

Electronic Supporting Information for:

Understanding How Lewis Acids Dope Organic Semiconductors: A “Complex” Story

Pablo Simón Marqués^a, Giacomo Londi^b, Brett Yurash^c, Thuc-Quyen Nguyen^c, Stephen Barlow^d, Seth R. Marder^d and David Beljonne^{b*}

a) Laboratoire MOLTECH-Anjou, UMR CNRS 6200, UNIV Angers, SFR MATRIX, 2 Bd Lavoisier, 49045 Angers Cedex, France

b) Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc, 20, 7000 Mons, Belgium

c) Center for Polymers and Organic Solids, Department of Chemistry & Biochemistry, University of California, Santa Barbara, California 93106, United States of America

d) Center for Organic Photonics and Electronics, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia, 30332-0400, United States of America

*email: david.beljonne@umons.ac.be

Contents

I.	PFPT	2
II.	PCPDTPT	6
III.	PCPDTBT	9
IV.	BCF complexes with H ₂ O	11

I. PFPT

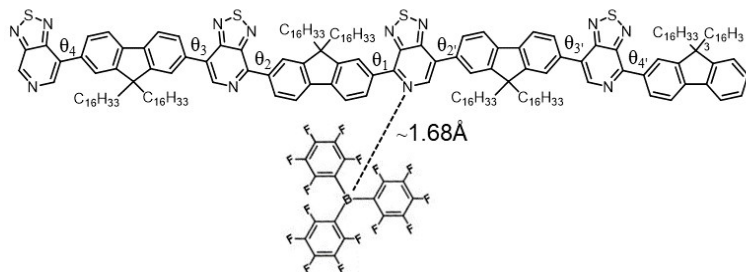


Figure S1: Chemical structure of the PFPT tetramer bound to BCF.

Table S1: Dihedral angles of the neat PFPT tetramer and the different adducts.

	θ_1	θ_2	$\theta_{2'}$	θ_3	$\theta_{3'}$	θ_4	$\theta_{4'}$
Neat	17	19	39	39	39	39	19
w/ BF_3	49	19	39	39	39	39	19
w/ BCF	51	19	41	39	39	39	19
w/ BBr_3	52	19	37	39	39	39	19

We performed a ground-state CM5 charge population analysis for the neat PFPT oligomer and when bound to LAs. While the PT group in the neat form carries a slightly negative partial charge ($-0.07|e|$), it acts as a LB within the coordinated complex, bearing a positive partial charge of about $+0.23|e|$, irrespective of the LA. As expected, the LA withdraws electron density from the PT group (making it more electron-poor), carrying a negative partial charge of $-0.40|e|$. The sum of the net charges upon binding is negative, as there is also a charge-transfer (CT) contribution arising from adjacent regions in the oligomer. The ground-state CT character of the adducts does not explain the trend observed on the EA, E_{gap} , and the absorption peak in Table 1 (see main text) with the nature of the LA. We found instead instructive to quantify the contribution of the LA to the LUMO wave function in the adduct: BF_3 contributes much less ($\sim 0.5\%$) to the LUMO than BCF ($\sim 3.0\%$) or BBr_3 ($\sim 2.6\%$). There is thus some partial hybridization of the oligomer molecular orbitals with the boron atom of the LA; the variation of this hybridization with LA, combined with the partial ground-state CT, helps rationalize why, in comparison to the other two LAs, BF_3 shows the smallest change in the EA and, in turn, the smallest impact on the E_{gap} of the adduct.

