Supporting Information

Molecular Origin of Efficient Hole Transfer from Non-Fullerene Acceptors: Insights from First-Principles Calculations

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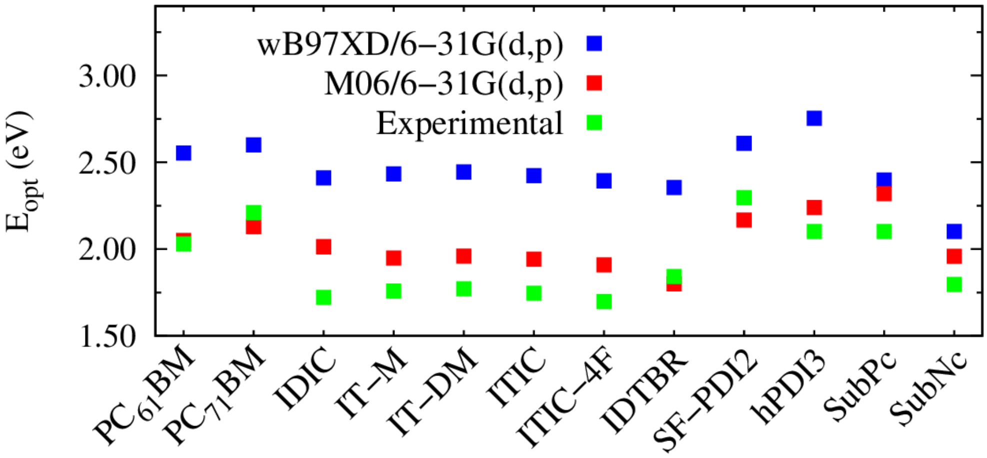


Figure S1 - Optical gap for non-fullerene molecules. Theoretical results of TD-DFT calculation with PCM and experimental results determined from the first maximum absorption wavelength (λ_{max}) in thin film (extracted in accordance with references of Table 2).

