Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Side Chain Effect on Conjugated Polymers/Fullerenes Interfaces in Organic Solar Cells – A DFT Study

Sarah A. (Ayoub)[1], Jolanta B. (Lagowski)[2]

[1] Department of Physics, King Abdulaziz University, Jeddah 21589, Kingdom of Saudi Arabia.

[2] Department of Physics and Physical Oceanography, Memorial University, St. John's, NL, A1B 3X7, Canada.

sayoub@kau.edu.sa , *jolantal@mun.ca*

Table S1: The results of B97-D3 and B3LYP-D3 binding energies of homogenous and heterogenous pairs with varying the lengths of side chains, and corresponding experimental determined PCEs.

Monomer	n_c	monomer/ monomer	Monomer/PCBM			Monomer/$PC_{71}BM$		
		ΔE_b (eV) B97-D3	ΔE_b (eV) B97-D3	ΔE_b (eV) B3LYP-D3	PCE (%)	ΔE_b (eV) B97-D3	ΔE_b (eV) B3LYP-D3	PCE (%)
P3BT	4	0.91	1.52	1.47	3.2 [1]	1.31	1.23	
P3PT	5	1.01	1.57	1.52	4.3 [1]	1.36	1.28	
P3HT	6	1.11	1.64	1.58	4.6 [1]	1.45	1.37	
P3T	8	1.31	1.69			1.49		
P3T	10	1.51	1.70			1.50		
P3T	12	1.71	1.70			1.51		
P3T	14	1.90	1.70			1.51		
PCDTBT-C2	2	1.84	1.93	1.82		1.77	1.67	
PCDTBT-C8	8	1.99	2.24	2.11	5.2 [2]	2.15	1.95	7.5 [2]
PCDTBT-C12	12	1.99	2.72			2.42		
PBDTTPD-2EH/C6	6	1.38	2.12			1.82		6.6 [3]
PBDTTPD-2EH/C7	7	1.66	2.27	2.36		1.91	1.95	8.5 [3]
PBDTTPD-2EH/C8	8	1.69	2.32	2.39		1.92	1.99	7.5 [3]
PBDTTPD-2EH/C12	12	1.73	2.43			2.09		
PNT4T-C6/C8	6/8	2.88	2.72			2.45		
PNT4T-2OD	8/10	2.76	3.01	2.83		2.80	2.57	10.1 [4]
PNT4T-2DT	10/12	1.77	2.54	2.44		2.33	2.14	
PBTff4T-C6/C8	6/8	1.67	2.17			2.14		
PBTff4T-2OD	8/10	1.65	2.42	2.33	9.6 [4]	2.38	2.22	10.4 [4]
PBTff4T-2DT	10/12	0.65	2.04	1.92		1.97	2.11	
PffBT4T-C6/C8	6/8	3.09	2.40			2.11		
PffBT4T-2OD	8/10	2.20	2.54	2.51	10.4 [4]	2.19	1.89	10.5 [4]
PffBT4T-2DT	10/12	0.88	1.98	2.09		1.73	1.37	7.64 [5]

Table S2: The results of B97-D3 and B3LYP-D3 binding energies of hom

ogenous and heterogenous pairs with varying the number of branched side chains, and corresponding experimental determined PCEs.

Monomer	n_B	monomer/ monomer	Monomer/PCBM			Monomer/$PC_{71}BM$		
		ΔE_b (eV) B97-D3	ΔE_b (eV) B97-D3	ΔE_b (eV) B3LYP-D3	PCE (%)	ΔE_b (eV) B97-D3	ΔE_b (eV) B3LYP-D3	PCE (%)
P3HT	0	1.11	1.64	1.58	3.48 [6]	1.45	1.37	
P3HT-*co*-EHT	1	0.99	1.69	1.68	3.85 [6]	1.39	1.47	
P3EHT	2	0.93	1.28	1.13	0.83 [6]	1.13	1.13	
PBDTTPD-C12/C8	0	2.49	2.53	2.83		2.17	2.61	3.2[3]
PBDTTPD-2EH/C8	1	1.69	2.32	2.39		1.99	1.99	6-7.5 [3, 7]
PBDTTPD-2EH/EH	2	1.36	2.12			1.75		3.2
PTB1	0	3.07	2.74		4.8[8]	2.40		5.6[8]
PTB4	1	2.10	2.37	2.25	6.1[8]	2.20	1.99	7.1[8]
PTB7	2	1.77	2.22	2.30		2.01	2.11	7.4

Table S3: The results of B97-D3 and B3LYP-D3 binding energies of homogenous and heterogenous pairs with varying the branching positions of branched side chains, and the corresponding experimental determined PCEs.

