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

Charge-transfer electronic states in organic solar cells: A TDDFT study

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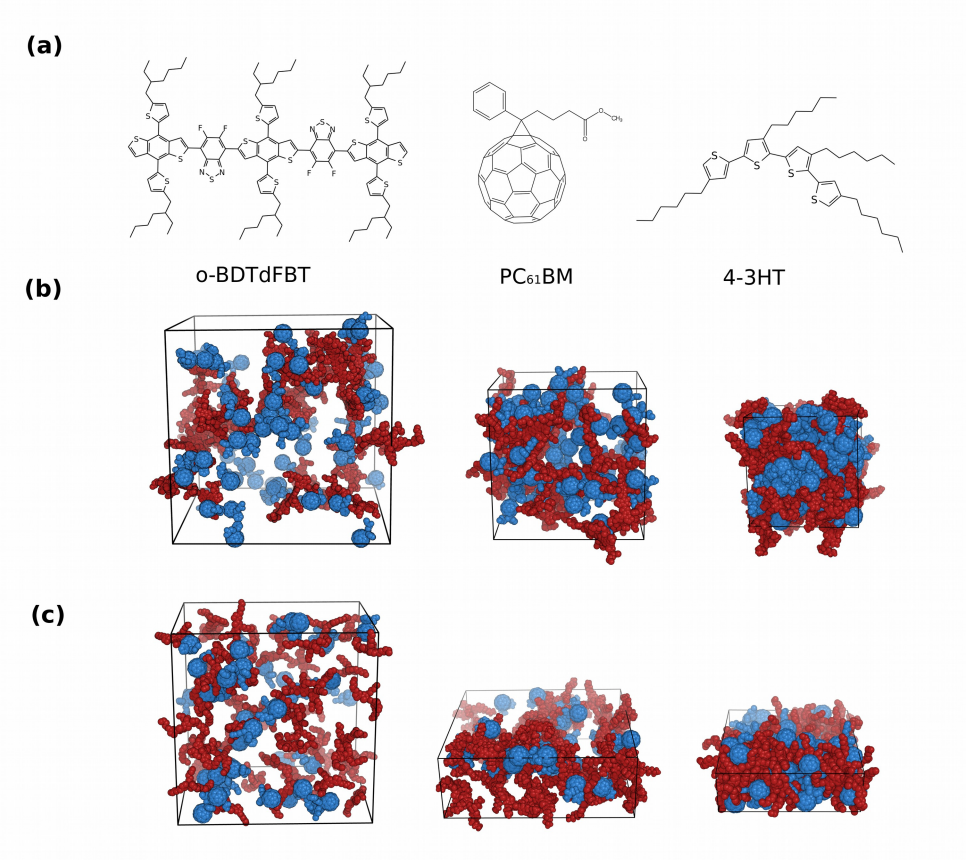

Figure S1. (a) Structures of electron acceptor PCBM ([6,6]-phenyl-C61-butyric acid methyl ester), donor molecules 4-3HT and o-BDTdFBT. (b) Solvent evaporation simulation for o-BDTdFBT/$PC_{61}BM$ and (c) 4-3HT/$PC_{61}BM$.

