Supporting Information

Effects of Fluorination on Exciton Binding Energy and Charge Transport of π-Conjugated Donor Polymers and the ITIC Molecular Acceptor: a Theoretical Study

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1. PCM parameters, *IP* values and DFT methods.

The geometry optimization of the materials to obtain the PCM parameters was done with ωB97XD/6-31G(d,p) theory level.

Table S1 - Electronic polarizability, molecular volume and dielectric constant.

Materials	Polarizability ($Bohr^3$)	Volume ($Bohr^3$/mol)	Dielectric constant
ITIC	1176.71	9183,411	4.48 (4.5[a])
ITIC-4f	1189.97	8966,444	4.75
DTBT-DT	488.04	4415,886	3.59
DTffBT-DT	488.30	4136,542	3.93
DTBT-NDT	664.90	5817,317	3.75
DTffBT-NDT	691.55	6048,953	3.76
PBDT-T	308.88	3731,677	2.59
PBDT-ffT	318.57	3673,560	2.71

[a] Experimental result obtained from capacitance-voltage measurements.[1]

Table S2 - Vertical ionization potential (*IP*) obtained in solid with PCM compared to measurements of literature. n is the number of mers and n=∞ is the linear extrapolation to a very large number of mers. All results in eV.

Materials	*IP* (eV)					
	n=1	n=2	n=3	n=∞	Exp.	Ref. for Exp.
ITIC	5.65	-	-	-	5.50[a]	[2]
ITIC-4f	5.69	-	-	-	5.66[a]	
DTBT-DT	5.59	5.42	5.34	5.22	5.31[b]	[3]
DTffBT-DT	5.64	5.45	5.40	5.27	5.38[b]	
DTBT-NDT	5.51	5.36	5.33	5.23	5.36[b]	[4]
DTffBT-NDT	5.53	5.39	5.35	5.26	5.41[b]	
PBDT-T	5.86	5.58	5.47	5.28	5.04[c]	[5]
PBDT-ffT	5.90	5.66	5.56	5.40	5.29[c]	

[a] Obtained from the ultraviolet photoelectron spectroscopy (UPS). [b] Electrochemical measurements with cyclic voltammetry. [c] Measured by photoelectron spectroscopy in air (PESA).

Table S3 - Summary of the DFT methods employed in these work for each of the calculations.

Calculation	Method
Geometry optimization, PCM parameters, dipole moment change ($\Delta\mu_{ge}$), electronic coupling (t) and binding energy of the complexes.	ωB97XD/6-31G(d,p)
IP, *EA* and E_{opt}.	M06/6-31G(d,p)
Reorganization energy (λ).	B3LYP/6-31G(d,p)

2. Exciton binding energy in the ground state geometry.

In these section, the geometry optimization was done with ωB97XD/6-31G(d,p) and thereafter single point calculations was done with M06/6-31G(d,p) to obtain the energies in which the PCM method was used.

Table S4 - PCM calculations of vertical ionization potential (*IP*), vertical electron affinity (*EA*), fundamental gap (E_{fund}), optical gap (E_{opt}) and exciton biding energy (E_b) for molecules and oligomers with one mer (n=1). All results in eV.

Materials	n=1				
	IP	*EA*	E_{fund}	E_{opt}	E_b
ITIC	5.65	3.20	2.45	1.94	0.51
ITIC-4f	5.69	3.31	2.38	1.91	0.47
DTBT-DT	5.59	2.29	3.30	2.36	0.94
DTffBT-DT	5.64	2.43	3.21	2.34	0.87
DTBT-NDT	5.51	2.34	3.17	2.31	0.86
DTffBT-NDT	5.53	2.46	3.07	2.25	0.82
PBDT-T	5.86	1.13	4.73	3.40	1.33
PBDT-ffT	5.90	1.36	4.54	3.27	1.28

Table S5 - PCM calculations of vertical ionization potential (*IP*), vertical electron affinity (*EA*), fundamental gap (E_{fund}), optical gap (E_{opt}) and exciton biding energy (E_b) for oligomers with two mers (n=2). All results in eV.

Materials	n=2				
	IP	*EA*	E_{fund}	E_{opt}	E_b
DTBT-DT	5.42	2.45	2.97	2.17	0.80
DTffBT-DT	5.45	2.58	2.87	2.14	0.73
DTBT-NDT	5.36	2.47	2.89	2.16	0.73
DTffBT-NDT	5.39	2.58	2.81	2.11	0.70
PBDT-T	5.58	1.75	3.83	2.76	1.07
PBDT-ffT	5.66	2.00	3.66	2.64	1.01

Table S6 - PCM calculations of vertical ionization potential (*IP*), vertical electron affinity (*EA*), fundamental gap (E_{fund}), optical gap (E_{opt}) and exciton biding energy (E_b) for oligomers with three mers (n=3). All results in eV.