Monomer/Monomer	P_B	monomer/ monomer	Monomer/PCBM			Monomer/$PC_{71}BM$		
		ΔE_b (eV) B97-D3	ΔE_b (eV) B97-D3	ΔE_b (eV) B3LYP-D3	PCE (%) [4]	ΔE_b (eV) B97-D3	ΔE_b (eV) B3LYP-D3	PCE (%) [4]
PNT4T-1ON	1	3.22	2.70	2.56		2.57	2.30	
PNT4T-2OD	2	2.76	3.01	2.83		2.80	2.57	10.1
PNT4T-3OT	3	3.22	2.43	2.27		2.83	2.23	
PBTff4T-1ON	1	1.50	2.38	2.49		2.09	1.91	
PBTff4T-2OD	2	1.65	2.42	2.33	9.6	2.38	2.22	10.4
PBTff4T-3OT	3	2.36	1.94	2.18		2.28	2.11	
PffBT4T-1ON	1	2.81	2.05	1.88		1.76	1.92	
PffBT4T-2OD	2	2.20	2.54	2.51	10.4	2.19	2.09	10.5
PffBT4T-3OT	3	2.92	2.21	2.76			2.56	

Table S4: The electronic offsets of isolated monomers and fullerenes calculated at the B3LYP method.

Isolated Monomers	Electronic Offsets from PCBM				Electronic Offsets from $PC_{71}BM$			
	$\Delta\epsilon_{HOMO}$	$\Delta\epsilon_{LUMO}$	$\Delta\epsilon_{H_D-L_A}-0$	$\frac{\Delta\epsilon_{H_D-L_A}-0.}{E_{g(monomer)}}$	$\Delta\epsilon_{HOMO}$	$\Delta\epsilon_{LUMO}$	$\Delta\epsilon_{H_D-L_A}-0.$	$\frac{\Delta\epsilon_{H_D-L_A}-0.}{E_{g(monomer)}}$
P3BT	0.22	1.98	2.03	0.47	0.22	2.00	2.01	0.47
P3PT	0.23	1.98	2.02	0.47	0.23	2.00	2.00	0.47
P3HT	0.22	1.99	2.03	0.47	0.22	2.01	2.01	0.47
P3HT-co-EHT	0.23	1.96	2.02	0.47	0.23	1.98	2.00	0.47
P3EHT	0.27	1.91	1.98	0.47	0.27	1.93	1.96	0.47
PCDTBT-C2	0.59	0.47	1.66	0.68	0.59	0.49	1.64	0.68
PCDTBT-C8	0.60	0.47	1.65	0.68	0.60	0.49	1.63	0.67
PBDTTPD-2EH/C7	0.40	0.86	1.85	0.61	0.40	0.88	1.83	0.61
PBDTTPD-2EH/C8	0.43	0.87	1.82	0.61	0.43	0.89	1.80	0.60
PBDTTPD-C12/C8	0.28	0.82	1.97	0.64	0.28	0.84	1.95	0.63
PTB4	0.43	1.01	1.82	0.58	0.43	1.03	1.80	0.58
PTB7	0.42	0.97	1.83	0.59	0.42	0.99	1.81	0.58
PNT4T-1ON	0.46	0.15	1.79	0.80	0.46	0.17	1.77	0.79
PNT4T-2OD	0.53	0.12	1.72	0.80	0.53	0.14	1.70	0.79
PNT4T-3OT	0.60	0.14	1.65	0.79	0.60	0.16	1.63	0.78
PNT4T-2DT	0.59	0.12	1.66	0.80	0.59	0.14	1.64	0.79
PBTff4T-1ON	0.52	0.39	1.73	0.72	0.52	0.41	1.71	0.71
PBTff4T-2OD	0.58	0.35	1.67	0.72	0.58	0.37	1.65	0.71
PBTff4T-3OT	0.59	0.39	1.66	0.71	0.59	0.41	1.64	0.70
PBTff4T-2DT	0.50	0.35	1.75	0.73	0.50	0.37	1.73	0.72
Pff4TBT-1ON	0.50	0.33	1.75	0.73	0.50	0.35	1.73	0.73
Pff4TBT-2OD	0.54	0.32	1.71	0.73	0.54	0.34	1.69	0.73

