Electronic Supplementary Information (ESI)

Effect of π-bridge units on properties of A-π-D-π-A type nonfullerene acceptors for organic solar cells

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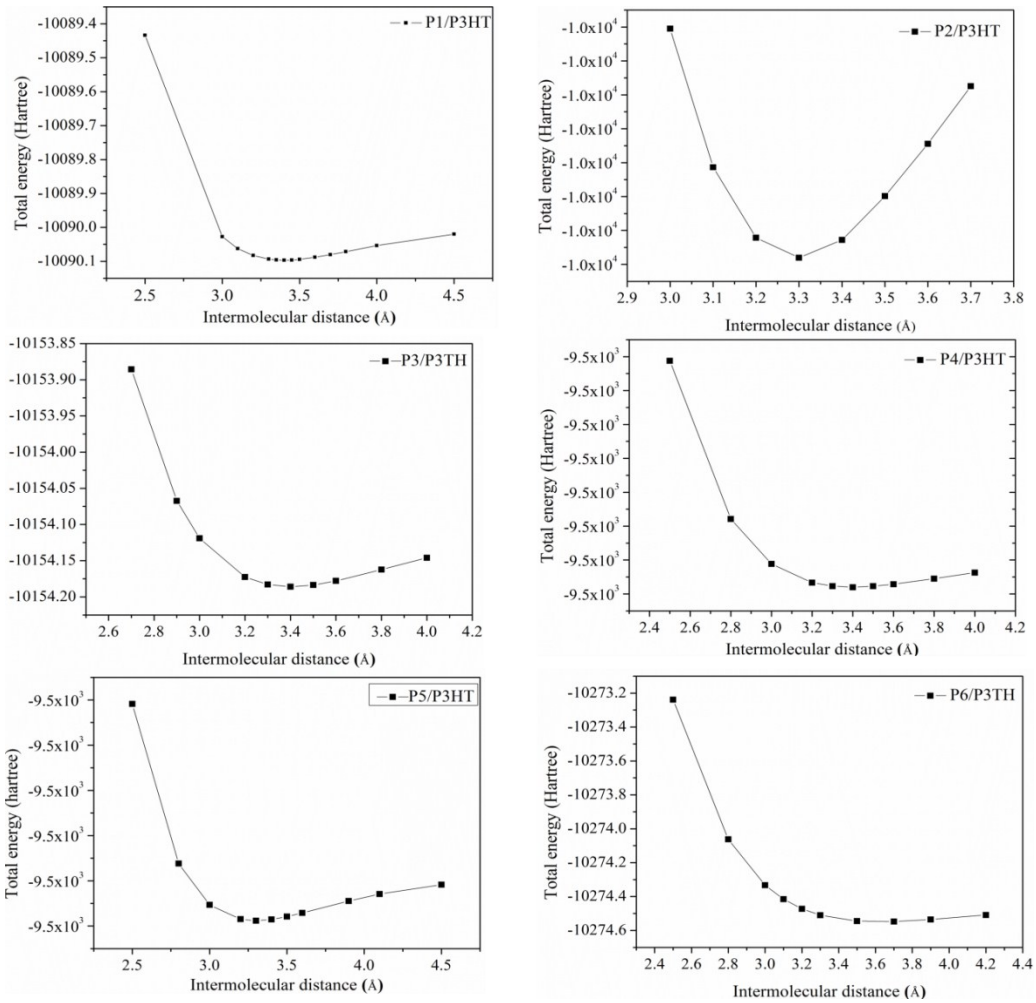

Fig. S1. The optimized total energies for adjacent fragments of P3HT/P1-P6 with respect to the intermolecular distance from M06-2X-D3/6-311G (d, p) calculation.

