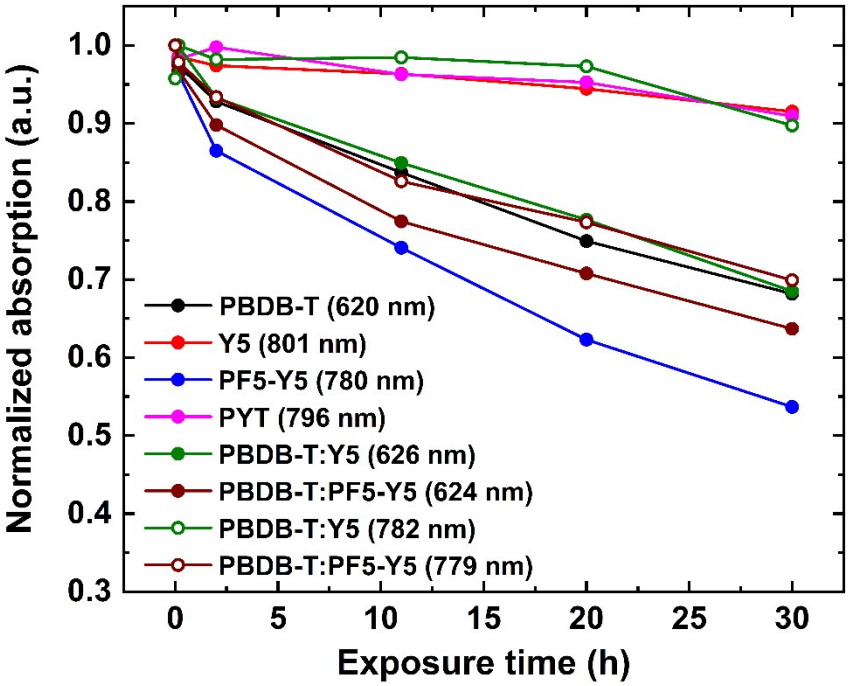


Figure S2: The relative change in absorbance of PBDB-T, Y5, PF5-Y5, PYT, PBDB-T:Y5 (1:0.75), and PBDB-T:PF5-Y5 (1:0.75) films as a function of exposure time.

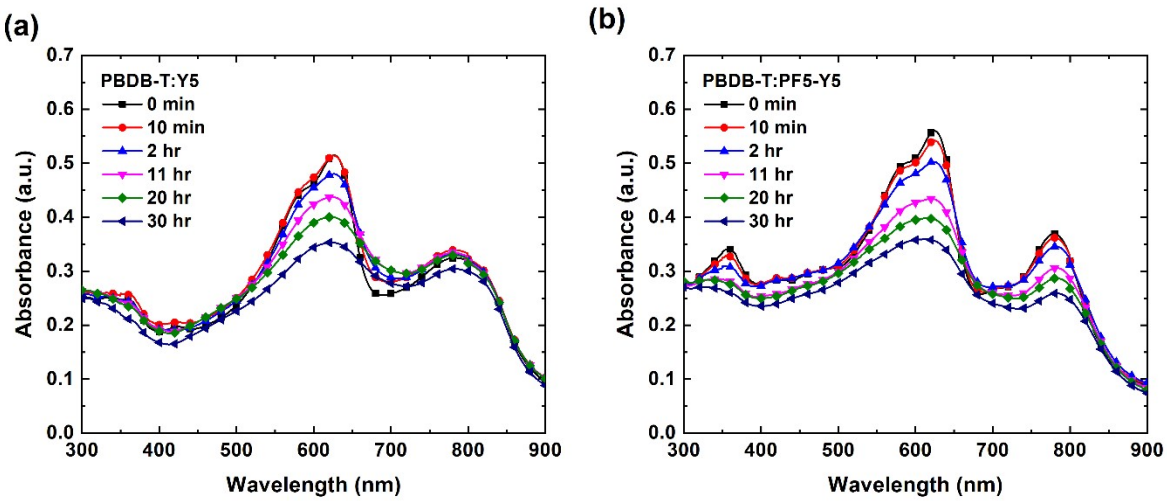


Figure S3: UV-vis spectra of (a) PBDB-T:Y5 (1:0.75), and (b) PBDB-T:PF5-Y5 (1:0.75) films exposed in ambient air for 0 min, 10 min, 2 hr, 11 hr, 20 hr, and 30 hr under AM 1.5 (one-sun-equivalent illumination).