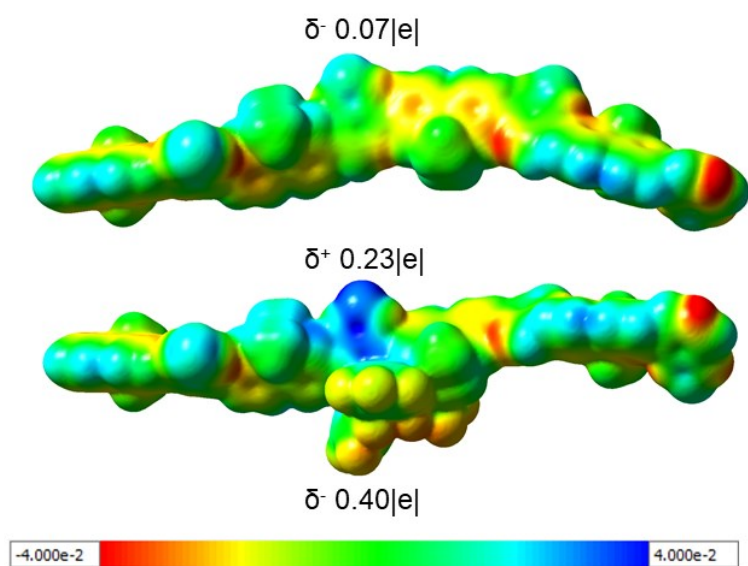


Figure S2: CM5 charge distribution of the neat tetramer (top) and the adduct with BCF (bottom).

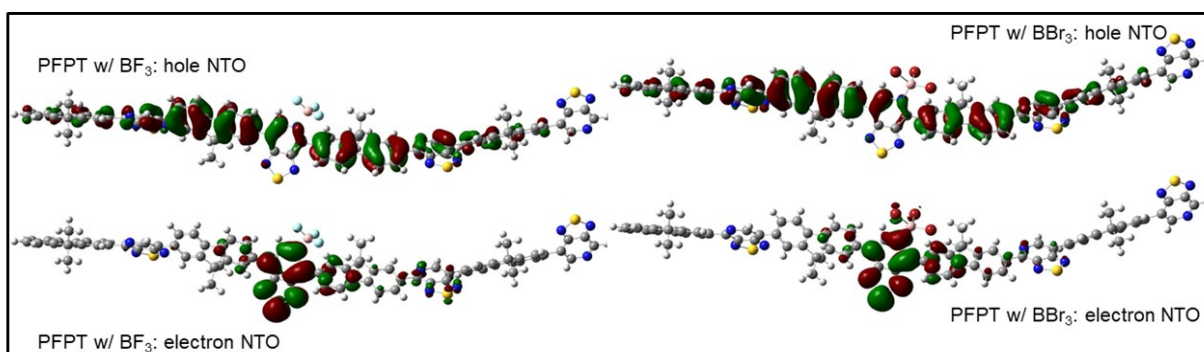


Figure S3: Lowest electronic excitation natural transition orbitals (NTOs) of the adduct with BF_3 (left) and BBr_3 (right).

Table S2: Calculated IP, EA and transport gap E_{gap} (in eV) for the neat PFPT tetramer and octamer and for their Lewis acid-base (LAB) adducts with BCF. Excitation wavelength (in nm), energy (in eV) and oscillator strength (f) of the lowest electronic transition S_0-S_1 are also reported.

	IP	EA	E_{gap}	$E(S_0-S_1)$	$f(S_0-S_1)$
PFPT tetramer	5.43	2.62	2.81	546 / 2.27	2.23
PFPT octamer	5.37	2.66	2.71	557 / 2.23	4.85
tetramer w/ BCF	5.57	3.01	2.56	607 / 2.04	0.92
octamer w/ BCF	5.43	3.01	2.42	610 / 2.03	1.11