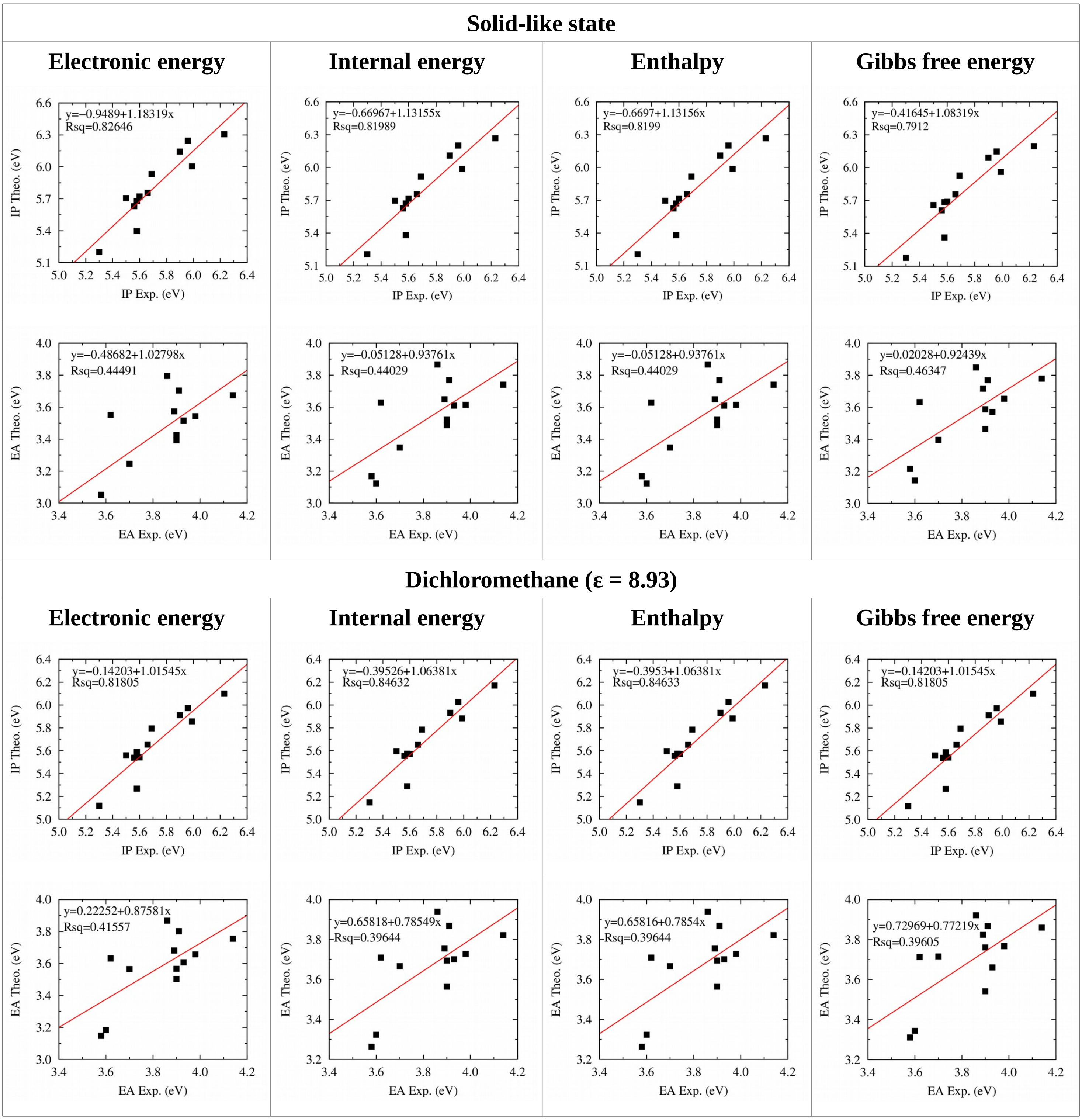


Figure S2 - Correlation between theoretical and experimental results of *IP* and *EA*. The linear equation and the the squared correlation coefficient (Rsq) are displayed in detail. Results for solid-like state (with PCM parameters of Table 1) and for molecules in dichloromethane solvent (ε = 8.93)[1]. We use the M06/6-311G(d,p) theory level for all these procedure.

Table S1 - Squared correlation coefficient (Rsq) of Figure S2.

	Rsq							
	Solid-like state				Dichloromethane			
	Electronic energy	Internal energy	Enthalpy	Gibbs free energy	Electronic energy	Internal energy	Enthalpy	Gibbs free energy
IP	0.82646	0.81989	0.8199	0.7912	0.81805	0.84632	0.84633	0.81805
EA	0.44491	0.44029	0.44029	0.46347	0.41557	0.39644	0.39644	0.39605

Table S2 - Theoretical results - in gas phase - of *IP*, *EA*, E_{opt} and E_b energies. Molecules in GS geometry. Results in eV.

Molecules	*IP*	*EA*	E_{opt}	E_b
NFAs				
IDIC	6.82	2.55	2.22	2.05
IT-M	6.35	2.44	2.10	1.81
IT-DM	6.31	2.39	2.11	1.81
ITIC	6.41	2.49	2.10	1.82
ITIC-4f	6.54	2.66	2.07	1.81
IDTBR	6.26	2.40	1.93	1.93
SF-PDI2	6.75	2.50	2.27	1.98
hPDI3	6.96	2.82	2.31	1.84
SubPc	6.54	1.38	2.49	2.67
SubNc	5.90	1.49	2.13	2.28
FAs				
PC$_{71}$BM	6.79	1.96	2.14	2.69
PC$_{61}$BM	6.94	1.94	2.06	2.94