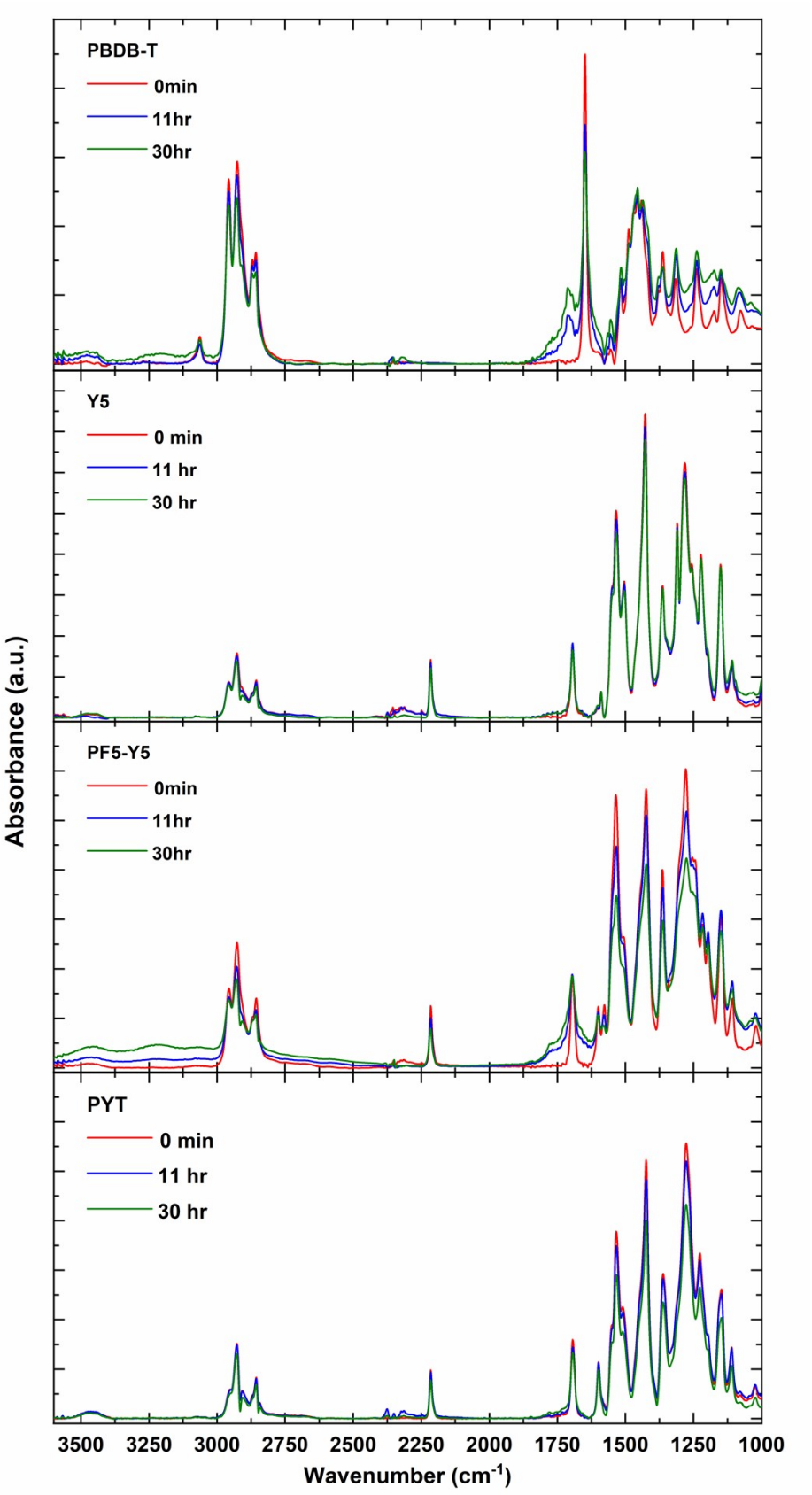


Figure S4: The wide FTIR spectra of PBDB-T, Y5, PF5-Y5, and PYT films, unexposed (0 min) and after exposure to light in air for exposure times 11 hr and 30 hr.

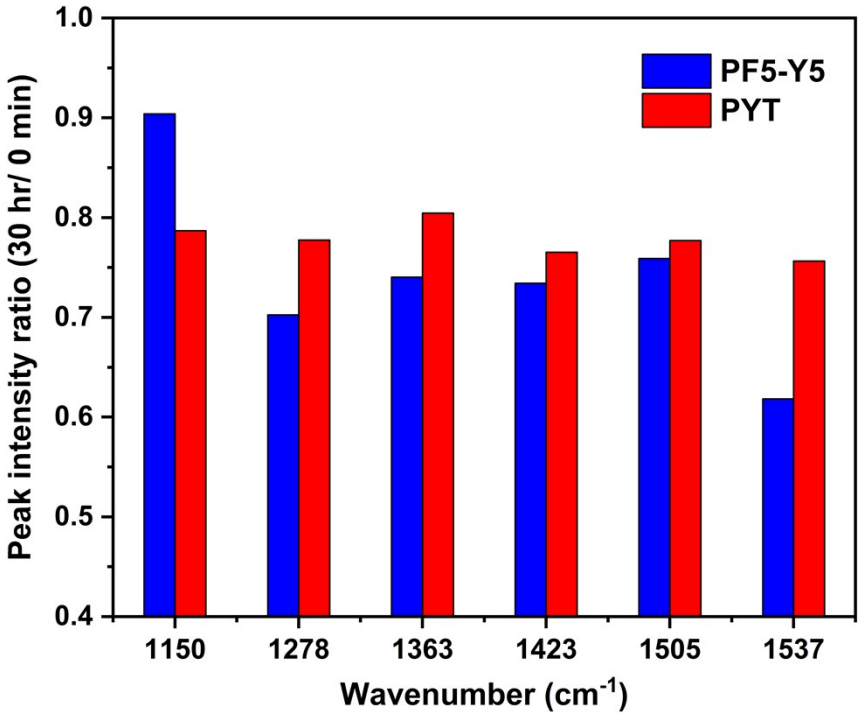


Figure S5: The peak intensity ratio (30 hr/0 min) for selected IR peaks of PF5-Y5 and PYT, extracted from figures 2c and 2d.