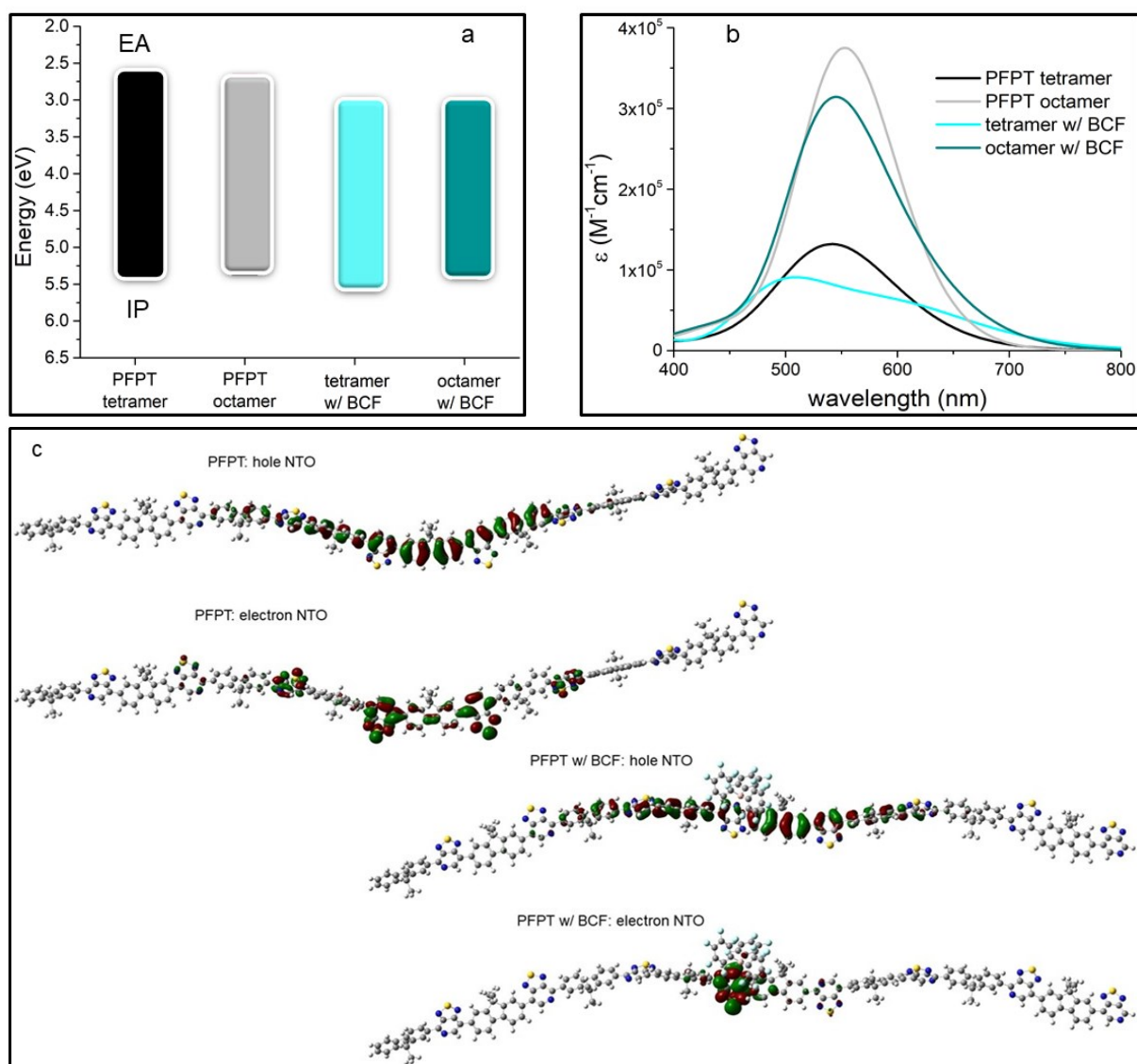


Figure S4: Energetic diagram showing IP and EA (in eV), b) calculated TD-DFT optical absorption spectra (in nm) for the different species and c) lowest electronic excitation NTOs of the neat PFPT octamer and the adduct with BCF. In panel b) absorption spectra were convoluted with a Full Width Half Maximum of 0.2 eV and the molar absorption coefficient ϵ is reported on the y-axis.

II. PCPDTPT

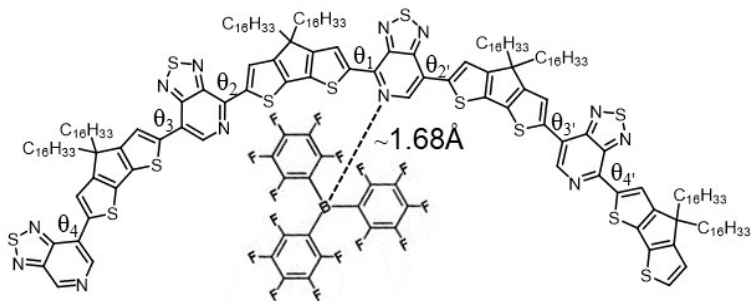


Figure S5: Chemical structure of the PCPDTPT tetramer bound to BCF.