Materials	n=3				
	IP	*EA*	E_{fund}	E_{opt}	E_b
DTBT-DT	5.34	2.51	2.83	2.10	0.73
DTffBT-DT	5.40	2.63	2.77	2.09	0.68
DTBT-NDT	5.33	2.52	2.81	2.12	0.69
DTffBT-NDT	5.35	2.63	2.72	2.07	0.65
PBDT-T	5.47	1.94	3.53	2.56	0.97
PBDT-ffT	5.56	2.20	3.36	2.45	0.91

Table S7 - Extrapolated results for a large number of mers (n=∞) of vertical ionization potential (*IP*), vertical electron affinity (*EA*), fundamental gap (E_{fund}), optical gap (E_{opt}) and exciton biding energy (E_b) (calculated with PCM). The linear extrapolation of these magnitudes is in relation of the reciprocal of the number of mers (1/n).[6] All results in eV.

Materials	n=∞				
	IP	*EA*	E_{fund}	E_{opt}	E_b
DTBT-DT	5.22	2.62	2.60	1.97	0.63
DTffBT-DT	5.27	2.73	2.54	1.96	0.58
DTBT-NDT	5.23	2.61	2.62	2.02	0.60
DTffBT-NDT	5.26	2.71	2.55	1.98	0.57
PBDT-T	5.28	2.35	2.93	2.13	0.80
PBDT-ffT	5.40	2.63	2.77	2.03	0.74