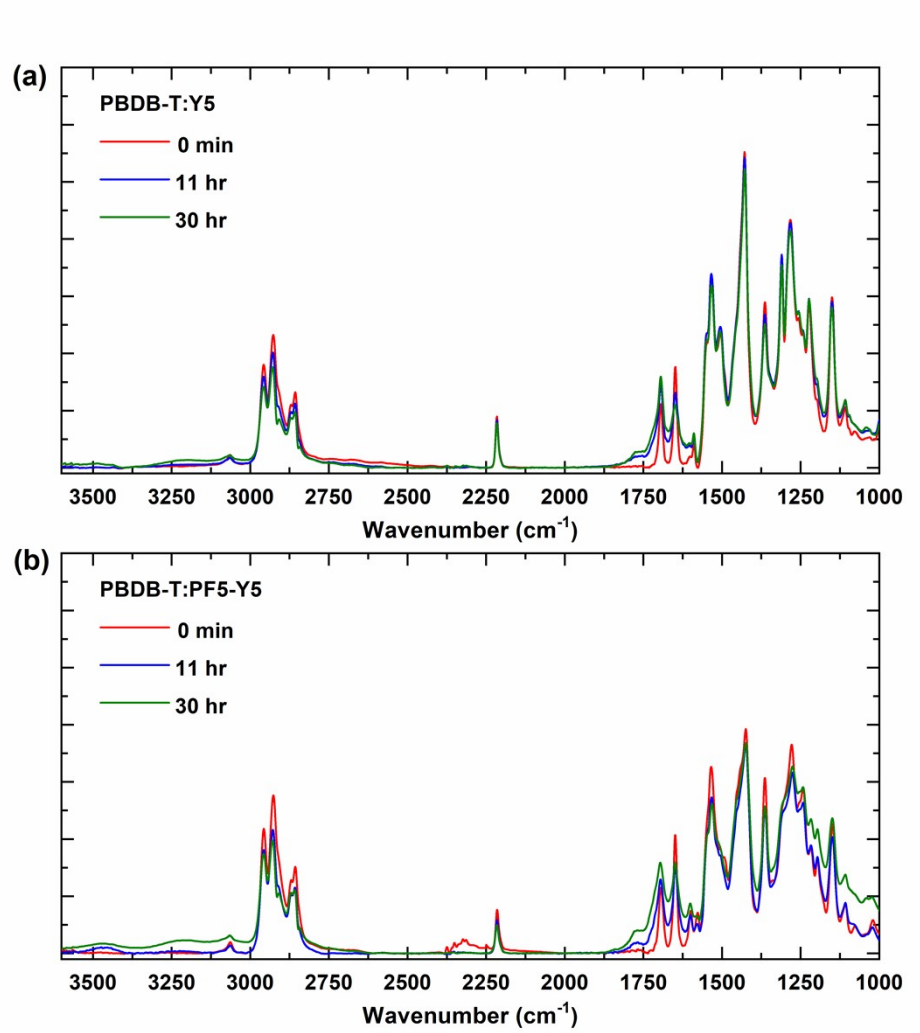


Figure S6: FTIR absorption spectra of PBDB-T:Y5 (1:0.75), and PBDB-T:PF5-Y5 (1:0.75), unexposed (0 min) and after exposure to light in air for exposure times 11 hr, and 30 hr.

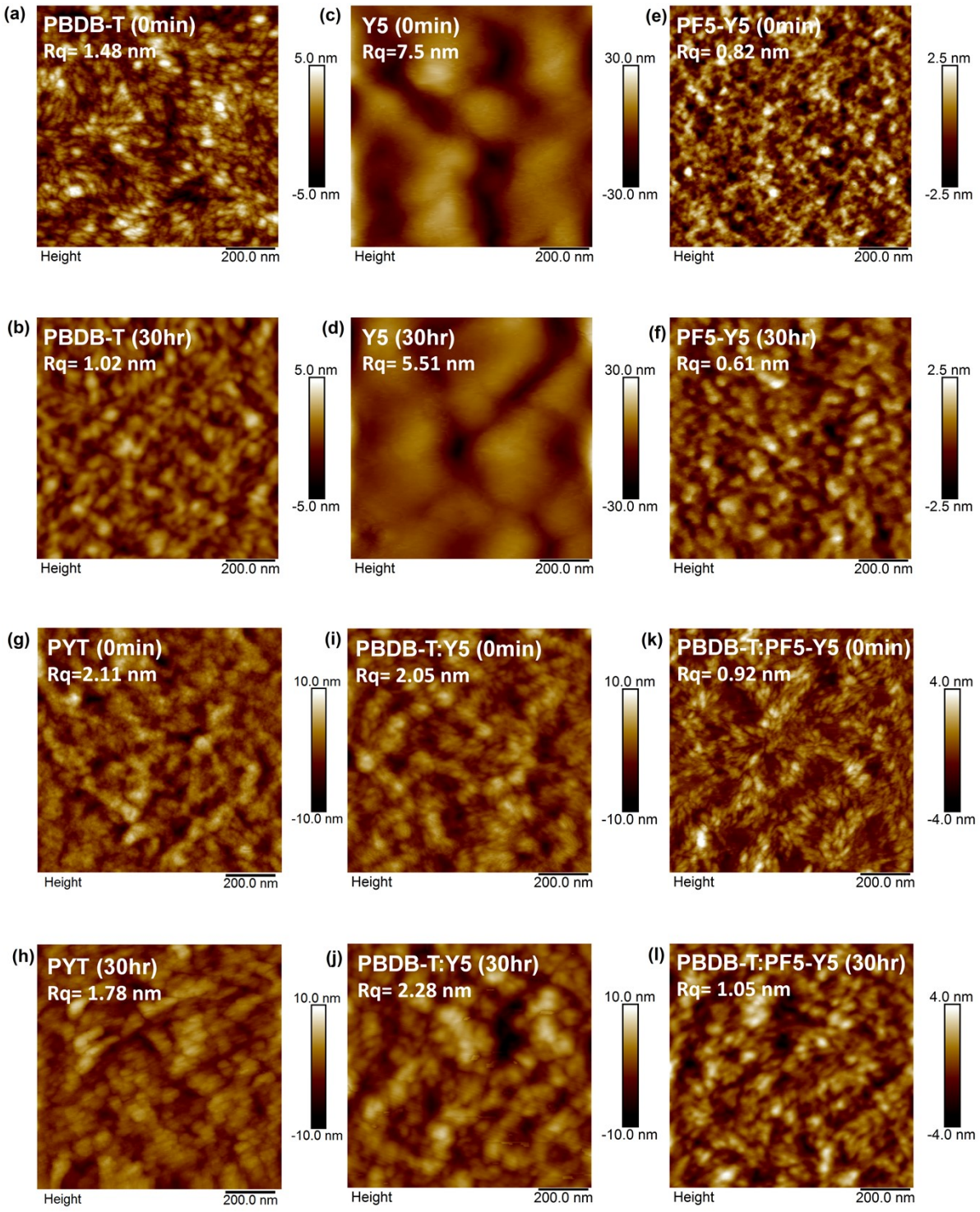


Figure S7: AFM images (1 μm × 1 μm) of spin coated PBDB-T, Y5, PF5-Y5, PYT, PBDB-T:Y5 (1:0.75), and PBDB-T:PF5-Y5 (1:0.75) films for 0 hr and 30 hr exposure times.