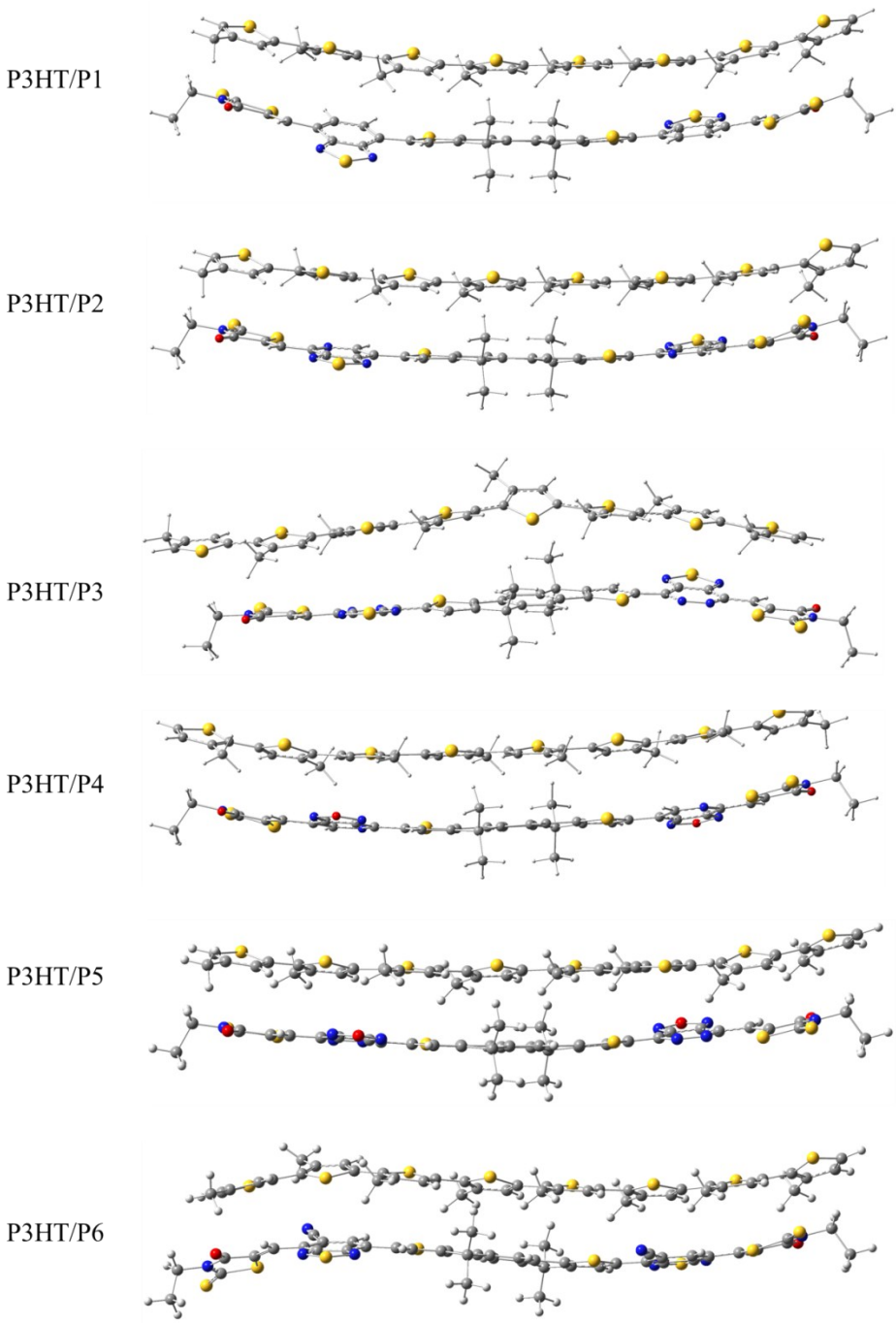

Fig.S2. The optimal three-dimensional models for P3HT/P1-P6 blends.