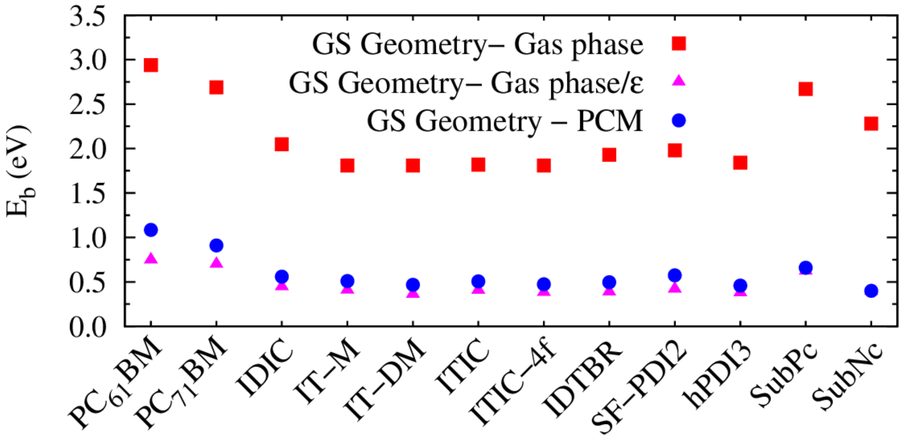


Figure S3 - Binding energy of Frenkel exciton for FAs and NFAs in ground state (GS) geometry calculated in gas phase and with PCM method. We also present the result in the gas phase divided by the dielectric constant.

Table S3 - Theoretical results - in solid with PCM - of IP, EA and E_{opt} energies. Molecules in ES geometry. Results in eV.

Molecules	IP	EA	E_{opt}	E_b
NFAs				
IDIC	5.73	3.47	1.77	0.49
IT-M	5.48	3.32	1.70	0.46
IT-DM	5.43	3.31	1.70	0.42
ITIC	5.50	3.35	1.69	0.46
ITIC-4f	5.55	3.45	1.67	0.43
IDTBR	5.21	3.25	1.53	0.43
SF-PDI2	5.67	3.45	1.68	0.54
hPDI3	6.07	3.59	2.04	0.44
SubPc	5.51	2.74	2.15	0.62
SubNc	4.96	2.83	1.77	0.36
FAs				
$PC_{71}BM$	5.71	3.09	1.64	0.96
$PC_{61}BM$	5.76	3.10	1.55	1.11

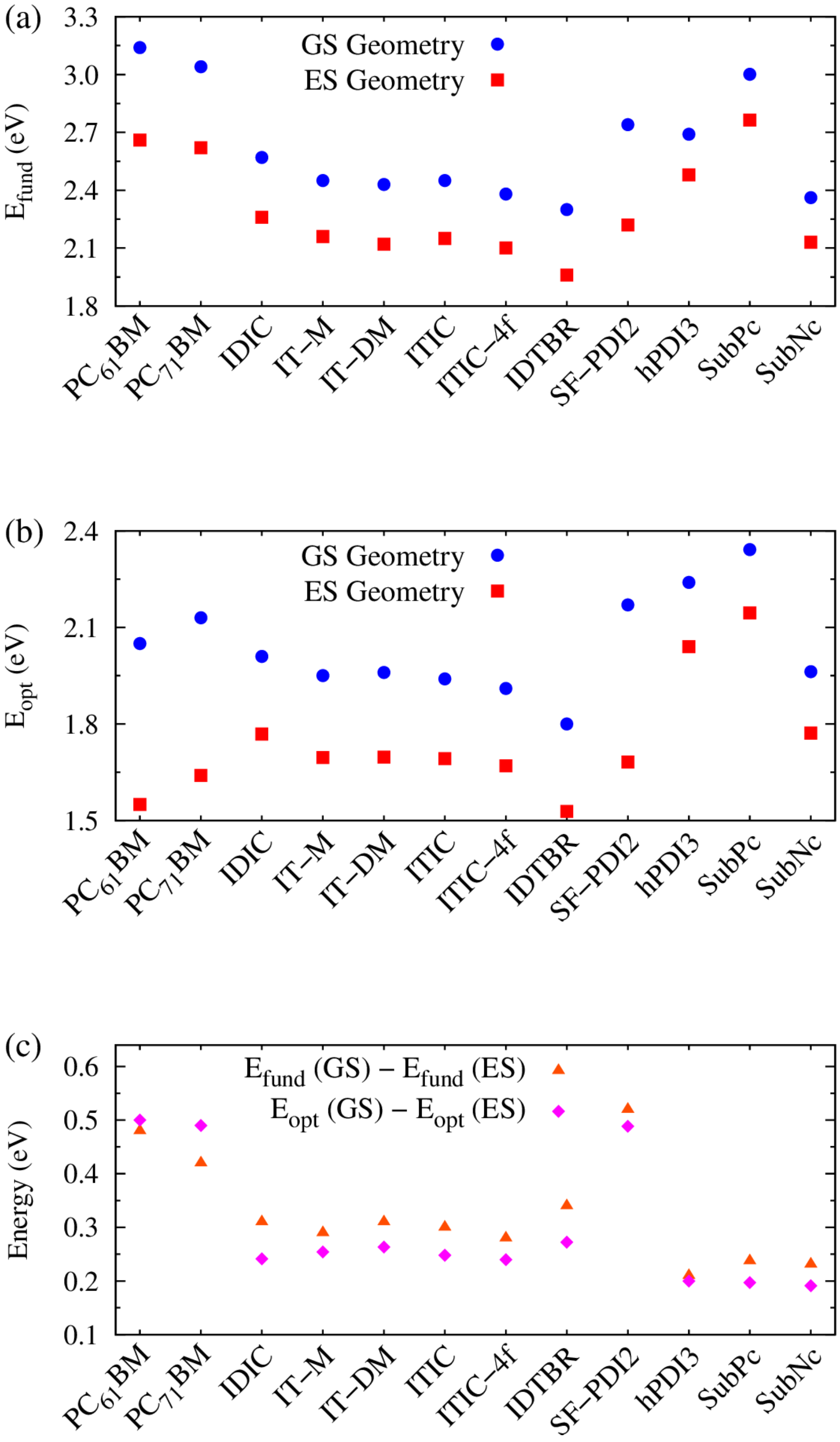
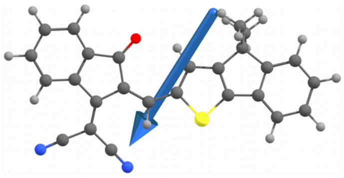
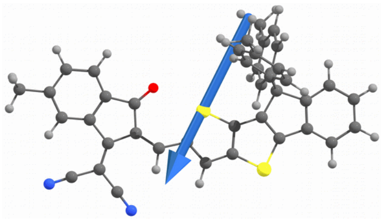


