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

Theoretical Studies on the Effect of a Bithiophene-bridge with Different Substituent Groups (R = H, CH_3, OCH_3 and CN) for Donor-π-Acceptor Copolymers in Organic Solar Cell Applications

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Table S1. The HOMO energy levels (eV) obtained in the gas phase with PBE0, B3LYP, B1B95and BHandHLYP methods at 6-31G** basis set.

Oligomer	PBE0	B3LYP	B1B95	BHandHLYP	Exp. (HOMO)
M1	-5.07	-4.81	-5.00	-5.80	-5.04
D1	-4.89	-4.65	-4.86	-5.68	

Table S2. Calculated electronic transitions, excitation energy, oscillator strength and main configurations of all the π-bridges by TD-B1B95/6-311G**//B1B95/6-311G** approach.

	Excitation energy (eV and nm)		*f*	Transition	Main configuration
π_1	4.30	288	0.367	$S_0 \rightarrow S_1$	H → L (98%)
π_2	4.28	290	0.393	$S_0 \rightarrow S_1$	H → L (98%)
π_3	3.72	333	0.383	$S_0 \rightarrow S_1$	H → L (99%)
π_4	4.06	306	0.337	$S_0 \rightarrow S_1$	H → L (98%)
π_5	3.92	316	0.340	$S_0 \rightarrow S_1$	H → L (98%)
π_6	3.63	341	0.267	$S_0 \rightarrow S_1$	H → L (98%)
$\pi_{6'}$	4.00	310	0.400	$S_0 \rightarrow S_1$	H → L (99%)