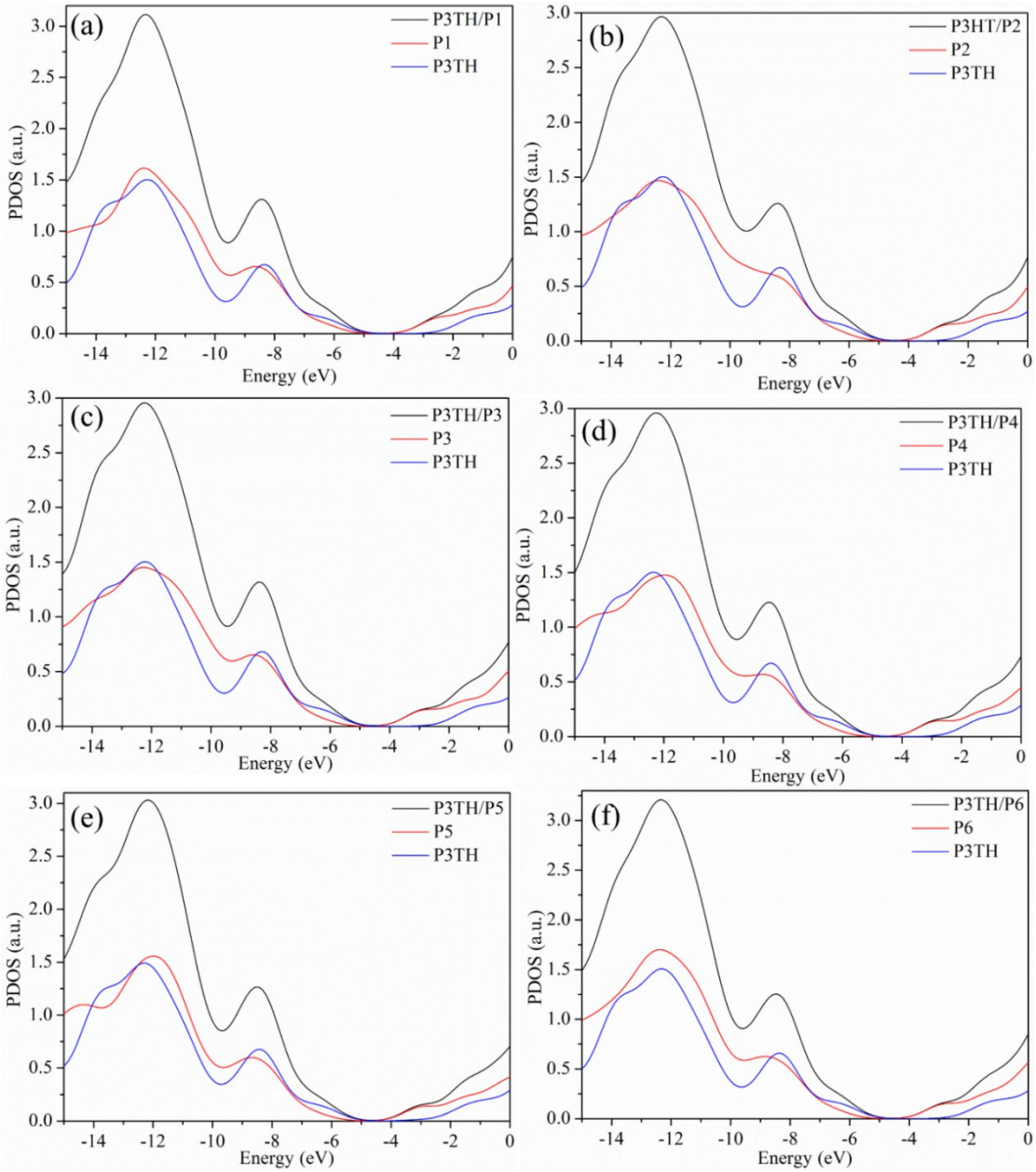

Fig.S3. Total densities of states (TDOS) and projected DOS (PDOS) for the donor/acceptor blends of active layers, which (a, b, c, d, e, f) represent P3TH/P1 to P3TH/P6 blends.

