Electronic Supplementary Information

Theoretical investigations on fluorinated and cyano copolymers for improvements of photovoltaic performances

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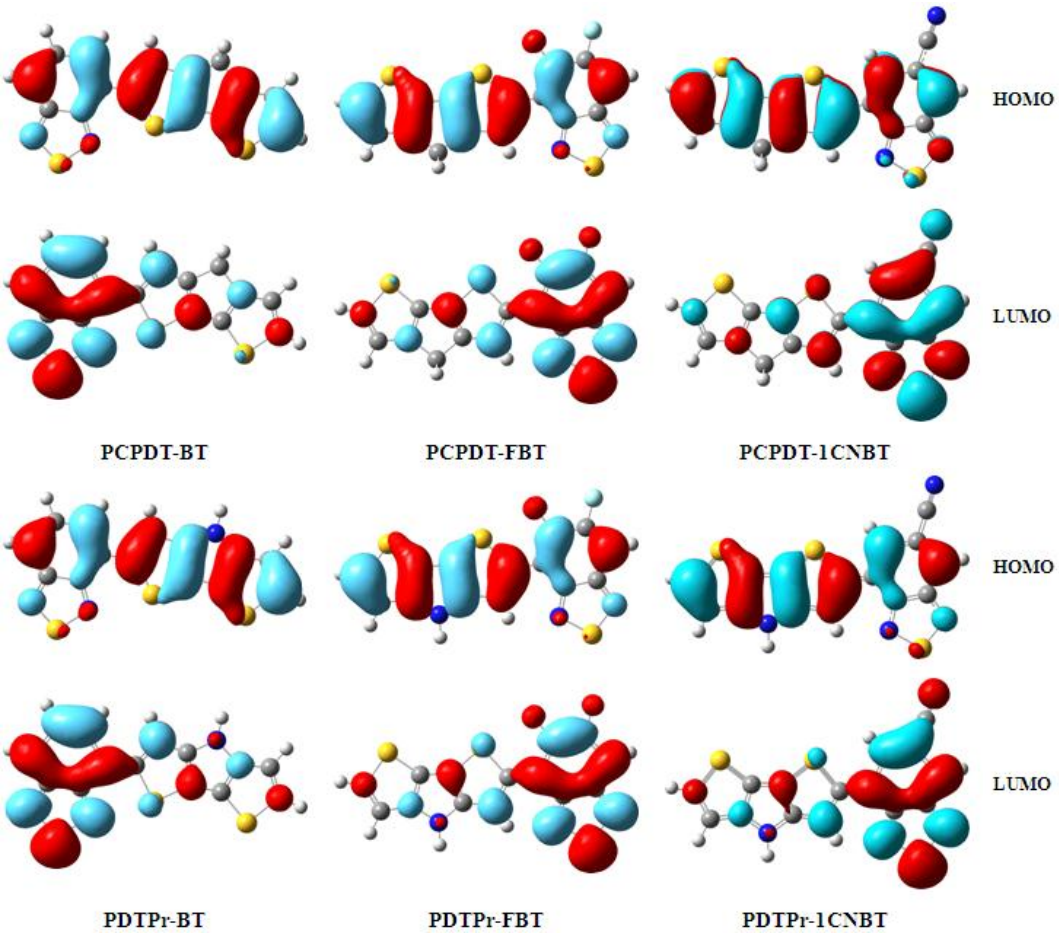

Fig. 1S Molecular orbital spatial distribution of all monomer models.