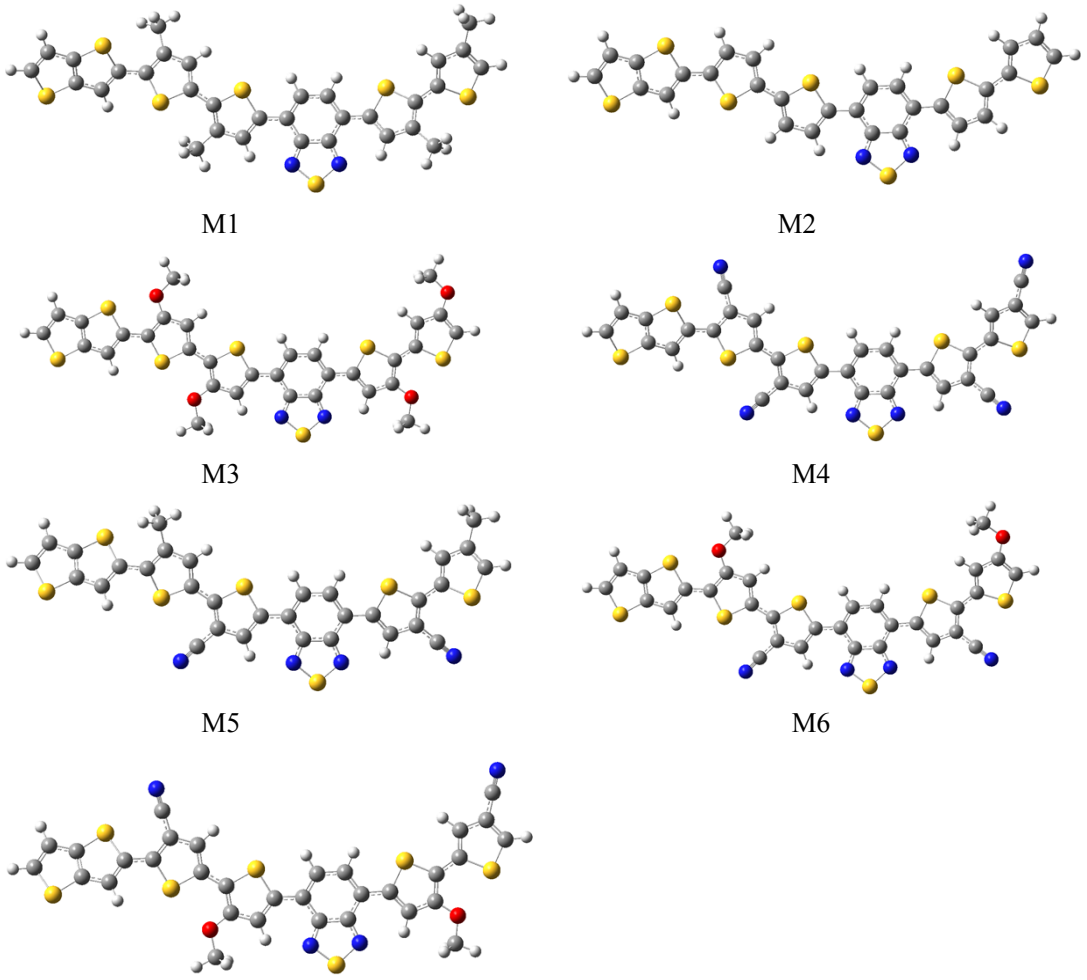
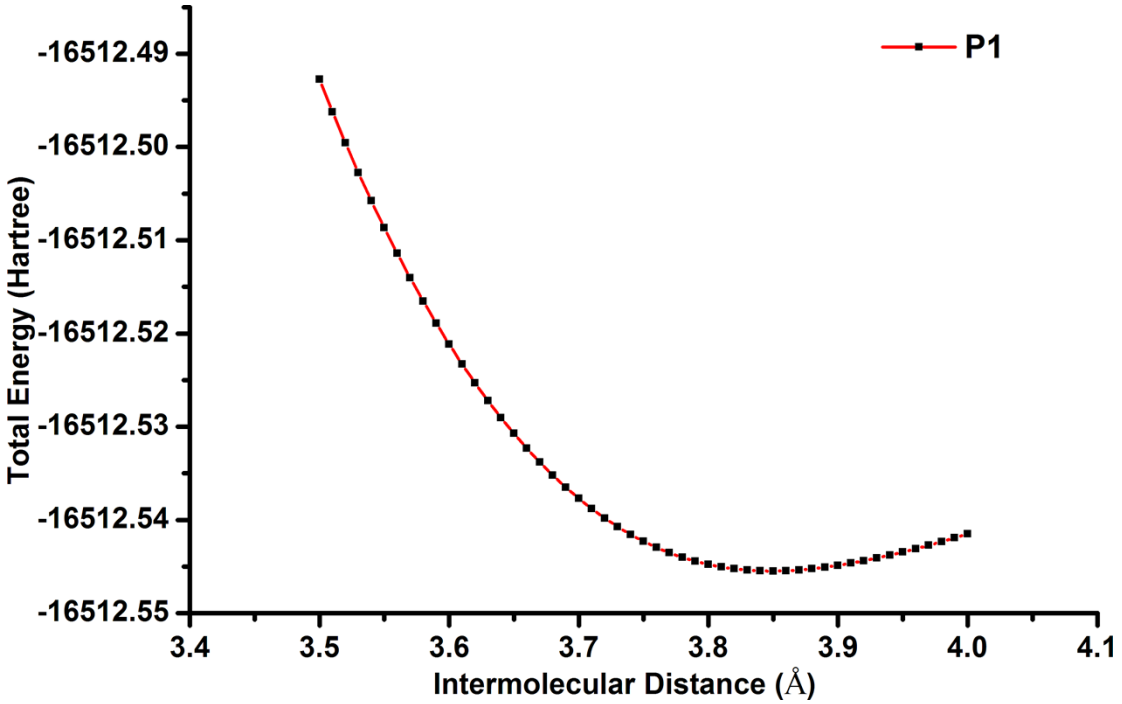
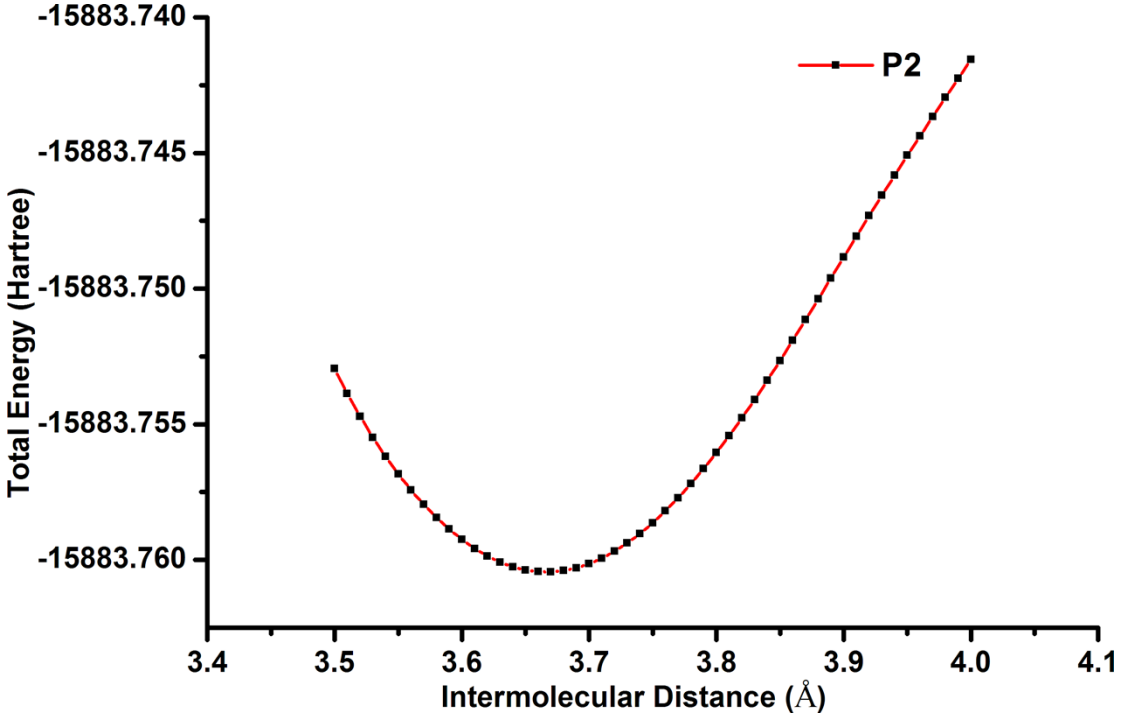