Pff4TBT-3OT	0.63	0.32	1.62	0.72	0.63	0.34	1.60	0.71
Pff4TBT-2DT	0.51	0.30	1.74	0.74	0.51	0.32	1.72	0.74

Table S5: The electronic offsets of the interacting monomers and fullerenes calculated at the SP B3LYP method using the B97-D3 optimized geometries.

Interacting Monomers	Electronic Offsets from PCBM				Electronic Offsets from $PC_{71}BM$			
	$\Delta\epsilon_{HOMO}$	$\Delta\epsilon_{LUMO}$	$\Delta\epsilon_{H_D-L_A}-0$	$\frac{\Delta\epsilon_{H_D-L_A}-0.}{E_{g(monomer)}}$	$\Delta\epsilon_{HOMO}$	$\Delta\epsilon_{LUMO}$	$\Delta\epsilon_{H_D-L_A}-0.$	$\frac{\Delta\epsilon_{H_D-L_A}-0.}{E_{g(monomer)}}$
P3BT	0.43	2.00	1.80	2.03	0.36	1.99	1.81	2.03
P3PT	0.44	2.00	1.79	2.02	0.37	2.00	1.81	2.03
P3HT	0.44	2.01	1.79	2.02	0.36	2.00	1.81	2.03
P3HT-co-EHT	0.38	2.02	1.85	2.08	0.38	1.98	1.79	2.02
P3EHT	0.38	2.00	1.85	2.08	0.23	2.14	1.94	2.17
PCDTBT-C2	0.68	0.56	1.55	1.73	0.58	0.53	1.59	1.76
PCDTBT-C8	0.64	0.51	1.60	1.77	0.59	0.53	1.59	1.76
PBDTTPD-2EH/C7	0.47	1.00	1.76	0.58	0.45	0.99	1.72	0.57
PBDTTPD-2EH/C8	0.45	1.01	1.78	0.58	0.46	0.99	1.71	0.57
PBDTTPD-C12/C8	0.42	0.96	1.81	0.59	0.38	0.95	1.80	0.59
PTB4	0.61	0.98	1.62	0.56	0.52	0.97	1.65	0.56
PTB7	0.61	0.97	1.62	0.56	0.52	0.95	1.66	0.57
PNT4T-1ON	0.55	0.19	1.69	0.78	0.45	0.18	1.73	0.78
PNT4T-2OD	0.75	0.19	1.49	0.75	0.71	0.18	1.47	0.76
PNT4T-3OT	0.70	0.22	1.54	0.75	0.43	0.18	1.75	0.78
PNT4T-2DT	0.75	0.19	1.49	0.75	0.71	0.18	1.47	0.76
PBTff4T-1ON	0.69	0.31	1.54	0.72	0.43	0.38	1.74	0.72
PBTff4T-2OD	0.60	0.41	1.64	0.70	0.50	0.37	1.67	0.71
PBTff4T-3OT	0.64	0.46	1.60	0.68	0.54	0.42	1.63	0.69
PBTff4T-2DT	0.59	0.40	1.65	0.70	0.50	0.36	1.68	0.72
Pff4TBT-1ON	0.61	0.41	1.63	0.70	0.48	0.35	1.70	0.72
Pff4TBT-2OD	0.65	0.44	1.59	0.68	0.40	0.32	1.77	0.74

Pff4TBT-3OT	0.67	0.35	1.56	0.71	0.51	0.32	1.66	0.73
Pff4TBT-2DT	0.59	0.30	1.64	0.73	0.47	0.29	1.69	0.74

Table S6: The electronic offsets of the interacting monomers and fullerenes calculated at the SP B3LYP method using the B3LYP-D3 optimized geometries.