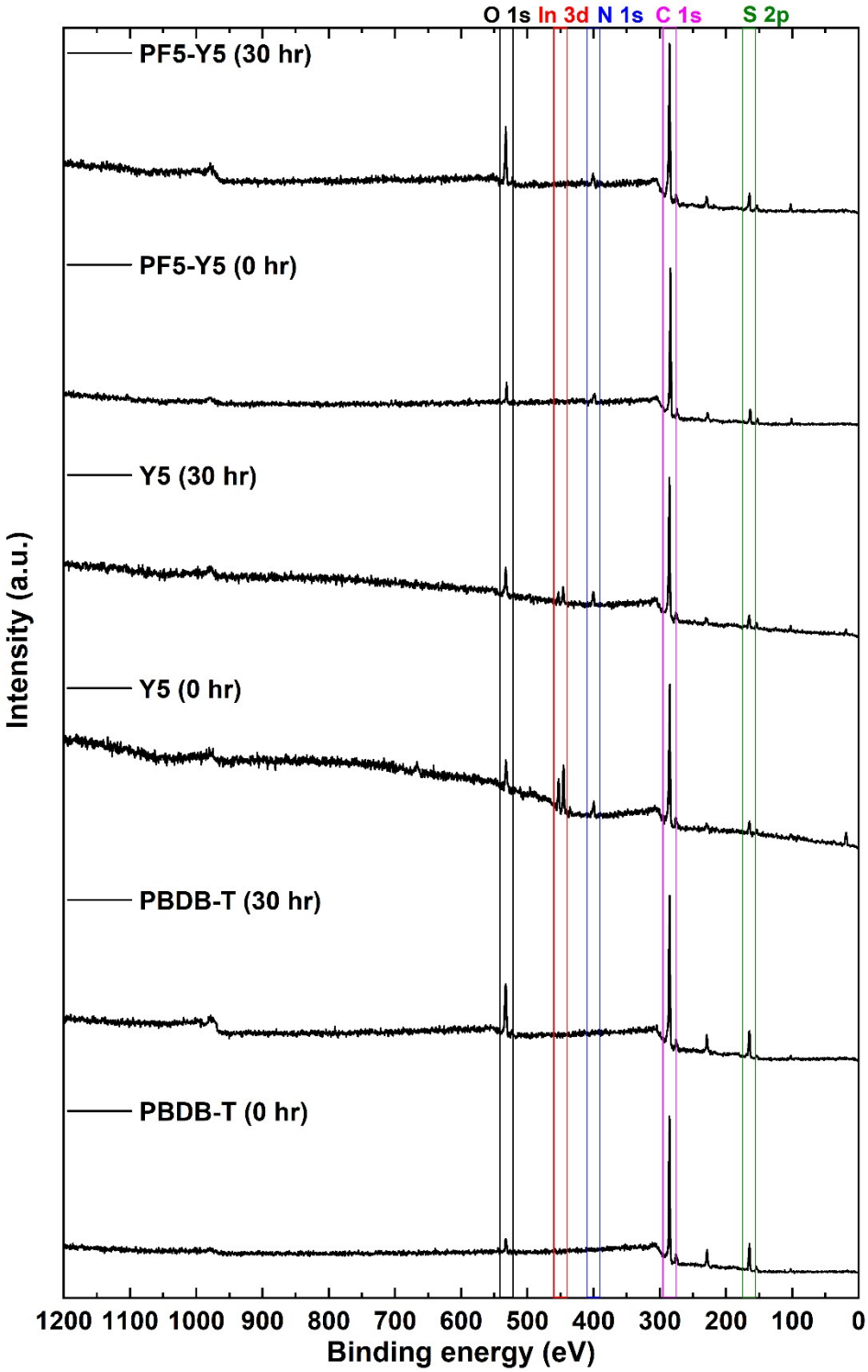


Figure S8: In-house XPS survey spectra of PBDB-T (bottom), Y5 (middle), and PF5-Y5 (top) for 0 hr and 30 hr under AM 1.5 solar simulator in ambient conditions. Apart from the assigned peak, smaller peaks in the spectrum are due to S 2s (229 eV), In 4d (19 eV) from the ITO substrate and traces of Si 2p (102 eV) and Si 2s (153 eV).

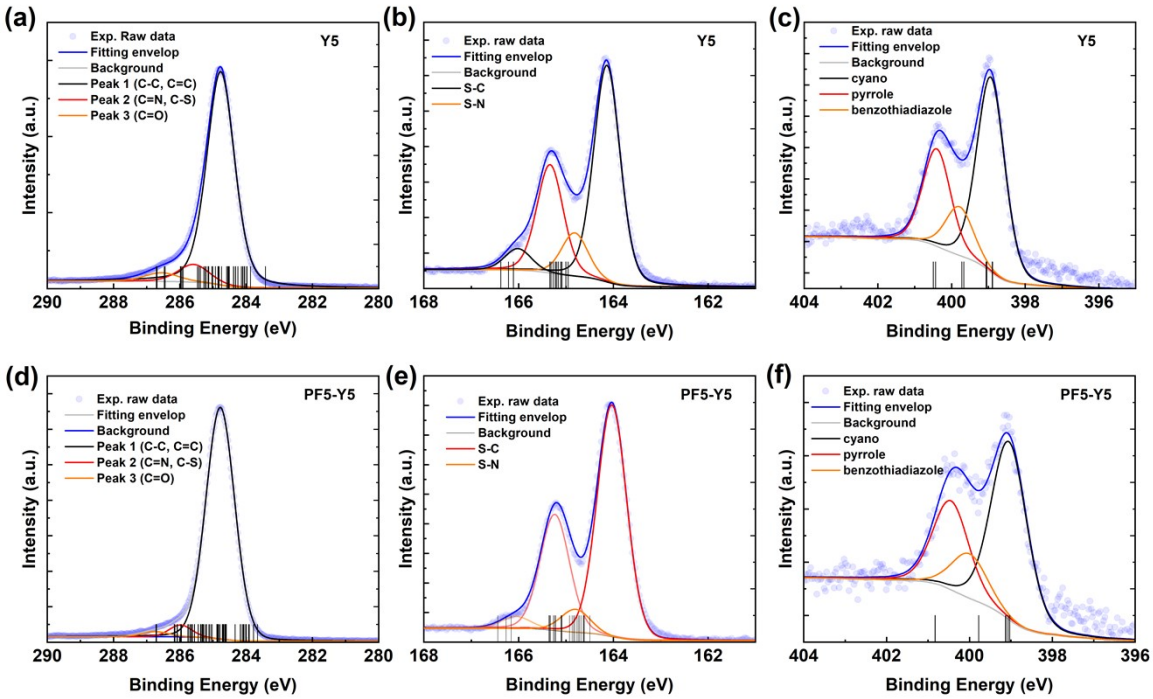


Figure S9: High-resolution and calculated XPS spectra of Y5 and PF5-Y5 (C1s, S2p, and N1s) for unexposed (0 hr) samples. The excitation photon energies used for C 1s, S 2p, and N 1s are 350 eV, 225 eV, and 465 eV.