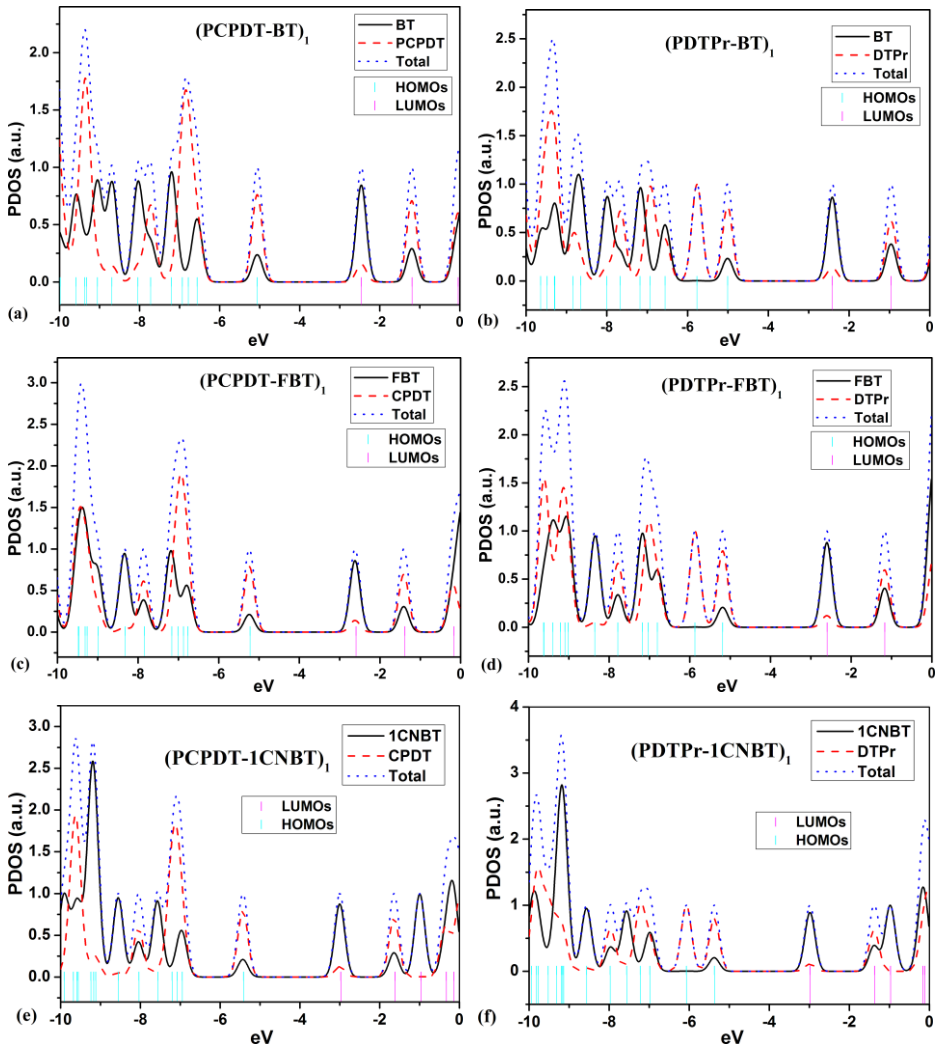

Fig. 2S Total densities of states (TDOS) and projected DOS (PDOS) for all monomer models.

Table 1S The orbital energy levels (HOMO and LUMO) and band gap (Eg) of monomer and dimer models at the B3LYP/6-31G(d) level. All the energy is eV.

	Dimers			Monomers		
	HOMO	LUMO	Eg	HOMO	LUMO	Eg
PCPDT-BT	-4.69	-2.73	1.96	-5.06	-2.46	2.60
PDTPr-BT	-4.64	-2.67	1.97	-5.00	-2.41	2.59
PCPDT-FBT	-4.88	-2.87	2.01	-5.24	-2.61	2.63
PDTPr-FBT	-4.83	-2.83	2.00	-5.18	-2.59	2.59
PCPDT-1CNBT	-5.08	-3.28	1.80	-5.43	-2.99	2.44
PDTPr-1CNBT	-5.00	-3.21	1.79	-5.37	-2.98	2.39

Table 2S The π-stacking of the six dimers from B97-D/6-31g(d) calculation and optimizations.

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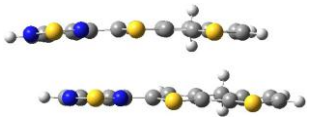
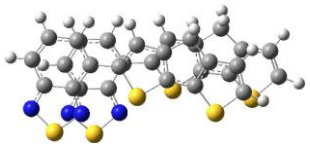
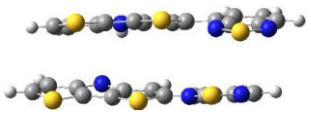
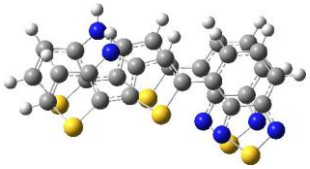
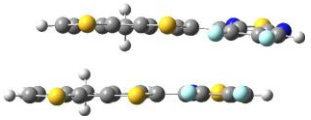
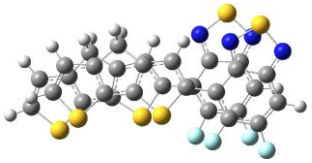
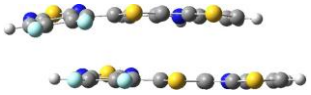
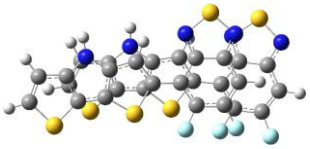
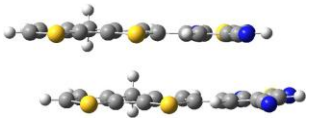
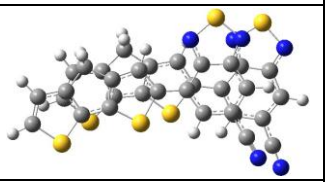
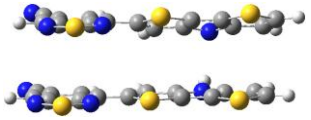
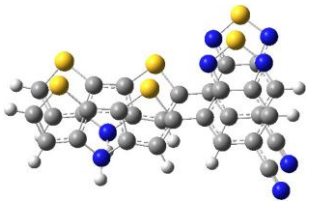
PCPDT-BT		
PDTPr-BT		
PCPDT-FBT		
PDTPr-FBT		
PCPDT-1CNBT		
PDTPr-1CNBT		