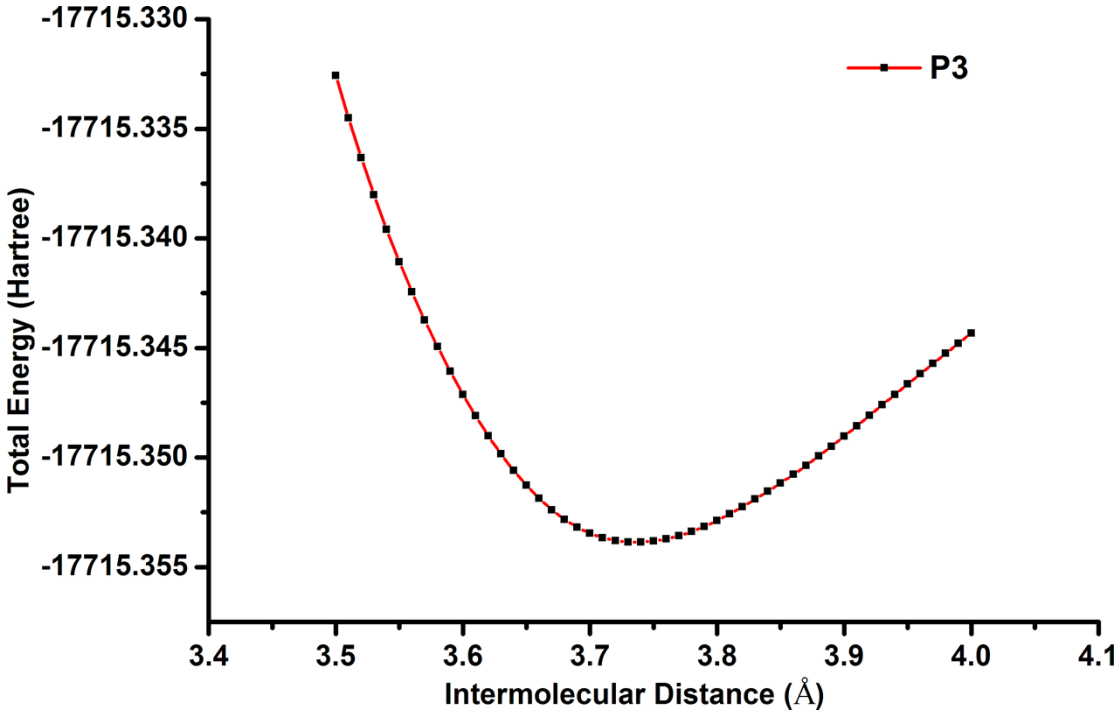
Fig. S1 The optimized geometries of all investigated monomers calculated at B1B95/6-311G**level. Color code: yellow (S), blue (N), black (C), red (O) and grey (H). In molecular structures, the alkyl (alkoxy) group has been replaced with methyl (methoxyl)