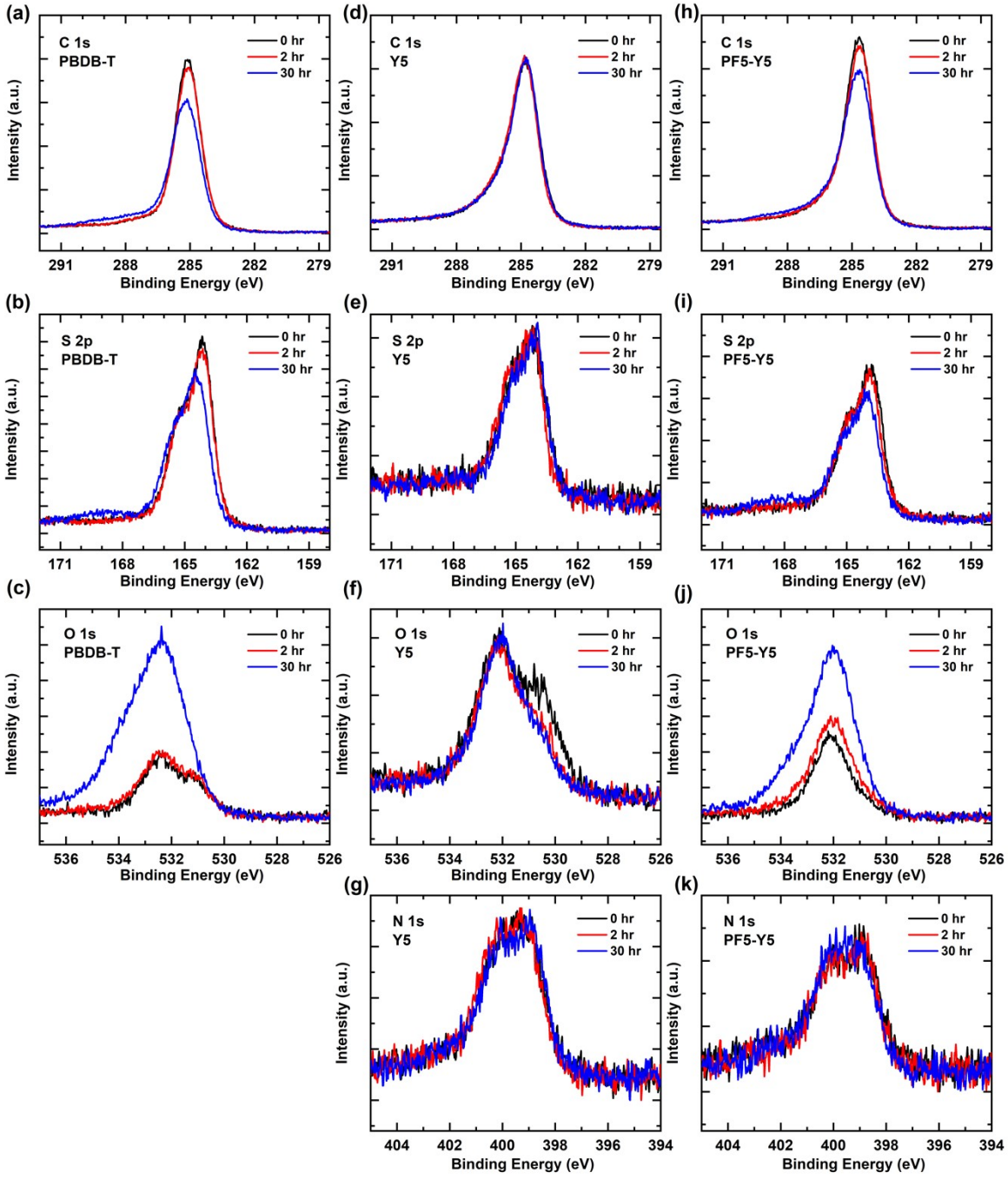


Figure S10: In-house XPS spectra of PBDB-T (left), Y5 (middle) and PF5-Y5 (right) for 0 hr and 30 hr of O 1s and N 1s under AM 1.5 solar simulator in ambient conditions.

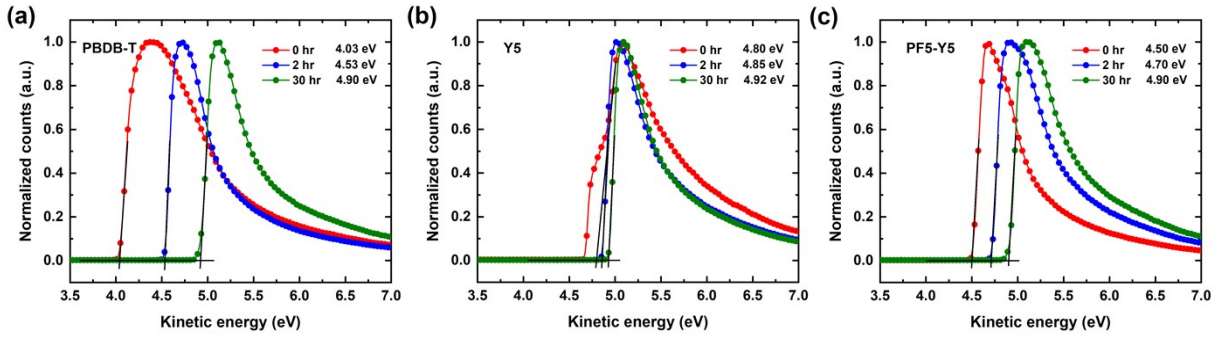
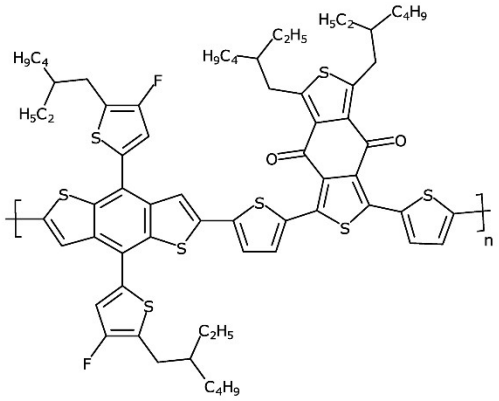
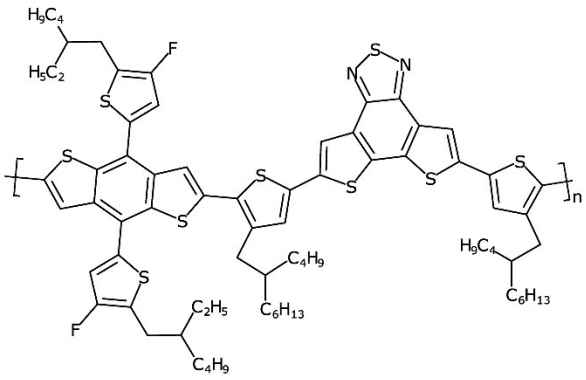


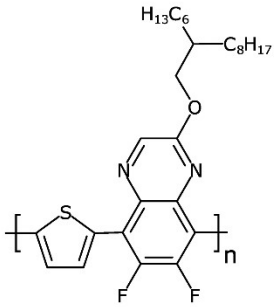
Figure S11: The secondary electron cut-off of (a) PBDB-T, (b) Y5, and (c) PF5-Y5 upon exposure for 0 hr, 2 hr, and 30 hr, measured by UV photoelectron spectroscopy.