Figure S4 - Molecular energies for molecules in ground state (GS) geometry and excited state (ES) geometry calculated with PCM method (a) Fundamental gap ($E_{fund} = IP - EA$). (b) Optical gap (E_{opt}). (c) Energy difference between E_{fund} (GS) and E_{fund} (ES) and between E_{opt} (GS) and E_{opt} (ES).

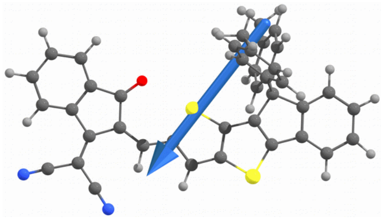
IDIC, D = 6.86



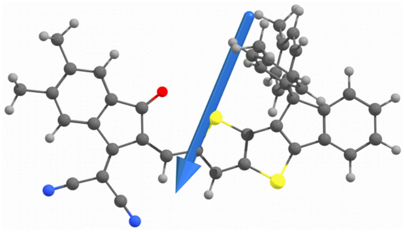
IT-M, D = 6.76



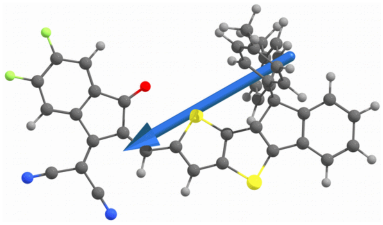
ITIC, D = 6.99



IT-DM, D = 7.06



ITIC-4F, D = 7.71



IDTBR, D = 5.82

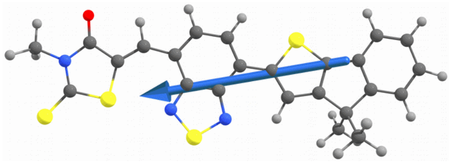
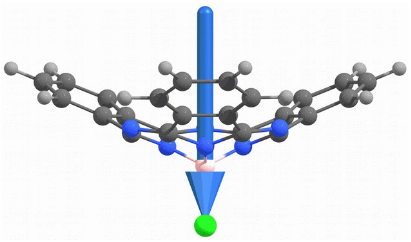


Figure S5 - Theoretical simulation of the intramolecular electronic dipole moments of half molecule models (dipole in Debyes).