P1
-16512.49
-16512.50
-16512.51
-16512.52
-16512.53
-16512.54
-16512.55
Total Energy (Hartree)
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
Intermolecular Distance (Å)

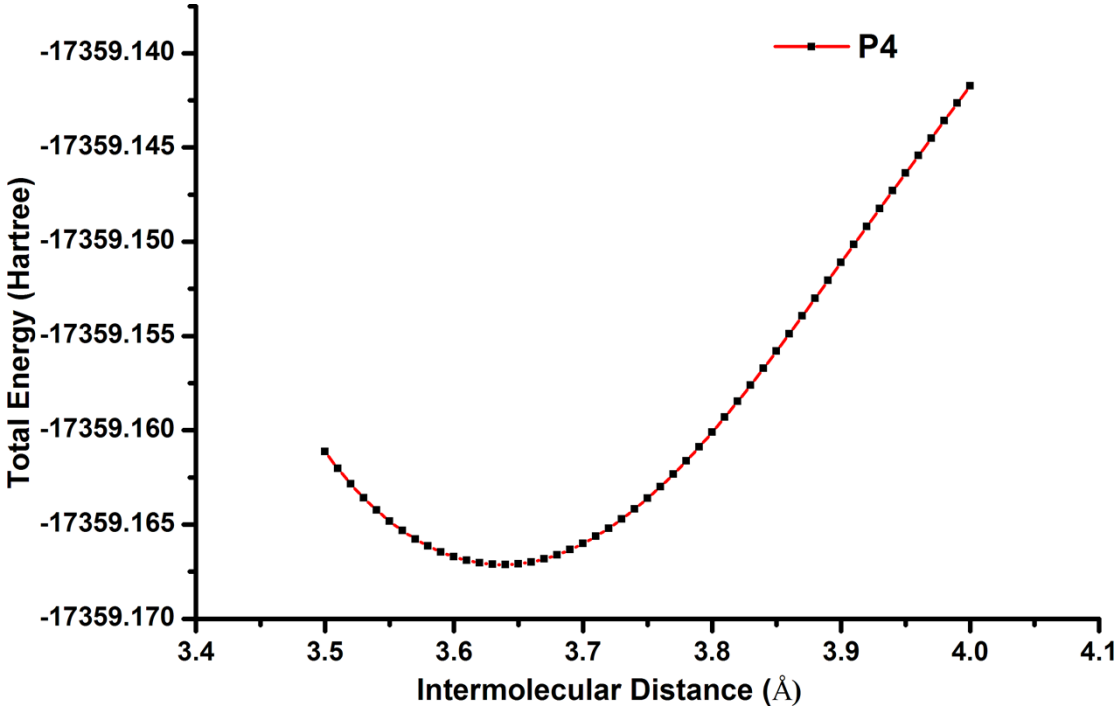
(a)