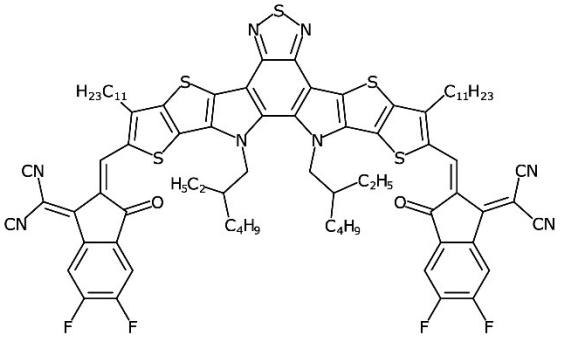
PM6



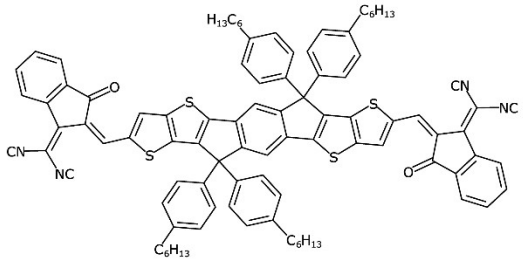
D18



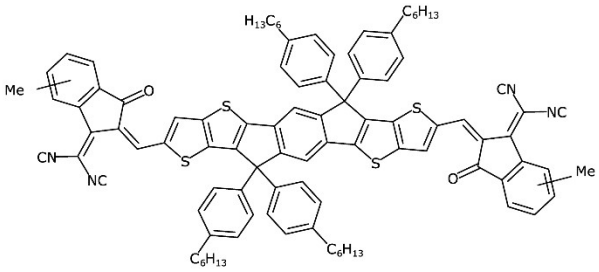
PTQ10



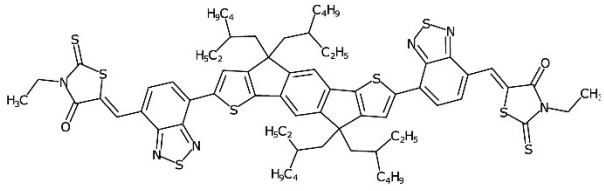
Y6



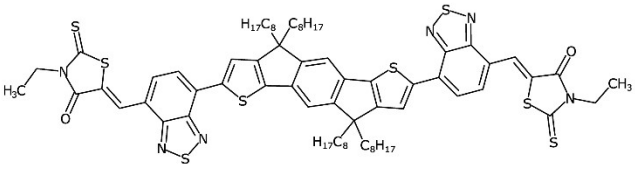
ITIC



ITIC-M



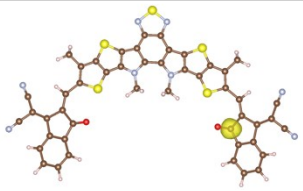
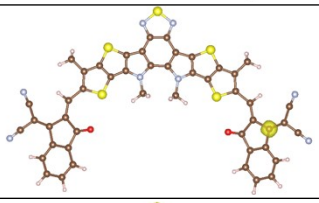
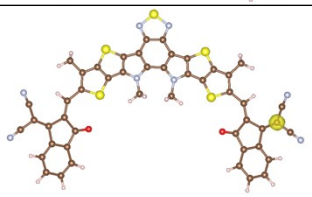
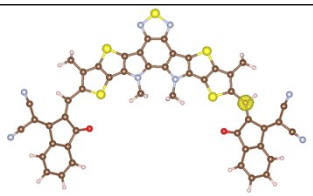
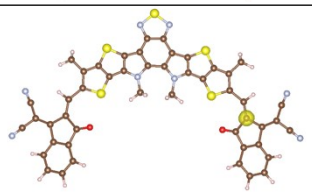
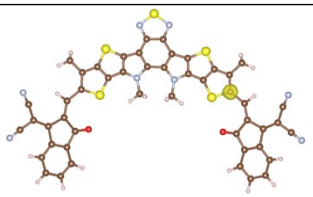
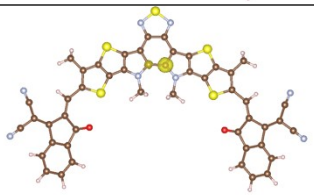
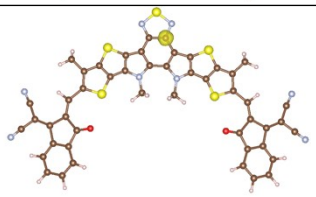
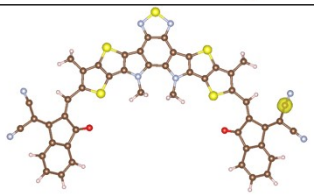
EH-IDTBR



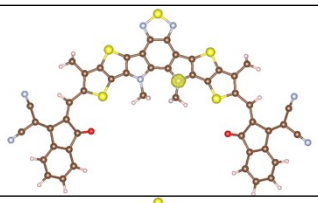
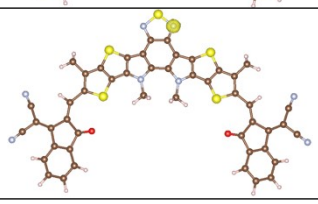
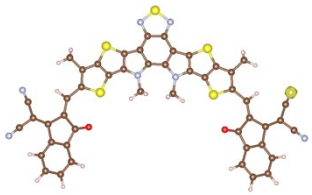
O-IDTBR

Figure S12: Molecular structures of donor polymers PM6, D18, and PTQ10, and NFAs Y6, ITIC, ITIC-M, EH-IDTBR, and O-IDTBR.

Table S1: Calculated Y5 C1s core orbitals.

Energy (eV)	Functional Group	Core Orbital
286.70	-C=O	
286.47	-C-C(CN)2	
285.98	-C-C(CN)2	
285.93	vinylene	
285.47	(CN)2-C-C-C-C=O	
285.43	C-S	
285.28	C-N pyrrole	
285.23	C=N BT	
285.15	C≡N	

Y5 N1s core orbitals.