1. The ralationship between the theoretical energy levels and experimental energy levels

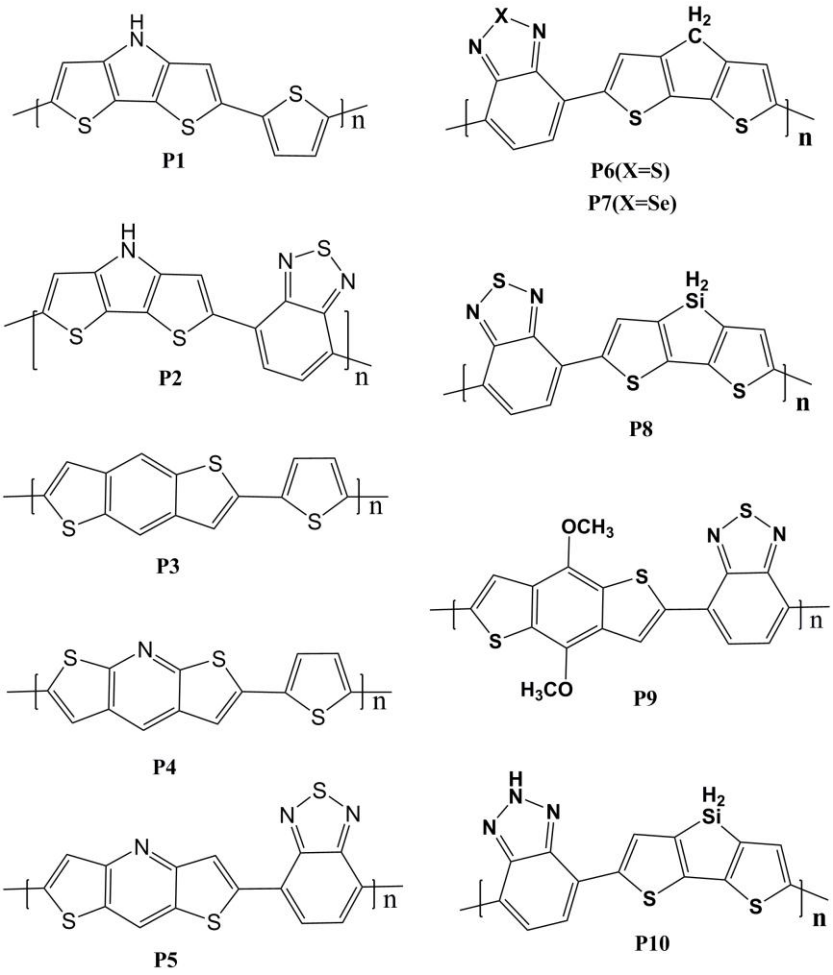
Recently, it is well known that for the energy levels and band gaps of organic conductor materials, there exists a great difference between theoretical calculations and experimentally measured values. Beaupré and co-works[1] proposed a reliable model that can be used to estimate the electronic properties (i.e., the HOMO, LUMO, and band gap energies) of conjugated polymers, which would be a great tool for applications in organic electronics such as light-emitting diodes, field-effect transistors, and photovoltaic cells. A similar model used to predict the energy levels of the new polymer was proposed by Blouin and co-works.[2] From the models, for a class of copolymers we found that the change trend for the energy levels values of density functional theory theoretical calculations and that of experimental data is consistent. Herein, we selected a class of donor-acceptor(D/A) polymers without bridge thiophene ring to calculate their orbital energy levels in comparison with the energy levels values obtained by cyclic voltammetry measurement of corresponding copolymers been reported in literatures.[3-7]