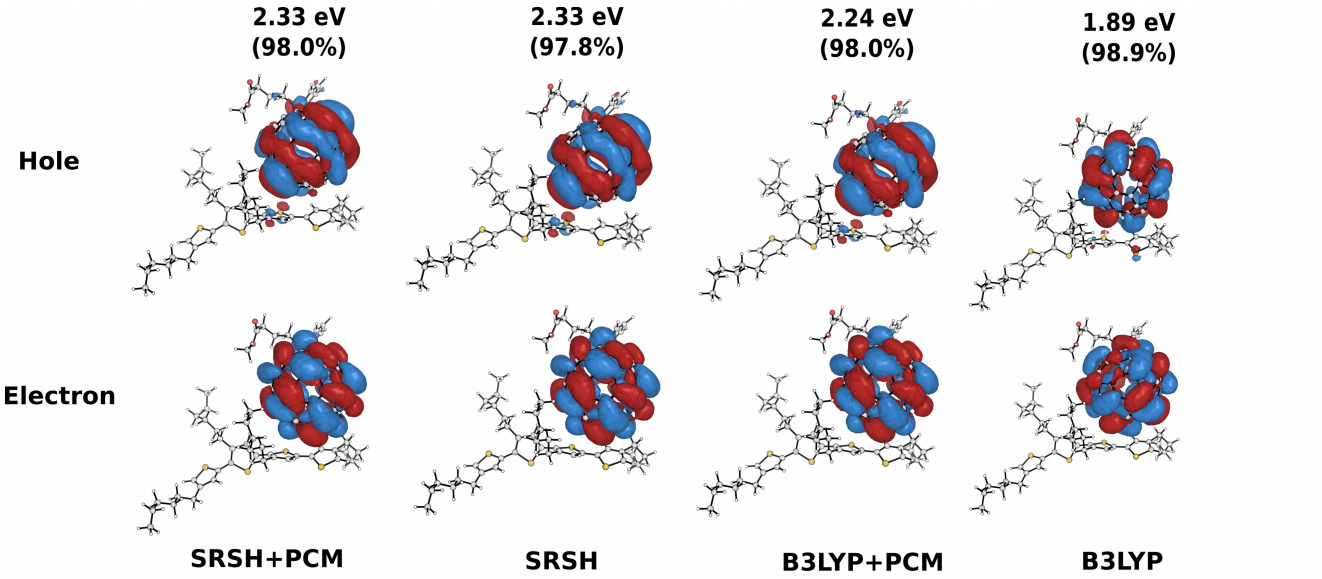

Figure S2. Electron-hole pair localization of the locally excited state LE computed from NTO, in the selected eD-eA adduct 4-3HT/$PC_{61}BM$, showing dependency for each scheme.

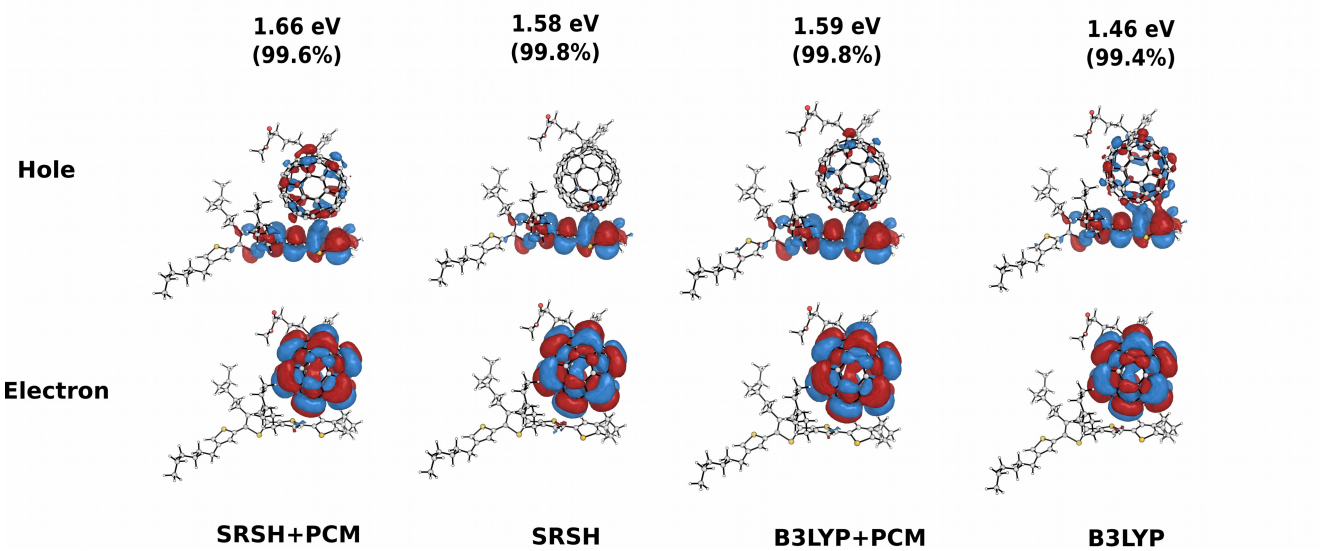

Figure S3. Electron-hole pair localization of charge transfer states CT_1 (CT_2) computed from natural transition orbital calculation (NTO) for one eD-eA adduct 4-3HT/$PC_{61}BM$ using different schemes. Curiously, the lowest charge tranfer state CT_1 is equal to the charge transfer state most coupled (CT_2) to the locally excited state LE.