Table S3: Dihedral angles of the neat PCPDTPT tetramer and the different adducts.

	θ_1	θ_2	$\theta_{2'}$	θ_3	$\theta_{3'}$	θ_4	$\theta_{4'}$
Neat	0	0	0	0	0	0	0
w/ BF_3	39	0	5	12	13	11	0
w/ BCF	112	0	22	14	14	11	0
w/ BBr_3	46	0	21	12	14	11	0

We performed a ground-state CM5 charge population analysis for the neat PCPDTPT oligomer and when bound to LAs. As in PFPT, the PT group in the neat form carries a slightly negative partial charge ($-0.10|e|$) and it acts as a LB within the coordinated complex, bearing a positive partial charge of about $+0.22|e|$. Therefore, the adduct features a partial CT, with the LA molecule carrying a negative partial charge of $-0.46|e|$. In this case, the boron atomic orbital contribution to the LUMO of the adduct is significantly smaller for BF_3 ($\sim 0.1\%$) compared to BCF ($\sim 3.5\%$) and BBr_3 ($\sim 2.3\%$).

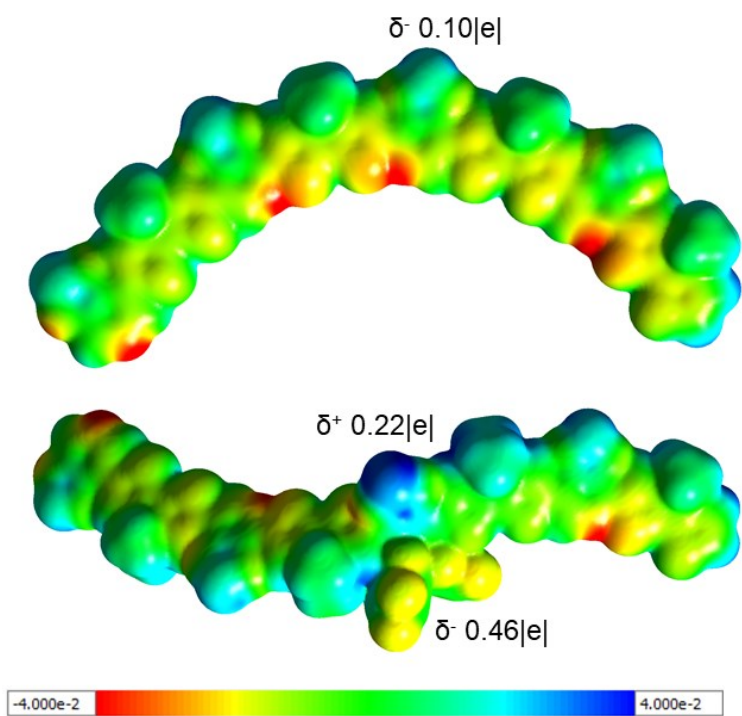


Figure S6: CM5 charge distribution of the neat tetramer (top) and the adduct with BCF (bottom).