Interacting Monomers	Electronic Offsets from PCBM				Electronic Offsets from $PC_{71}BM$			
	$\Delta\epsilon_{HOMO}$	$\Delta\epsilon_{LUMO}$	$\Delta\epsilon_{H_D-L_A}-0.$	$\frac{\Delta\epsilon_{H_D-L_A}-0.}{E_{g(monomer)}}$	$\Delta\epsilon_{HOMO}$	$\Delta\epsilon_{LUMO}$	$\Delta\epsilon_{H_D-L_A}-0.$	$\frac{\Delta\epsilon_{H_D-L_A}-0.}{E_{g(monomer)}}$
P3BT	0.38	2.02	1.89	0.45	0.32	2.00	1.91	0.45
P3PT	0.39	2.02	1.89	0.45	0.33	2.00	1.91	0.45
P3HT	0.39	2.02	1.88	0.45	0.33	2.00	1.91	0.45
P3HT-co-EHT	0.27	2.09	2.00	0.46	0.34	1.98	1.89	0.45
P3EHT	0.35	2.00	1.92	0.45	0.19	2.15	2.05	0.45
PCDTBT-C2	0.62	0.59	1.65	0.65	0.53	0.54	1.70	0.67
PCDTBT-C8	0.59	0.61	1.68	0.65	0.53	0.56	1.71	0.67
PBDTTPD-2EH/C7	0.42	1.08	1.85	0.57	0.43	0.99	1.80	0.58
PBDTTPD-2EH/C8	0.43	1.07	1.84	0.57	0.44	1.01	1.79	0.58
PBDTTPD-C12/C8	0.42	1.00	1.85	0.59	0.38	0.98	1.86	0.59
PTB4	0.55	1.01	1.72	0.57	0.51	0.99	1.73	0.57
PTB7	0.56	1.00	1.71	0.57	0.49	0.97	1.75	0.58
PNT4T-1ON	0.34	0.18	1.93	0.80	0.41	0.22	1.83	0.78
PNT4T-2OD	0.61	0.23	1.66	0.76	0.64	0.19	1.60	0.77
PNT4T-3OT	0.56	0.26	1.72	0.76	0.55	0.26	1.69	0.75
PNT4T-2DT	0.61	0.22	1.66	0.76	0.63	0.19	1.61	0.77
PBTff4T-1ON	0.61	0.35	1.66	0.72	0.20	0.42	2.04	0.74
PBTff4T-2OD	0.54	0.44	1.74	0.70	0.46	0.36	1.77	0.73
PBTff4T-3OT	0.60	0.54	1.67	0.67	0.50	0.44	1.74	0.68
PBTff4T-2DT	0.51	0.45	1.76	0.70	0.46	0.35	1.78	0.73

Pff4TBT-1ON	0.49	0.43	1.79	0.71	0.41	0.33	1.82	0.74
Pff4TBT-2OD	0.38	0.46	1.89	0.71	0.32	0.37	1.92	0.74
Pff4TBT-3OT	0.33	0.45	1.93	0.72	0.41	0.37	1.82	0.73
Pff4TBT-2DT	0.34	0.47	1.93	0.72	0.30	0.37	1.93	0.74