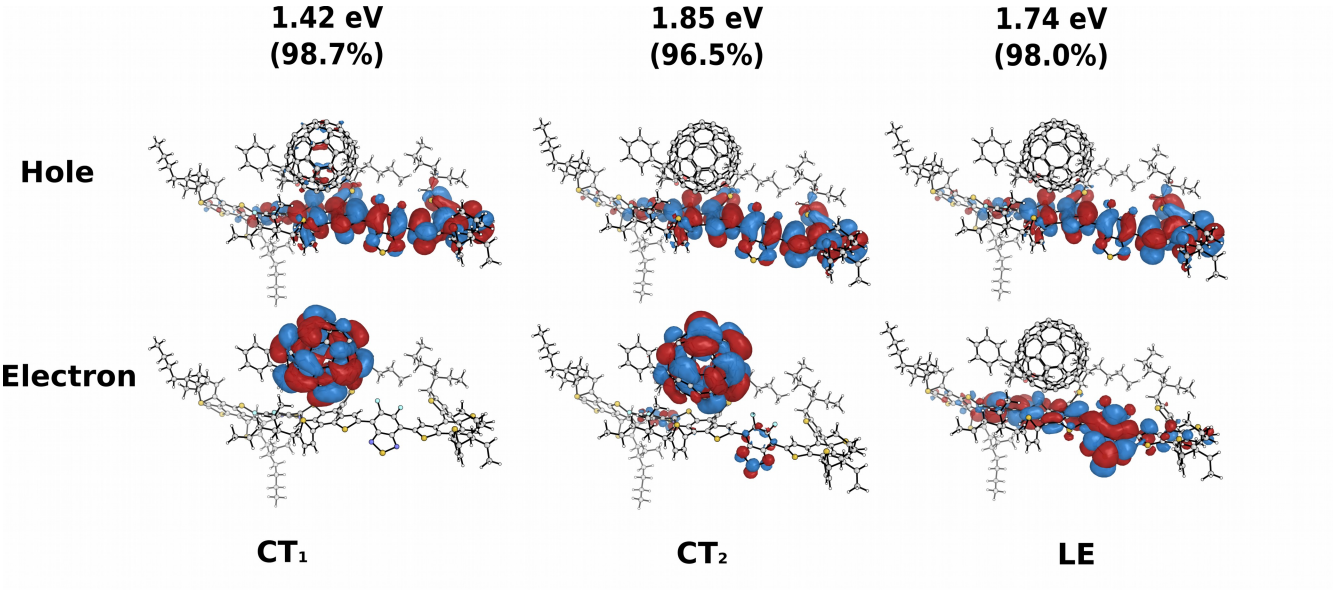

Figure S4. Electron-hole pairs computed for each electronic excited states in one adduct o-BDTdFBT/$PC_{61}BM$ using B3LYP scheme and NTO implementation.