The chemical structure of a class of D/A copolymers were shown in Scheme 1S. The energy levels and energy band-gap of theoretical calculation and experimental values for a class of copolymers (dimer models) are listed in Table 3S. The correlation of theoretical and experimental HOMO and LUMO are in figure 3S. The empirical correlations between theoretical energy levels ($HOMO_{th}$ and $LUMO_{th}$) and experimental energy levels (HOMO and LUMO) for the class of DA copolymers are in following equations:

$$HOMO = 0.65 \times HOMO_{th} - 1.97 \quad (R = 0.97) \qquad (1)$$

$$LUMO = 0.83 \times LUMO_{th} - 0.94 \quad (R = 0.93) \qquad (2)$$

From the Eq (1) and (2), one can see that the ten-pointsmodel gave relatively good correlation coefficients ($R > 0.92$) and these equations have been used to estimate the HOMO and LUMO energy levels of several analogous derivatives.



Scheme 1S. The chemical structure of a class of DA copolymers.

Table 3S The energy levels and energy band-gap of theoretical calculation and experimental values for a class of copolymers (dimer models), all energy is eV.

		Experimental values			Theory[a]		
	Ref.	HOMO	LUMO	Eg	HOMO	LUMO	Eg
P1	[3]	-4.89	-2.56	2.33	-4.5	-1.89	2.61
P2	[3]	-4.94	-3.07	1.87	-4.64	-2.67	1.97
P3	[3]	-5.35	-2.62	2.73	-5.06	-2.18	2.88
P4	[3]	-5.43	-2.97	2.46	-5.37	-2.3	3.07
P5	[3]	-5.56	-3.33	2.23	-5.54	-2.97	2.57
P6	[4]	-5.00	-3.40	1.60	-4.66	-2.72	1.94
P7	[4]	-4.90	-3.28	1.62	-4.58	-2.77	1.81
P8	[6]	-5.05	-3.27	1.78	-4.87	-2.83	2.03
P9	[7]	-5.10	-3.19	1.91	-4.67	-2.76	1.91
P10	[5]	-5.09	-2.76	2.33	-4.77	-2.39	2.38

[a]The energy levels and energy band-gap of theoretical calculation carried at the levels of DFT/B3LYP/6-31G(d) in dimer models

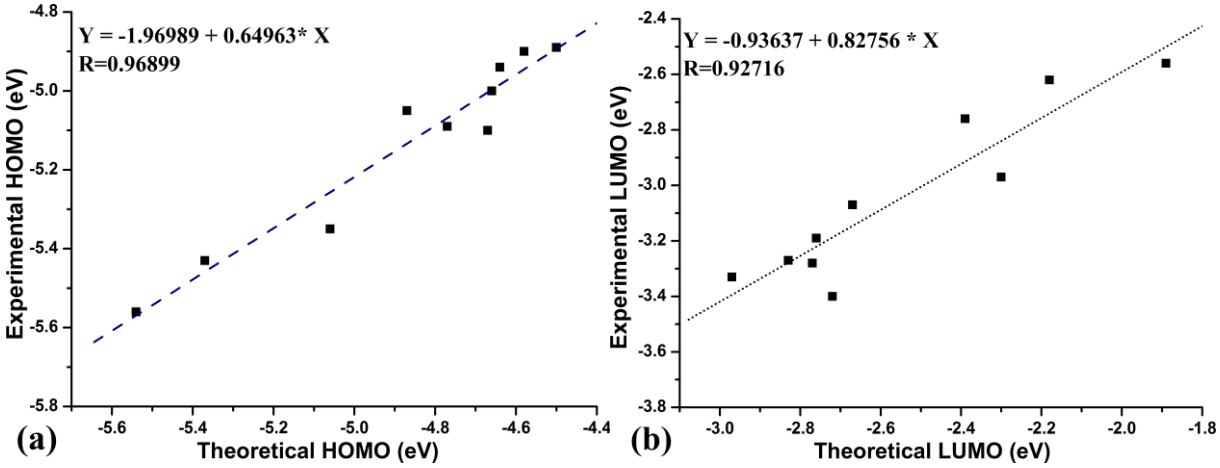


Figure 3S. Theoretical and experimental HOMO (a) and LUMO (b).

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