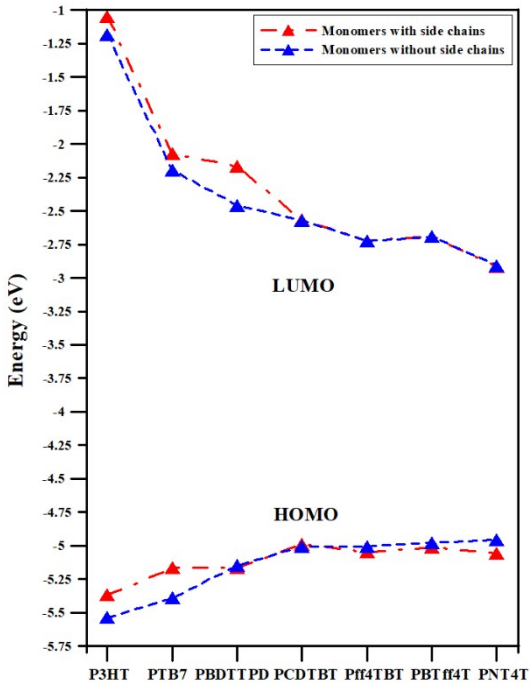
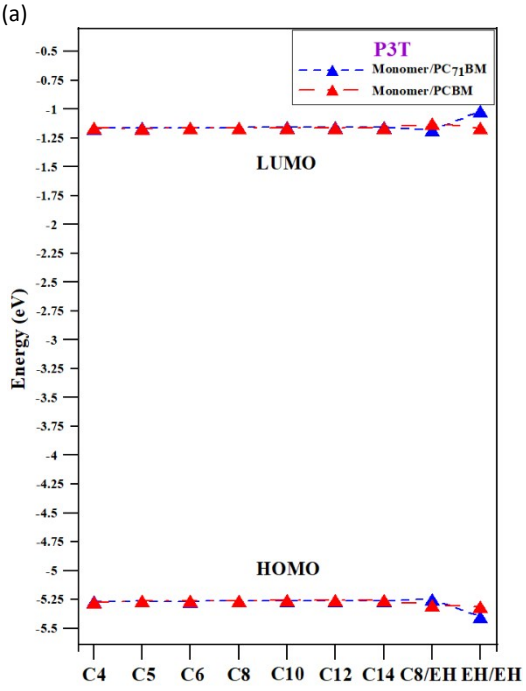
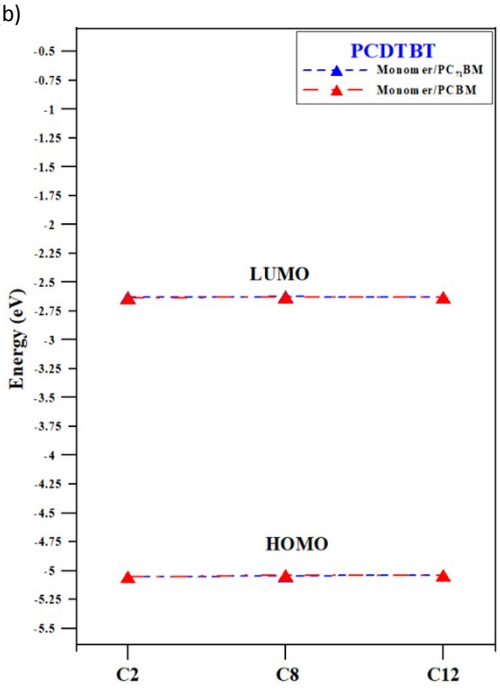


Figure S1: Energy levels of gas phase monomers with and without side chains calculated at the B3LYP method.

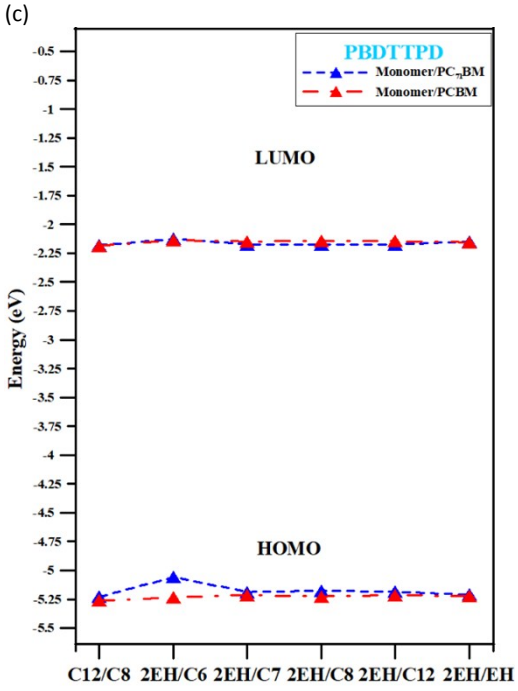
(a)


P3T
Monomer/PC71BM
Monomer/PCBM
LUMO
HOMO
Energy (eV)
-0.5
-0.75
-1
-1.25
-1.5
-1.75
-2
-2.25
-2.5
-2.75
-3
-3.25
-3.5
-3.75
-4
-4.25
-4.5
-4.75
-5
-5.25
-5.5
C4
C5
C6
C8
C10
C12
C14
C8/EH
EH/EH