P2
-15883.740
-15883.745
-15883.750
-15883.755
-15883.760
Total Energy (Hartree)
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
Intermolecular Distance (Å)

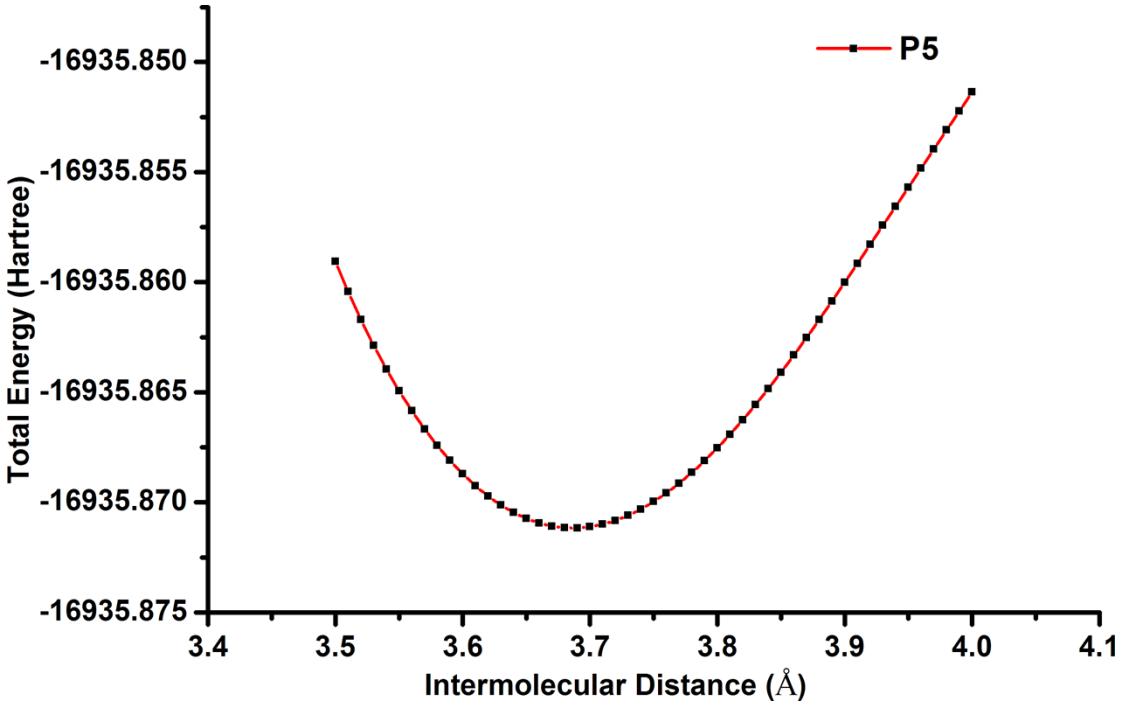
(b)


P3
Total Energy (Hartree)
-17715.330
-17715.335
-17715.340
-17715.345
-17715.350
-17715.355
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
Intermolecular Distance (Å)