Energy (eV)	Functional Group	Core Orbital
400.50 400.44	N-C (pyrrole)	
399.72 399.67	N=C (BT)	
399.07 399.05 398.90 398.89	N≡C (cyano)	

Y5 S2p core orbitals.

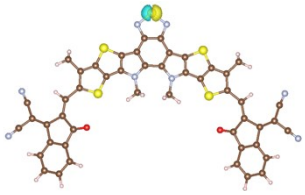
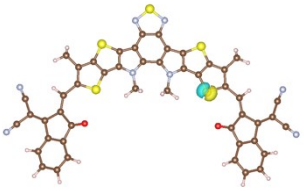
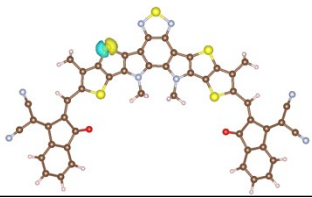
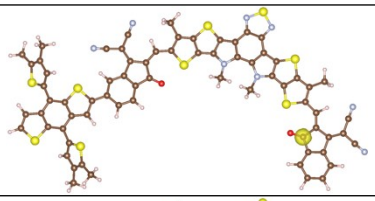
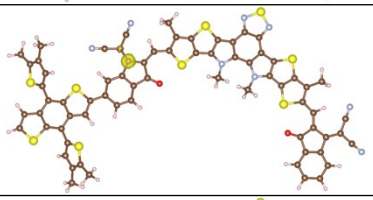
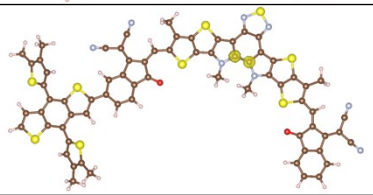
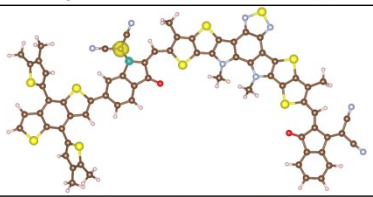
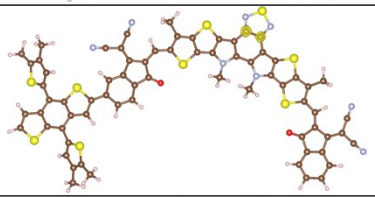
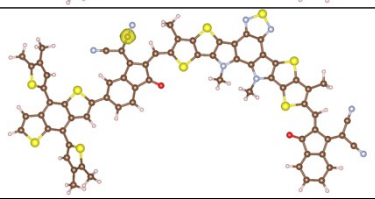
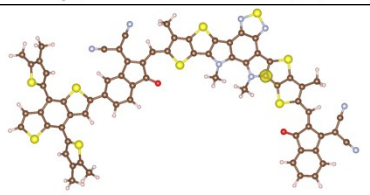
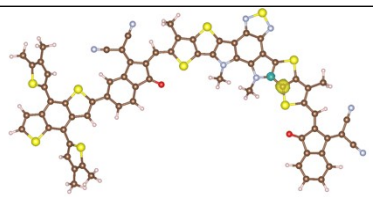
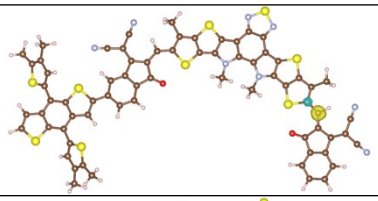
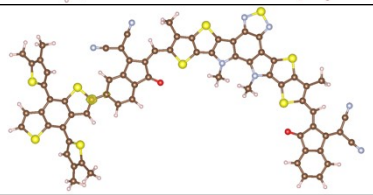
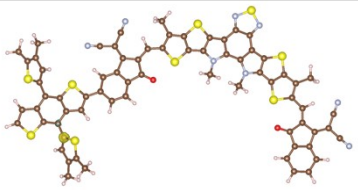
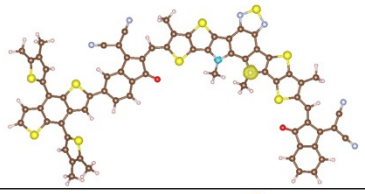
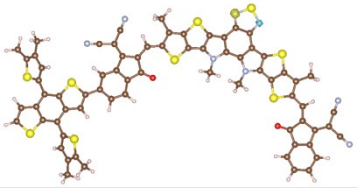
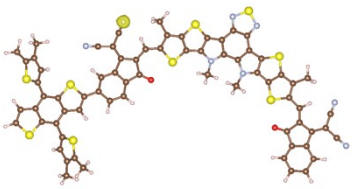
Energy (eV)	Functional Group	Core Orbital
166.38 166.21 166.11	S-N (BT)	
165.34 165.32 165.22 165.19 165.11 165.08	S-C (outer)	
165.27 165.22 165.16 165.11 165.00 164.95	S-C (inner)	

Table S2: Calculated PF5-Y5 C1s core orbitals.

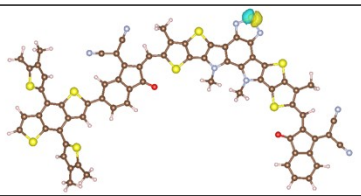
Energy (eV)	Functional Group	Core Orbital
281.32	-C=O	
280.77	-C-C(CN)2	
280.687	C-N pyrrole	
280.547	-C(CN)2	
280.356	C=N BT	
280.296 280.292 280.247 280.222	-C≡N	
280.249 280.244	-C-N (pyrrole)	
280.161 280.153 280.049 280.045 279.909 279.907 279.880	-C-S (Y5 co-monomer)	

279.878		
279.976 279.963	vinylene	
279.822 279.721 279.663	-C-S (BDT fused)	
279.460 279.435	-C-S (BDT side)	

PF5-Y5 N1s core orbitals.

Energy (eV)	Functional Group	Core Orbital
400.83	N-C (pyrrole)	
399.73	N=C (BT)	
399.13 399.12 399.07 399.03	N≡C (cyano)	

PF5-Y5 S2p core orbitals.