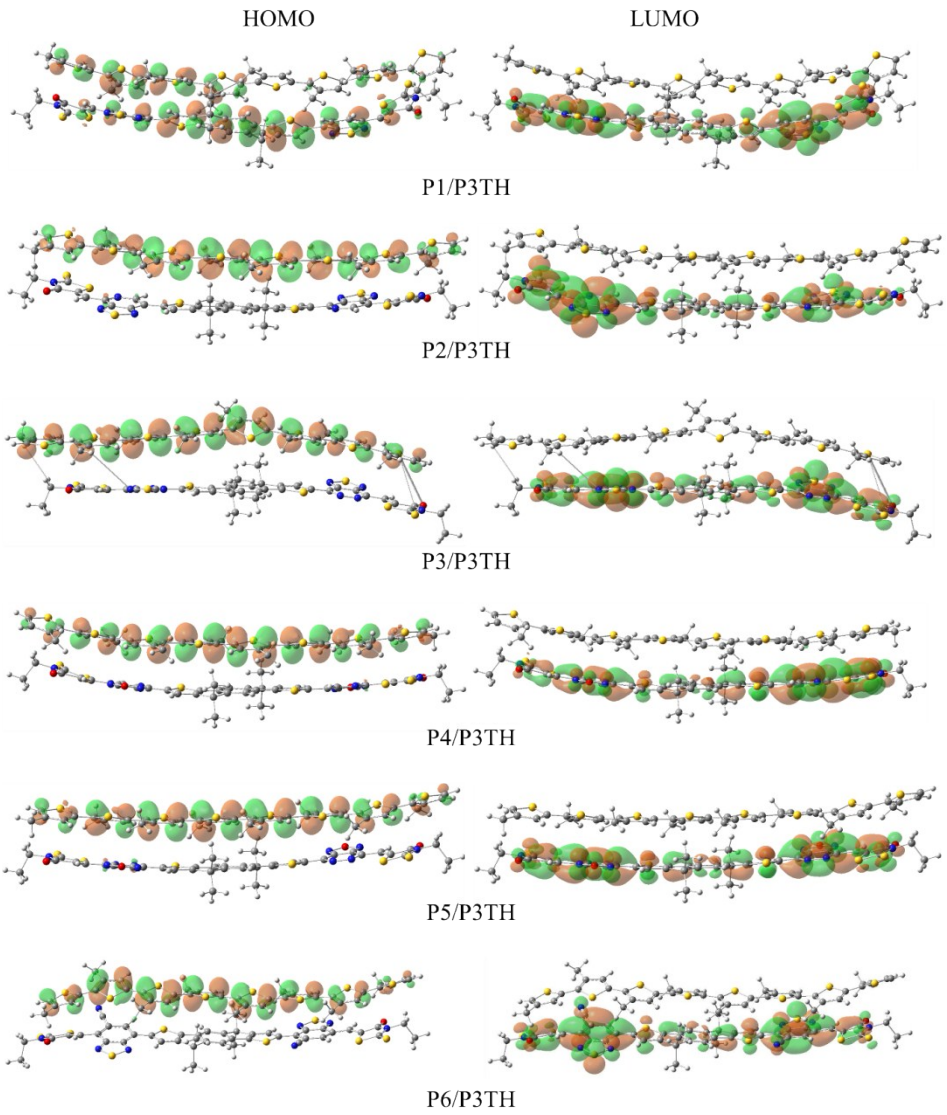

Fig. S4. The contour plot of the HOMO and the LUMO orbitals of P3TH/P1-P6 blends.

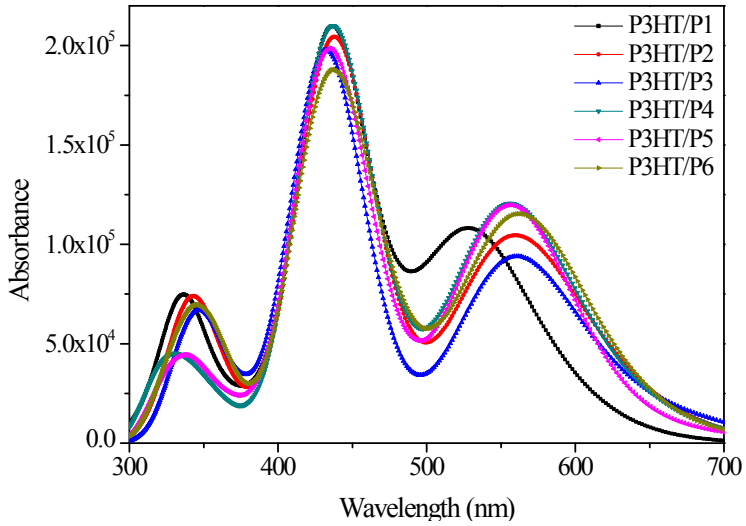

Fig. S5 Simulated absorption spectra of P3HT/P1-P6 at TD-M06-2X-D3/6-311G(d, p) level.