SubPc, D = 4.83



SubNc, D = 5.15

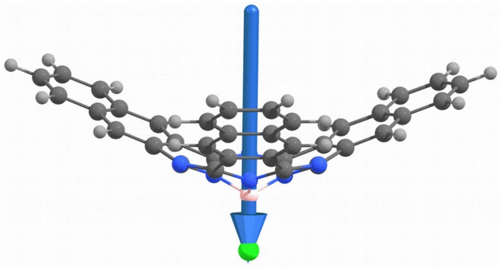


Figure S6 - Electronic dipole moment of subphitalocianines (dipole in Debyes).

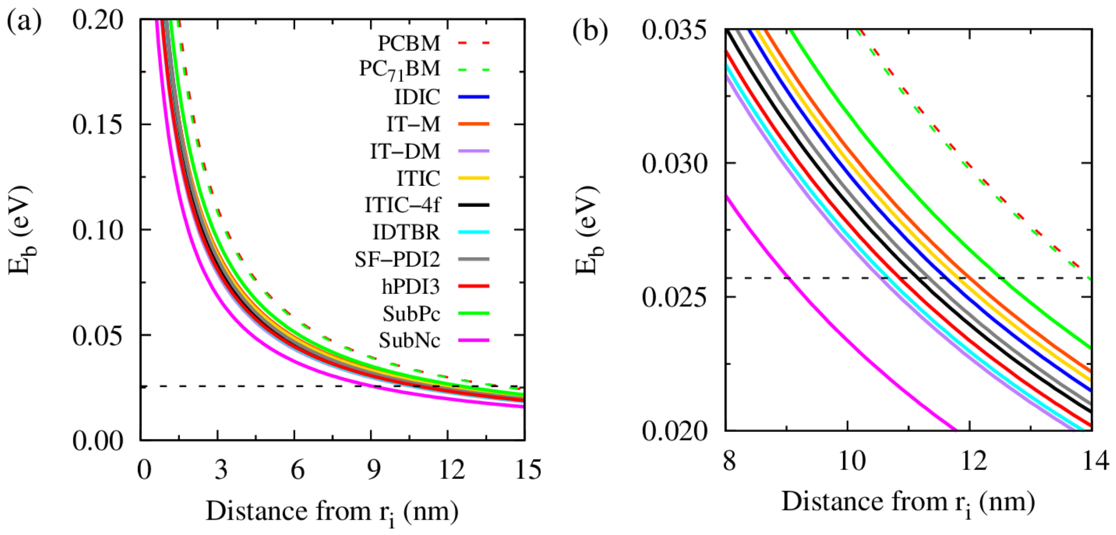


Figure S7 - (a) Exciton binding energy increasing the distance from r_i. (b) Zoom-in the region of the exciton binding energy equals k_bT (dotted black line).

Table S4 - Theoretical results of initial electron-hole par distance r_i, Onsager radius r_c and the difference between $r_c - r_i$. All results in nm obtained from $E_b(r)=e^2/4\pi\varepsilon\varepsilon_0 r$. r_i is the initial electron-hole distance (of the Frenkel exciton) and r_c is the Coulomb capture radius (or Onsager radius), defined as the distance at which the Coulomb attraction energy equals the thermal energy k_BT.[2] When $E_b(\mathrm{r}) = k_BT$ it is considered that the electron-hole pair is dissociated.