Energy (eV)	Functional Group	Core Orbital
166.40 166.28 166.16	S-N (BT)	

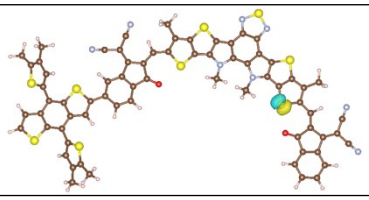
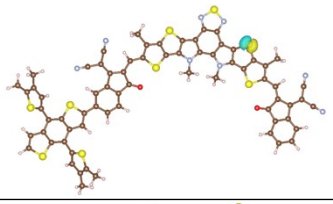
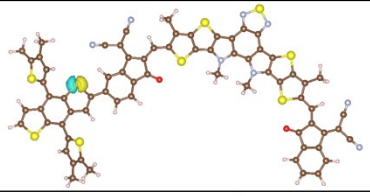
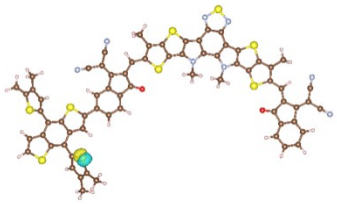
165.34 165.23 165.22 165.09	S-C (outer)	
165.36 165.26 165.16 165.10	S-C (inner)	
164.92 164.87 164.82 164.77 164.70	BDT (fused)	
164.84 164.74 164.71 164.63 164.61 164.49	BDT (side)	

Table S3: Atomic percentage of PBDB-T, Y5, and PF5-Y5 for fresh, 2 hr, and 10 hr, extracted from the survey XPS spectra by CASA XPS.

	Element and Line	Expected	Fresh	2 hr	30 hr
PBDB-T ($C_{68}H_{78}O_2S_8$)	C1s	87.17	87.23	85.37	78.37
	O1s	2.56	1.51	4.22	13.08
	S2p	10.25	11.26	10.24	8.55
	In3d	0.00	0.00	0.11	0.00
	Sn3d	0.00	0.00	0.00	0.00
Y5 ($C_{82}H_{90}N_8O_2S_5$)	C1s	86.31	79.78	82.48	81.75
	N1s	8.42	7.25	5.08	5.75
	O1s	2.10	7.94	6.53	5.13
	S2p	5.26	3.54	5.14	7.20
	In3d	0.00	1.42	0.71	0.17
	Sn3d	0.00	0.07	0.06	0.00
PF5-Y5 ($C_{128}H_{154}N_8O_2S_9$)	C1s	87.07	84.53	84.78	80.72
	N1s	5.44	6.00	4.16	4.58
	O1s	1.36	3.95	5.95	9.50
	S2p	6.12	5.43	5.12	5.19
	In3d	0.00	0.08	0.00	0.00
	Sn3d	0.00	0.00	0.00	0.00

Table S4: Assignment of components and their relative contributions in the XPS C 1s and S 2p core level spectra of PBDB-T, Y5 and PF5-Y5 in Figure 3.

	PBDB-T		Y5		PF5-Y5	
Orbital	Binding energy (eV)	Area (%)	Binding energy (eV)	Area (%)	Binding energy (eV)	Area (%)
C 1s (0 hr)	285.10 (C-C, C=C) 286.64 (C-S), (C=O)	93.04 6.96	284.78 (C-C, C=C) 286.26 (C-S), (C-N), (C=O)	77.75 22.25	284.68 (C-C, C=C) 286.18 (C-S), (C=N), (C=O)	83.97 16.03
C 1s (30 hr)	285.18 (C-C, C=C) 286.68 (C-S), (C=O) 288.64 (Anhydride)	79.43 10.76 9.82	284.78 (C-C, C=C) 286.26 (C-S), (C-N), (C=O)	76.46 23.54	284.68 (C-C, C=C) 286.18 (C-S), (C-N), (C=O) 288.18 (Anhydride)	74.20 18.66 7.14
S 2p (0 hr)	164.13 (S $2p_{3/2}$) (C-S) 165.31 (S $2p_{1/2}$) (C-S)	66.67 33.33	164.08 (S $2p_{3/2}$) (C-S) 165.26 (S $2p_{1/2}$) (C-S) 164.82 (S $2p_{3/2}$) (N-S) 166.00 (S $2p_{1/2}$) (N-S)	54.30 27.15 12.37 6.18	163.74 (S $2p_{3/2}$) (C-S) 164.92 (S $2p_{1/2}$) (C-S) 164.48 (S $2p_{3/2}$) (N-S) 165.66 (S $2p_{1/2}$) (N-S)	56.10 28.05 10.57 5.28
S 2p (30 hr)	164.42 (S $2p_{3/2}$) (C-S) 165.60 (S $2p_{1/2}$) (C-S) 169.12 (S $2p_{3/2}$) (SO_X) 169.30 (S $2p_{1/2}$) (SO_X)	59.71 29.85 6.96 3.483	164.00 (S $2p_{3/2}$) (C-S) 165.18 (S $2p_{1/2}$) (C-S) 164.76 (S $2p_{3/2}$) (N-S) 165.94 (S $2p_{1/2}$) (N-S)	55.50 27.75 11.17 5.58	163.94 (S $2p_{3/2}$) (C-S) 165.12 (S $2p_{1/2}$) (C-S) 164.68 (S $2p_{3/2}$) (N-S) 165.86 (S $2p_{1/2}$) (N-S) 167.74 (S $2p_{3/2}$) (SO_X) 168.92 (S $2p_{1/2}$) (SO_X)	46.95 23.47 8.05 4.02 11.67 5.84

Table S5: The valence band onset (Vb_{onset}), positions of Fermi level (E_f), and highest occupied molecular orbital (HOMO) of PBDB-T, Y5, and PF5-Y5 for 0 hr, 2hr, and 30 hr exposure time. The valence band onset is measured by UPS and the position of the Fermi level (E_f), with respect to the vacuum level, (i.e. the work function) is extracted from the secondary electron cut-off (SECO) in the UPS spectra (figure S11).

Sample	Vb_{onset} (eV)	Fermi level, E_f (eV)	*HOMO (eV)
PBDB-T (0 hr)	1.06	-4.03	-5.09
PBDB-T (2 hr)	0.61	-4.53	-5.14
PBDB-T (30 hr)	0.57	-4.90	-5.47
Y5 (0 hr)	0.92	-4.80	-5.72
Y5 (2 hr)	0.85	-4.85	-5.70
Y5 (30 hr)	0.79	-4.92	-5.71
PF5-Y5 (0 hr)	1.07	-4.50	-5.57
PF5-Y5 (2 hr)	0.99	-4.70	-5.69
PF5-Y5 (30 hr)	0.75	-4.90	-5.65

*HOMO= $E_f + Vb_{onset}$