Table S1 Selected bond lengths L_i (Å) and dihedral Angles φ (deg) of all molecules from the PBE0/6-311G (d, p) level calculations, where L_1-L_3 and φ_1-φ_6 see Fig.1

	L_1	L_2	L_3	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
P1	1.35	1.43	1.44	0.17	0.99	2.28	2.61	0.84	0.17
P2	1.35	1.43	1.43	0.22	0.33	5.44	-0.29	-0.17	0.05
P3	1.35	1.43	1.43	0.00	0.04	0.06	0.10	0.04	0.00
P4	1.35	1.42	1.43	0.26	0.59	1.95	-0.68	-1.64	0.65
P5	1.35	1.43	1.42	0.16	0.27	0.23	0.09	0.30	0.02
P6	1.35	1.43	1.44	5.19	42.5	4.32	22.9	-4.74	0.45

Table S2 Molecular orbital compositions (%) of donor segments and acceptor segments for all donor-acceptor blends of active layers

	Orbital	H-4	H-3	H-2	H-1	H	L	L+1	L+2	L+3	L+4
	Energy (eV)	-7.33	-6.94	-6.66	-6.32	-6.05	-2.63	-2.47	-1.57	-1.39	-1.35
P3TH/P1	Donor (%)	53	47	73	29	93	2	2	82	10	15
	Acceptor (%)	47	53	27	71	7	98	98	18	90	85
	Energy (eV)	-7.41	-6.93	-6.68	-6.3	-6.03	-2.85	-2.67	-1.61	-1.46	-1.45
P3TH/P2	Donor (%)	43	57	56	45	97	2	2	57	21	24
	Acceptor (%)	57	43	44	55	3	98	98	43	79	76
	Energy (eV)	-7.48	-7.01	-6.73	-6.34	-6.03	-2.98	-2.82	-1.64	-1.62	-1.48
P3TH/P3	Donor (%)	9	95	4	98	99	1	1	4	1	76
	Acceptor (%)	91	5	96	2	1	99	99	96	99	24
	Energy (eV)	-7.53	-7.04	-6.81	-6.43	-6.12	-2.98	-2.77	-1.68	-1.53	-1.45
P3TH/P4	Donor (%)	35	66	47	53	98	2	2	69	36	3
	Acceptor (%)	65	34	53	47	2	98	98	31	64	97
	Energy (eV)	-7.62	-7.05	-6.85	-6.44	-6.07	-3.06	-2.87	-1.76	-1.67	-1.53
P3TH/P5	Donor (%)	30	78	34	69	88	89	7	2	13	64
	Acceptor (%)	70	22	66	31	12	91	92	73	87	36
	Energy (eV)	-7.41	-7.05	-6.66	-6.41	-6.18	-2.92	-2.76	-1.66	-1.57	-1.48
P3TH/P6	Donor (%)	36	65	46	54	98	2	2	43	45	3
	Acceptor (%)	64	35	54	46	2	98	98	57	55	97

Table S3 Calculated excitation energy, oscillator strength (*f*), electronic transition, and main configuration of P3TH/P1-P6 using TD-M06-2X-D3/6-311G(d, p) approach

	Excitation energy (eV, nm)	*f*	transition	Main configuration
P3HT/P1	2.84, 436	2.849	$S_0 \rightarrow S_5$	H→L+2 (71%)
P3HT/P2	2.80, 443	2.003	$S_0 \rightarrow S_5$	H→L+2 (38%)
P3HT/P3	2.86, 433	1.636	$S_0 \rightarrow S_8$	H→L+4 (30%)
P3HT/P4	2.24, 554	1.583	$S_0 \rightarrow S_3$	H-2→L (34%)
P3HT/P5	2.87, 432	2.172	$S_0 \rightarrow S_9$	H→L+4 (34%)
P3HT/P6	2.90, 428	1.564	$S_0 \rightarrow S_7$	H→L+2 (20%)

Table S4 Calculated excitation energy, oscillator strength (*f*), electronic transition, light absorption efficiency (η) and main configuration of P3TH/P1-P6 using TD-PBE0/6-311G(d, p) approach

	Excitation energy (eV, nm)	*f*	transition	Main configuration	η
P3HT/P1	2.45, 506	1.186	$S_0 \rightarrow S_8$	H→L+2 (58%), H-3→L (20%)	0.9348
P3HT/P2	2.33, 532	1.414	$S_0 \rightarrow S_9$	H→L+3 (44%), H→L+2 (28%)	0.9615
P3HT/P3	2.50,497	1.600	$S_0 \rightarrow S_{14}$	H→L+4 (79%)	0.9749
P3HT/P4	2.44,509	2.055	$S_0 \rightarrow S_9$	H→L+2 (72%)	0.9912
P3HT/P5	2.29, 542	1.508	$S_0 \rightarrow S_9$	H→L+3 (65%)	0.9690
P3HT/P6	2.37, 523	1.108	$S_0 \rightarrow S_9$	H→L+2 (65%)	0.92201