Molecules	r_i	r_c	r_c - r_i
NFAs			
IDIC	0.56	12.18	11.62
IT-M	0.64	12.64	12.00
IT-DM	0.61	11.16	10.55
ITIC	0.63	12.45	11.82
ITIC-4F	0.64	11.79	11.15
IDTBR	0.58	11.25	10.67
SF-PDI2	0.53	11.87	11.34
hPDI3	0.64	11.50	10.86
SubPc	0.51	13.03	11.48
SubNc	0.62	9.66	8.96
FAs			
$PC_{71}BM$	0.41	14.36	13.95
$PC_{61}BM$	0.34	14.36	14.02

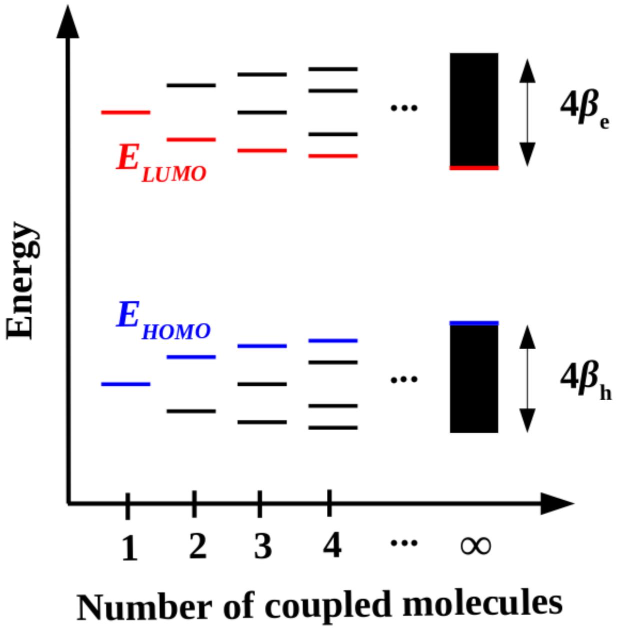


Figure S8 - Diagram representing the energy band formation and band gap decrease due to the intermolecular electronic coupling as a function of the number molecules.

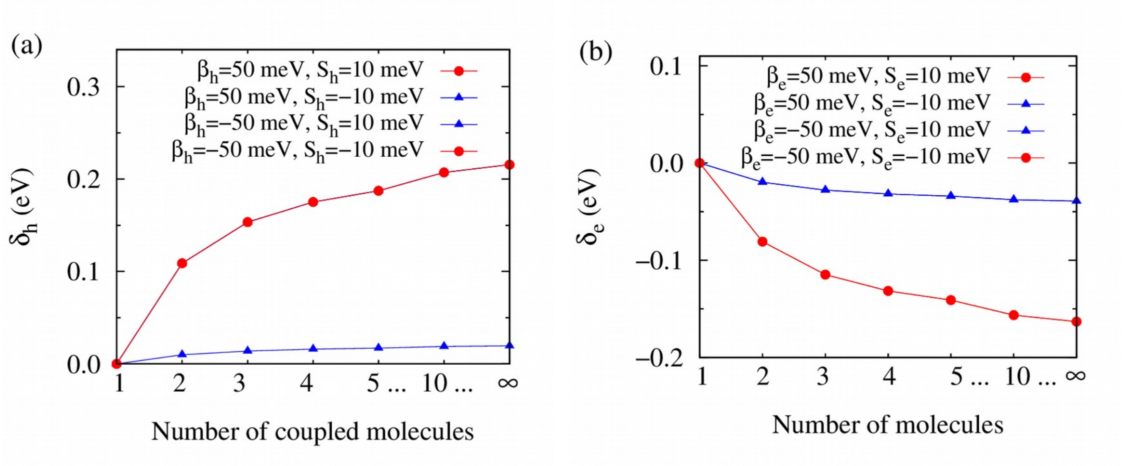


Figure S9 - (a) δ_h and (b) δ_e variation as a function of the number of molecules considering $S_{h/e}$ = ± 10 meV and $\beta_{h/e}$ = ± 50 meV.