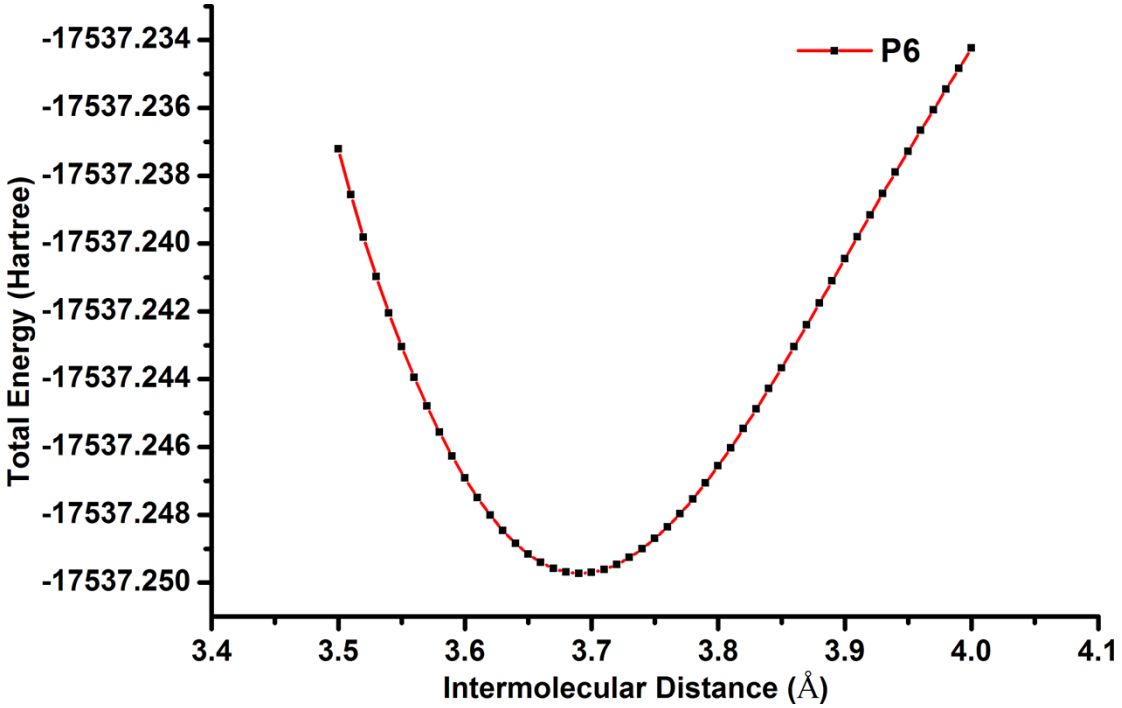
(c)


P4
Total Energy (Hartree)
-17359.140
-17359.145
-17359.150
-17359.155
-17359.160
-17359.165
-17359.170
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
Intermolecular Distance (Å)

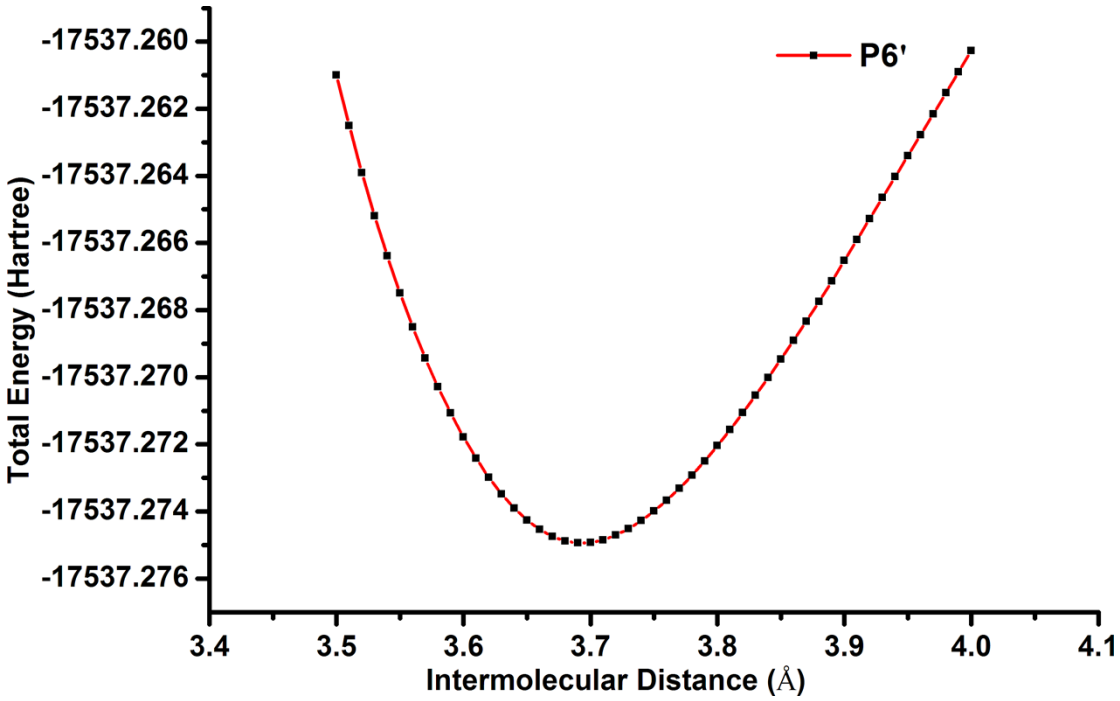
(d)