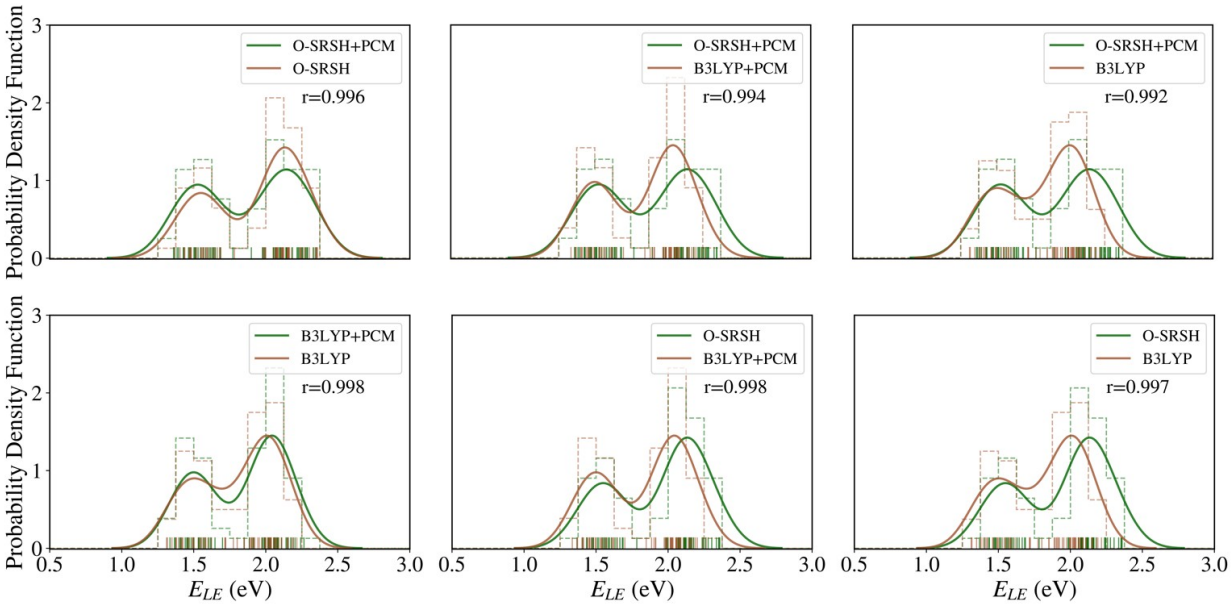

Figure S5. Probability density function of LE state schemes for 4-3HT/$PC_{61}BM$ system using O-SRSH+PCM, O-SRSH, B3LYP+PCM and B3LYP schemes. Pearson correlation coefficent *r* between schemes was evaluated with kernel density stimation values.

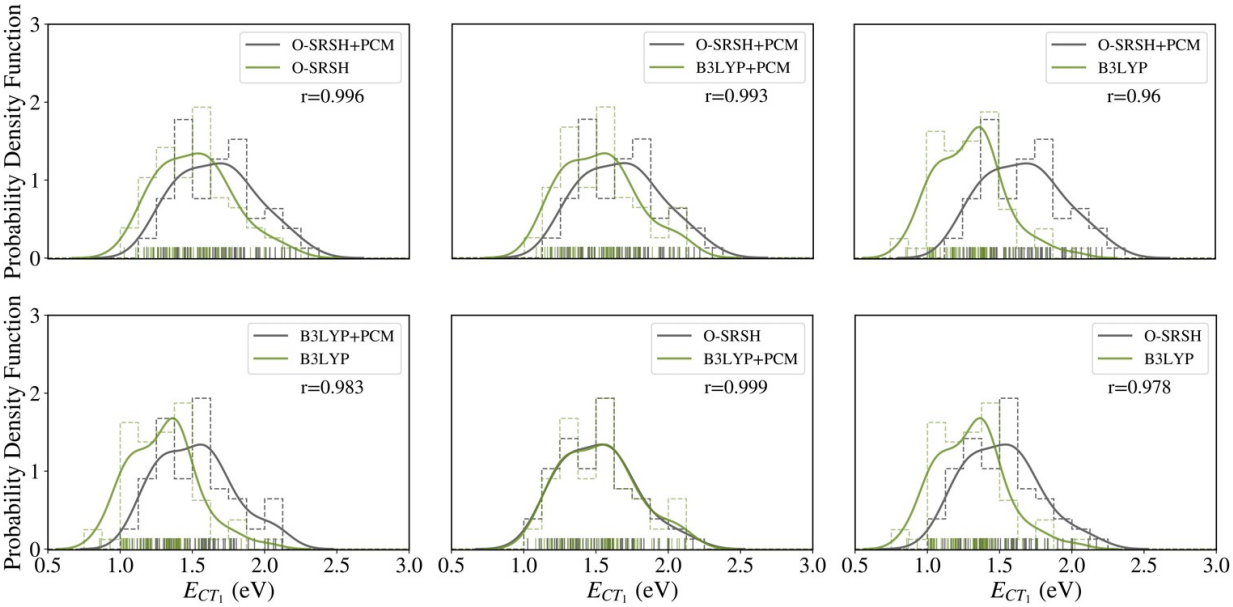

Figure S6. Probability density function of CT_1 state calculated from O-SRSH+PCM, O-SRSH, B3LYP+PCM and B3LYP schemes schemes in the 4-3HT/$PC_{61}BM$ system. Pearson correlation coefficent *r* between schemes was computed with kernel density stimation values.