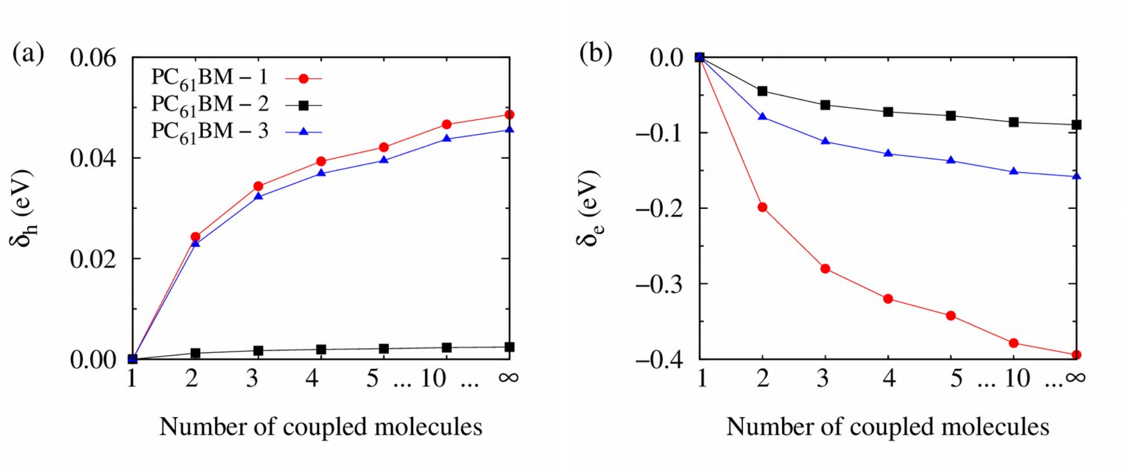


Figure S10 - (a) δ_h and (b) δ_e change as a function of the number of coupled molecules considering the results of $S_{h/e}$ and $\beta_{h/e}$ of three **PC$_{61}$BM** dimers.

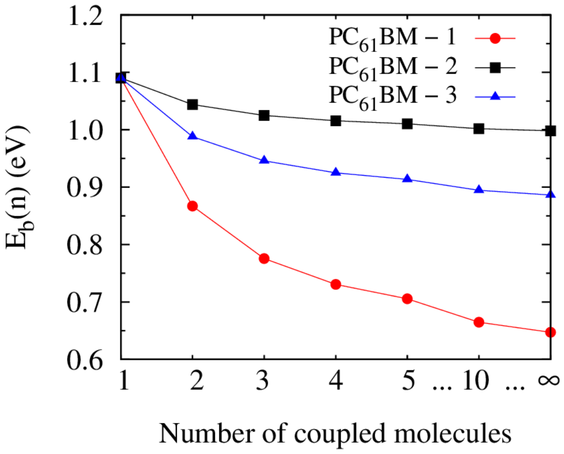


Figure S11 - Exciton binding energy as a function of the number of coupled molecules for **PC$_{61}$BM - 1**, **PC$_{61}$BM - 2** and **PC$_{61}$BM - 3**.

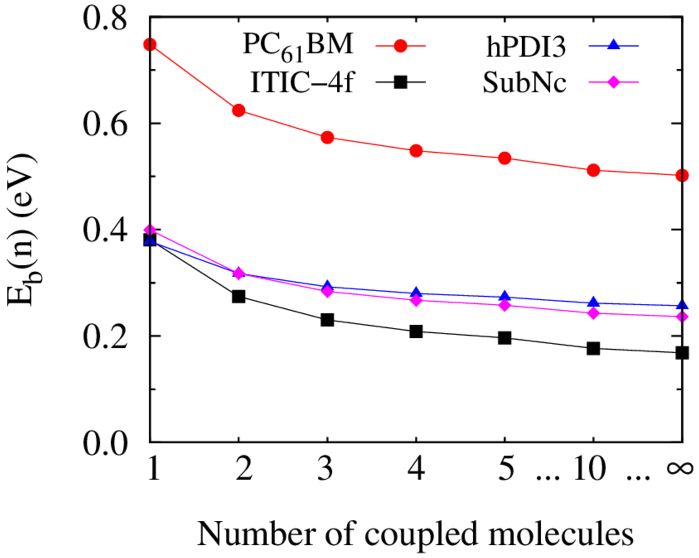


Figure S12 - Exciton binding energy as a function of the number of molecules. The results of **PC$_{61}$BM** are the average between the simulated dimers. $E_b(1)$ is the binding energy of Frenkel exciton calculated with E_b^{vac}/ε method for molecules in GS geometry.

References

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, X. Li and M. Caricato, *Gaussian, Inc., Wallingford CT*.

2 T. M. Clarke and J. R. Durrant, *Chem. Rev.*, 2010, **110**, 6736–6767.