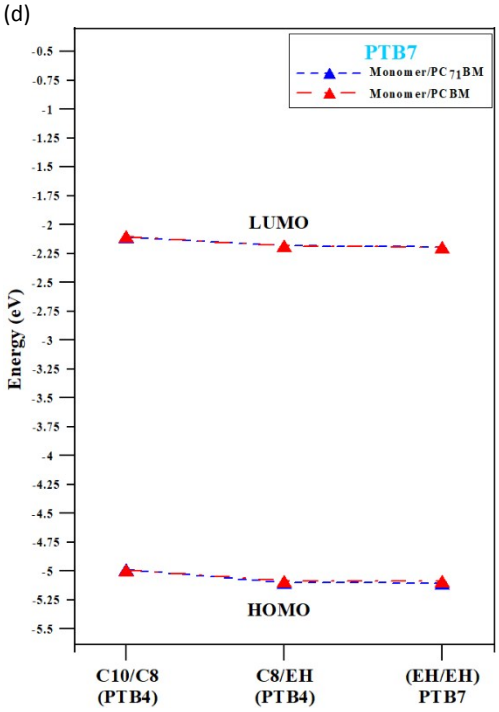
(b)


PCDTBT
Monomer/PCnBM
Monomer/PCBM
LUMO
HOMO
Energy (eV)
-0.5
-0.75
-1
-1.25
-1.5
-1.75
-2
-2.25
-2.5
-2.75
-3
-3.25
-3.5
-3.75
-4
-4.25
-4.5
-4.75
-5
-5.25
-5.5
C2
C8
C12

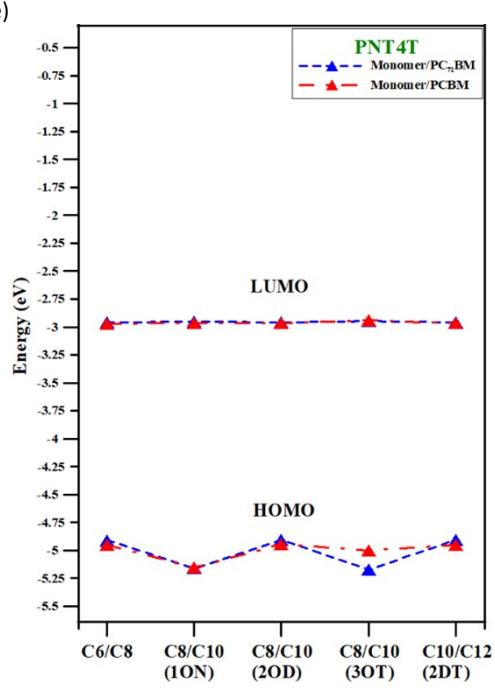
(c)


PBDTTPD
Monomer/PC71BM
Monomer/PCBM
LUMO
HOMO
Energy (eV)
-0.5
-0.75
-1
-1.25
-1.5
-1.75
-2
-2.25
-2.5
-2.75
-3
-3.25
-3.5
-3.75
-4
-4.25
-4.5
-4.75
-5
-5.25
-5.5
C12/C8
2EH/C6
2EH/C7
2EH/C8
2EH/C12
2EH/EH

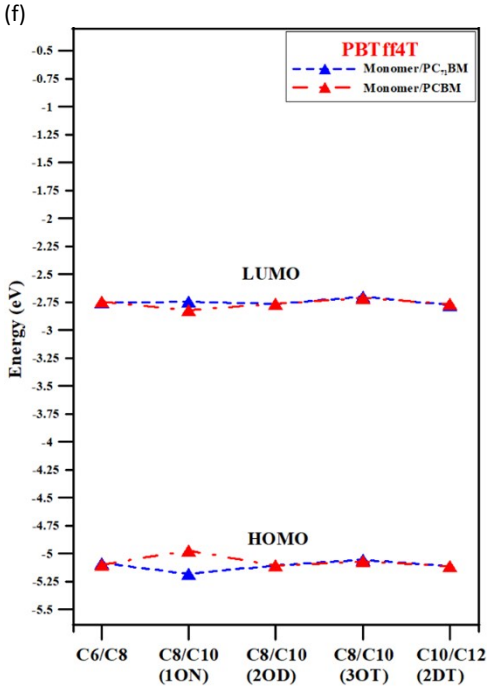
(d)


PTB7
Monomer/PC71BM
Monomer/PCBM
LUMO
HOMO
Energy (eV)
-0.5
-0.75
-1
-1.25
-1.5
-1.75
-2
-2.25
-2.5
-2.75
-3
-3.25
-3.5
-3.75
-4
-4.25
-4.5
-4.75
-5
-5.25
-5.5
C10/C8
(PTB4)
C8/EH
(PTB4)
(EH/EH)
PTB7

(e)