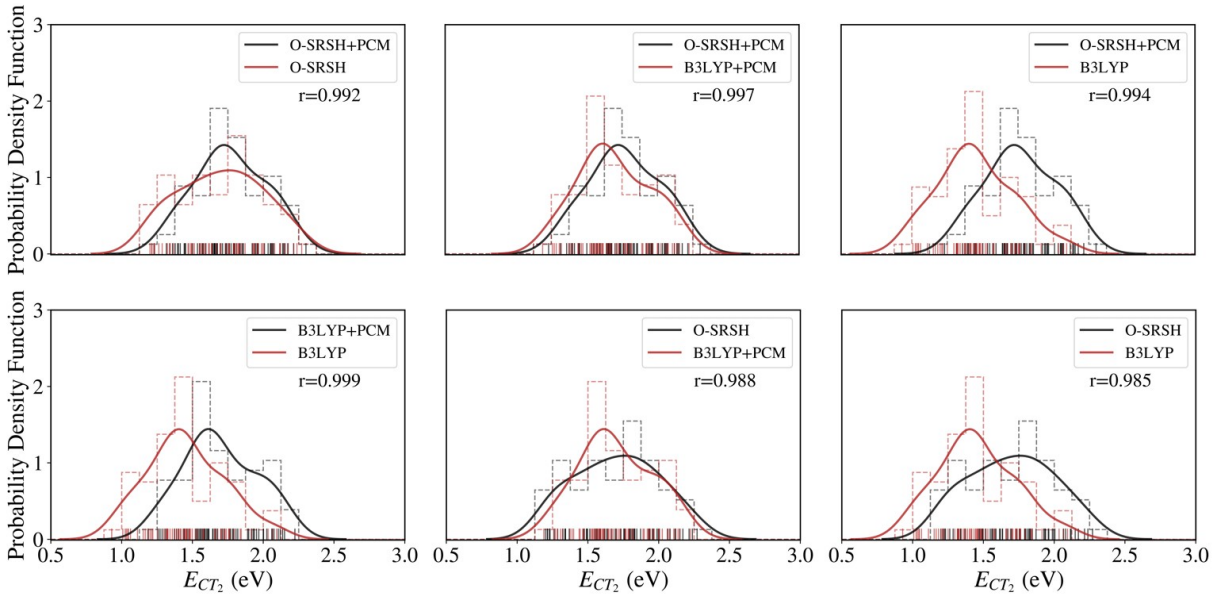

Figure S7. Probability density function of CT_2 state schemes for 4-3HT/$PC_{61}BM$ system using O-SRSH+PCM, O-SRSH, B3LYP+PCM and B3LYP schemes. Pearson correlation coefficent *r* between schemes was computed with kernel density stimation values.

Table S1. Charge difference relation δ calculated between two states that are involved in charge transfer processes.

	$\delta = \frac{1}{2}\left\|Q_{ii}^{DA} + Q_{jj}^{DA}\right\|$		
	LE-CT_1	CT_1-GS	LE-CT_2
	4-3HT/$PC_{61}BM$		
SRSH+PCM	0.90±0.09	0.88±0.10	0.90±0.09
SRSH	0.92±0.08	0.88±0.07	0.91±0.06
B3LYP+PCM	0.89±0.09	0.86±0.10	0.88±0.09
B3LYP	0.91±0.11	0.85±0.10	0.91±0.10
	o-BDTdFBT/$PC_{61}BM$		
B3LYP	0.94±0.07	0.90±0.04	0.93±0.07

Where $Q_{ii}^{DA} = Q_i^D - Q_i^A$ represents the charge difference between donor-fragment and acceptor-fragment charges in the state *i*.