P5
-16935.850
-16935.855
-16935.860
-16935.865
-16935.870
-16935.875
Total Energy (Hartree)
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
Intermolecular Distance (Å)

(e)


P6
-17537.234
-17537.236
-17537.238
-17537.240
-17537.242
-17537.244
-17537.246
-17537.248
-17537.250
Total Energy (Hartree)
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
Intermolecular Distance (Å)

(f)



(g)

Fig. S2 The calculated total energies of two adjacent dimmers (P1 (a), P2 (b), P3 (c), P4 (d), P5 (e), P6 (f) and P6′ (g)) as the function of intermolecular distance (scanning step length is 0.01 Å)

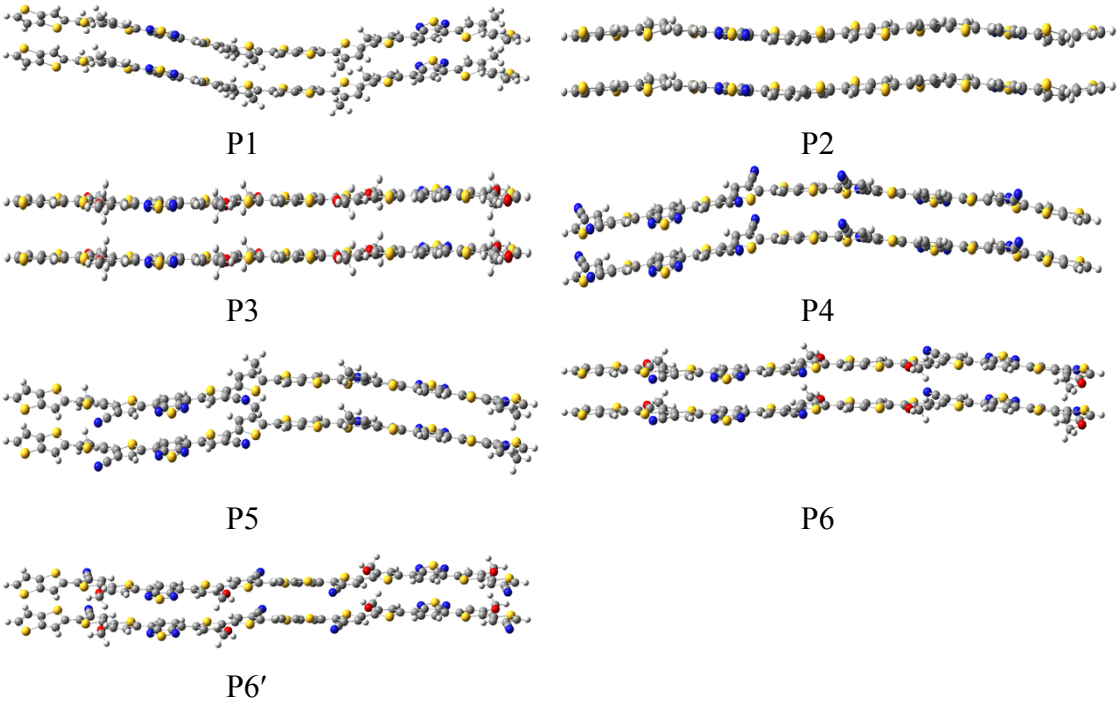


Fig. S3 3D models of two adjacent dimer fragments of those copolymers