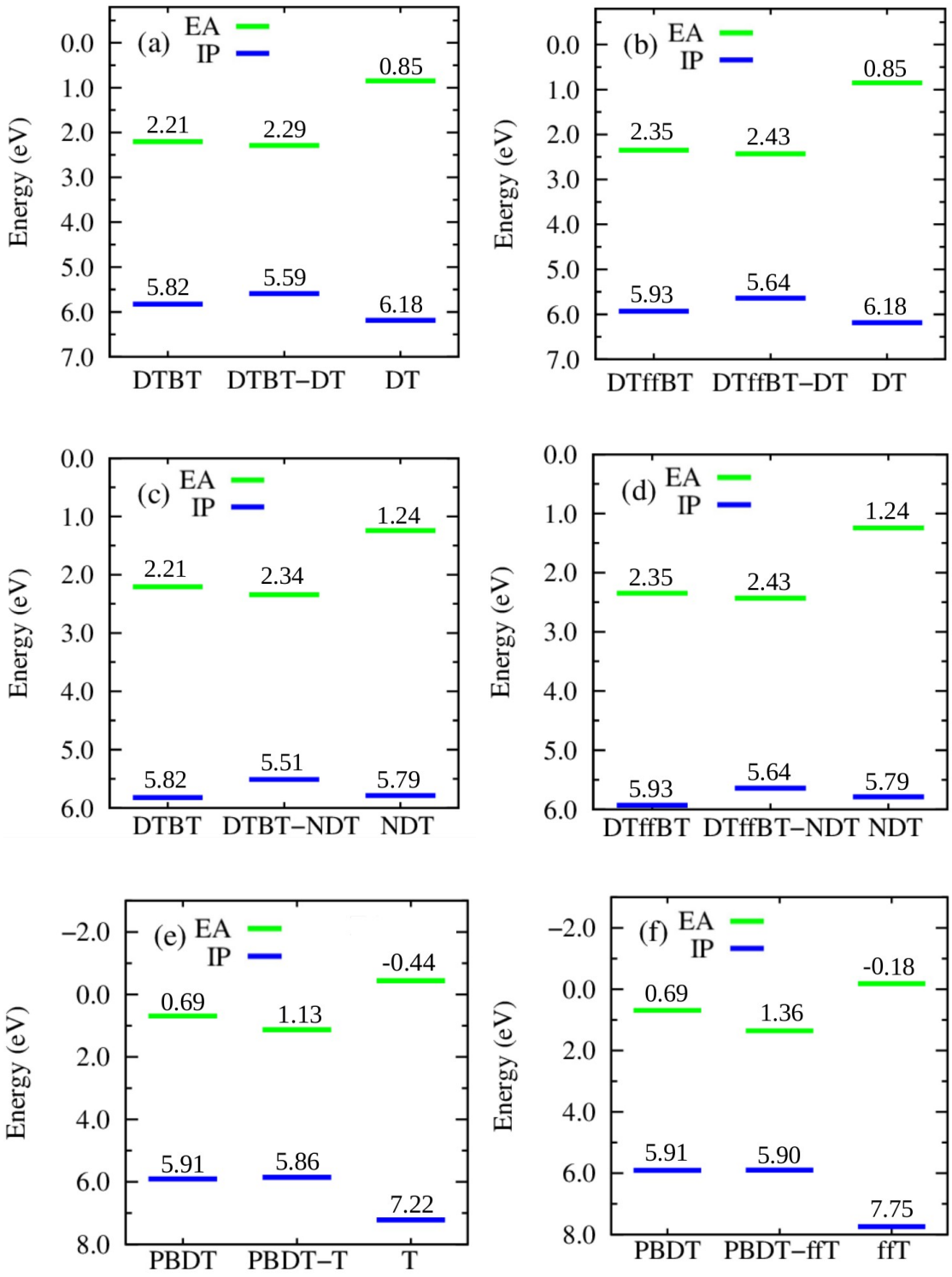

Figure S1 – Calculation of the vertical *EA* and *IP* energies with PCM for monomers and for isolated chemical groups that compose them. (a) DTBT-DT, (b) DTffBT-DT, (c) DTBT-NDT, (d) DTffBT-NDT, (e) PBDT-T and (f) PBDT-ffT.

Table S8 - Gas phase calculations of vertical ionization potential (*IP*), vertical electron affinity (*EA*), fundamental gap (E_{fund}), optical gap (E_{opt}) and exciton biding energy (E_b) for molecules and oligomers with two mers (n=2). All results in eV.

Materials	n=2				
	IP	*EA*	E_{fund}	E_{opt}	E_b
ITIC	6.41	2.49	3.9	2.10	1.82
ITIC-4f	6.54	2.66	3.88	2.07	1.81
DTBT-DT	5.97	1.75	4.22	2.22	2.00
DTffBT-DT	6.04	1.90	4.14	2.17	1.97
DTBT-NDT	5.86	1.77	4.09	2.18	1.91
DTffBT-NDT	5.90	1.92	3.99	2.12	1.86
PBDT-T	6.15	0.99	5.16	2.84	2.32
PBDT-ffT	6.27	1.26	5.01	2.73	2.28

3. Dipole moment change $\Delta\mu_{ge}$.

Table S9 - The calculation results of dipole moment for simulated materials (ωB97XD/6-31G(d,p)).

Materials	μ_g (xyz)	μ_g	μ_e (xyz)	μ_e	$\Delta\mu_{ge}$
ITIC	0.0080 0.3679 -0.0180	0.3684	0.0028 0.4991 -0.0185	0.4994	0.1313
ITIC-4f	-0.0518 0.0201 -0.0215	0.0595	-0.2008 -0.0209 -0.0297	0.2041	0.1548
DTBT-DT	0.7000 0.6658 0.8065	1.2584	0.8475 0.0931 0.7912	1.1632	0.5916
DTffBT-DT	0.1375 0.3743 0.5934	0.7150	0.0053 0.9605 0.6826	1.1783	0.6075
DTBT-NDT	-0.9866 0.6812 -1.1567	1.6660	-1.0971 0.1183 -0.9925	1.4842	0.5967
DTffBT-NDT	1.9809 -0.4848 -1.7039	2.6575	1.4128 -0.5688 -2.3789	2.8247	0.8862
PBDT-T	-0.1043 -0.0941 0.6873	0.7015	0.3024 -0.4194 0.8081	0.9594	0.5346
PBDT-ffT	0.8377 0.1193 -1.1524	1.4297	0.5166 0.8014 -1.0550	1.4220	0.7602

4. Exciton binding energy in the excited state geometry.

In these case, the results are for the materials in geometry of the first excited state obtained with TD-DFT optimization with ωB97XD/6-31G(d,p) and thereafter single point calculations was done with M06/6-31G(d,p) to obtain the energies.

Table S10 - PCM calculations of vertical ionization potential (*IP*), vertical electron affinity (*EA*), fundamental gap (E_{fund}), optical gap (E_{opt}) and exciton biding energy (E_b) for molecules and oligomers with one mer (n=1). All results in eV.