PNT4T
Monomer/PC71BM
Monomer/PCBM
LUMO
HOMO
Energy (eV)
-0.5
-0.75
-1
-1.25
-1.5
-1.75
-2
-2.25
-2.5
-2.75
-3
-3.25
-3.5
-3.75
-4
-4.25
-4.5
-4.75
-5
-5.25
-5.5
C6/C8
C8/C10 (1ON)
C8/C10 (2OD)
C8/C10 (3OT)
C10/C12 (2DT)

(f)


PBTff4T
Monomer/PC71BM
Monomer/PCBM
LUMO
HOMO
Energy (eV)
-0.5
-0.75
-1
-1.25
-1.5
-1.75
-2
-2.25
-2.5
-2.75
-3
-3.25
-3.5
-3.75
-4
-4.25
-4.5
-4.75
-5
-5.25
-5.5
C6/C8
C8/C10 (1ON)
C8/C10 (2OD)
C8/C10 (3OT)
C10/C12 (2DT)

(g)

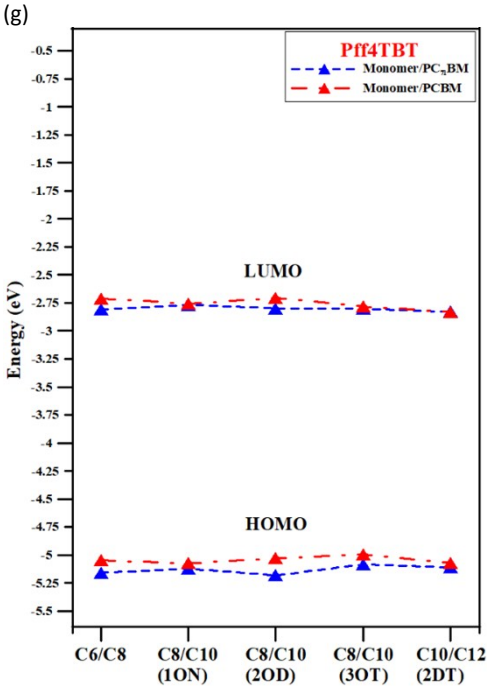


Figure S2: The energy levels of interacting (a) P3T, (b) PCDTBT, (c) PBDTTPD, (d) PTB7, (e) PNT4T, (f) PBTff4T, and (g) Pff4TBT with various side chains, and with two types of fullerenes, calculated at the SP B3LYP using the B97-D3 optimized geometries.

References

1. A. Gadisa, W. D. Oosterbaan, K. Vandewal, J. C. Bolsee, S. Bertho, J. D'Haen, L. Lutsen, D. Vanderzande and J. V. Manca, *Advanced Functional Materials*, 2009, **19**, 3300-3306.
2. S. Beaupre and M. Leclerc, *Journal of Materials Chemistry A*, 2013, **1**, 11097-11105.
3. C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. J. Frechet, M. D. McGehee and P. M. Beaujuge, *Journal of the American Chemical Society*, 2013, **135**, 4656-4659.
4. Y. H. Liu, J. B. Zhao, Z. K. Li, C. Mu, W. Ma, H. W. Hu, K. Jiang, H. R. Lin, H. Ade and H. Yan, *Nature Communications*, 2014, **5**, 5293.
5. Z. H. Chen, P. Cai, J. W. Chen, X. C. Liu, L. J. Zhang, L. F. Lan, J. B. Peng, Y. G. Ma and Y. Cao, *Advanced Materials*, 2014, **26**, 2586-2591.
6. B. Burkhart, P. P. Khlyabich and B. C. Thompson, *Macromolecules*, 2012, **45**, 3740-3748.
7. K. R. Graham, C. Cabanetos, J. P. Jahnke, M. N. Idso, A. El Labban, G. O. N. Ndjawa, T. Heumueller, K. Vandewal, A. Salleo, B. F. Chmelka, A. Amassian, P. M. Beaujuge and M. D. McGehee, *Journal of the American Chemical Society*, 2014, **136**, 9608-9618.
8. J. M. Szarko, J. C. Guo, Y. Y. Liang, B. Lee, B. S. Rolczynski, J. Strzalka, T. Xu, S. Loser, T. J. Marks, L. P. Yu and L. X. Chen, *Advanced Materials*, 2010, **22**, 5468-5472.