Materials	n=1				
	IP	*EA*	E_{fund}	E_{opt}	E_b
ITIC	5.50	3.35	2.15	1.69	0.46
ITIC-4f	5.55	3.45	2.10	1.67	0.43
DTBT-DT	5.01	2.80	2.21	1.50	0.71
DTffBT-DT	5.17	2.80	2.37	1.69	0.68
DTBT-NDT	5.08	2.72	2.36	1.64	0.72
DTffBT-NDT	5.18	2.79	2.39	1.68	0.71
PBDT-T	5.51	1.54	3.97	2.79	1.18
PBDT-ffT	5.60	1.70	3.90	2.75	1.15

Table S11 - PCM calculations of vertical ionization potential (*IP*), vertical electron affinity (*EA*), fundamental gap (E_{fund}), optical gap (E_{opt}) and exciton biding energy (E_b) for oligomers with two mers (n=2). All results in eV.

Materials	n=2				
	IP	*EA*	E_{fund}	E_{opt}	E_b
DTBT-DT	4.95	2.80	2.15	1.49	0.66
DTffBT-DT	5.05	2.90	2.15	1.54	0.61
DTBT-NDT	4.97	2.83	2.14	1.51	0.63
DTffBT-NDT	5.05	2.91	2.14	1.52	0.62
PBDT-T	5.24	2.15	3.09	2.15	0.94
PBDT-ffT	5.36	2.33	3.03	2.13	0.90

Table S12 - Extrapolated results for a large number of mers (n=∞) of vertical ionization potential (*IP*), vertical electron affinity (*EA*), fundamental gap (E_{fund}), optical gap (E_{opt}) and exciton biding energy (E_b) (calculated with PCM). The linear extrapolation of these magnitudes is in relation of the reciprocal of the number of mers (1/n).[6] All results in eV.

Materials	n=∞				
	IP	*EA*	E_{fund}	E_{opt}	E_b
DTBT-DT	4.89	2.80	2.09	1.48	0.61
DTffBT-DT	4.93	3.00	1.93	1.39	0.54
DTBT-NDT	4.86	2.94	1.92	1.38	0.54
DTffBT-NDT	4.92	3.03	1.89	1.36	0.53
PBDT-T	4.97	2.76	2.21	1.51	0.70
PBDT-ffT	5.12	2.96	2.16	1.51	0.65

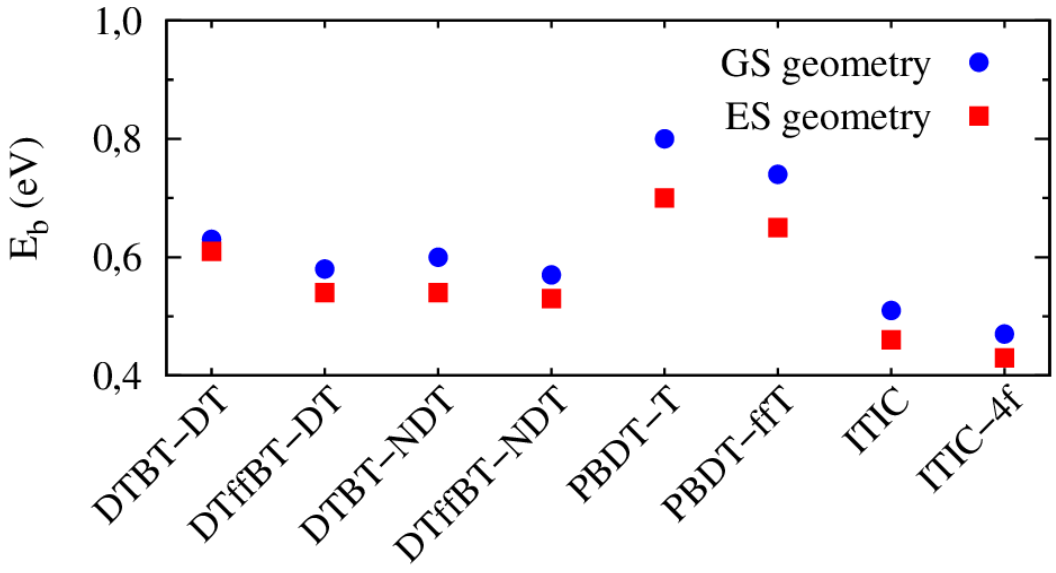

Figure S2 - Exciton binding energy with the materials in ground state (GS) geometry and excited state (ES) geometry. The results for polymers is the extrapolated value for a large number of mers.

5. References.

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