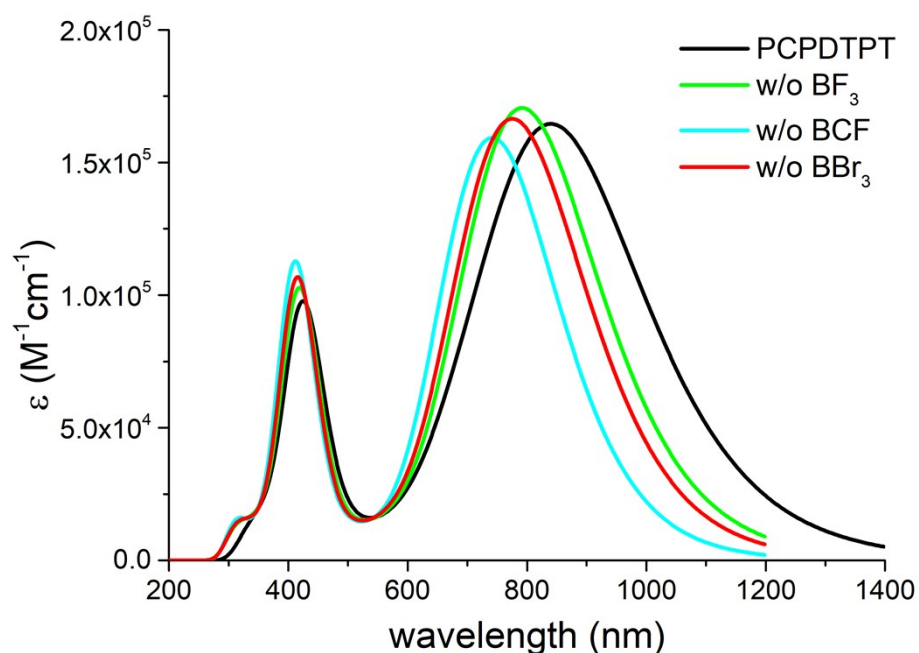


Figure S7: Calculated TD-DFT optical absorption spectra without the LA. Absorption spectra were convoluted with a Full Width Half Maximum of 0.2 eV and the molar absorption coefficient ϵ is reported on the y-axis.

Table S4: Calculated E_{gap} (in eV), excitation wavelength (in nm), energy (in eV) and oscillator strength (f) of the lowest electronic transition S_0-S_1 for the pristine PCPDTPT tetramer without the different LAs.

	E_{gap}	$E(S_0-S_1)$	$f(S_0-S_1)$
PCPDTPT	1.84	864 / 1.43	2.68
w/o BF_3	1.97	805 / 1.54	2.82
w/o BCF	2.12	750 / 1.65	2.69
w/o BBr_3	2.01	789 / 1.57	2.70

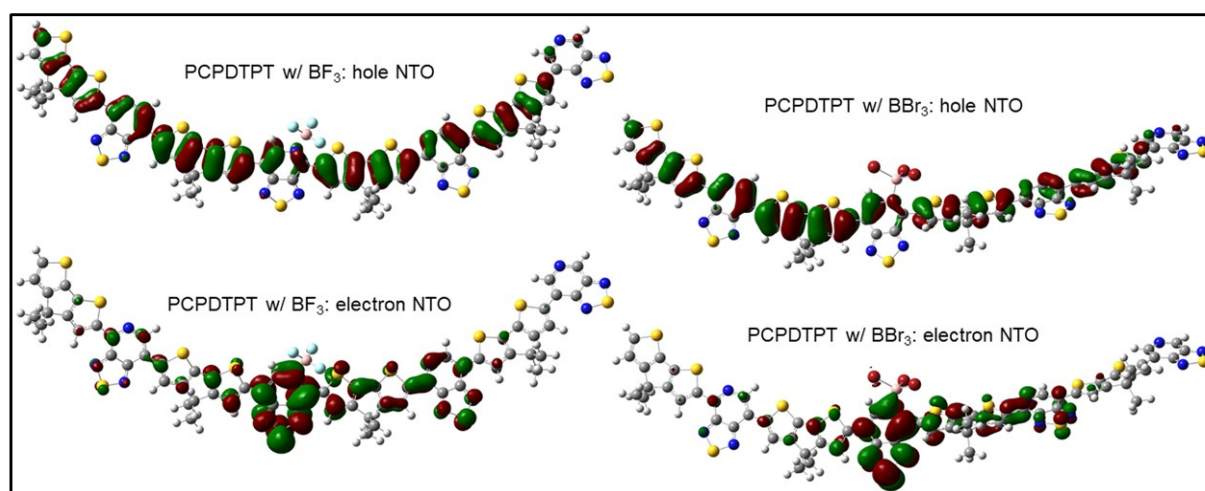


Figure S8: Lowest electronic excitation natural transition orbitals (NTOs) of the adduct with and BF_3 (left) and BBr_3 (right).

III. PCPDTBT

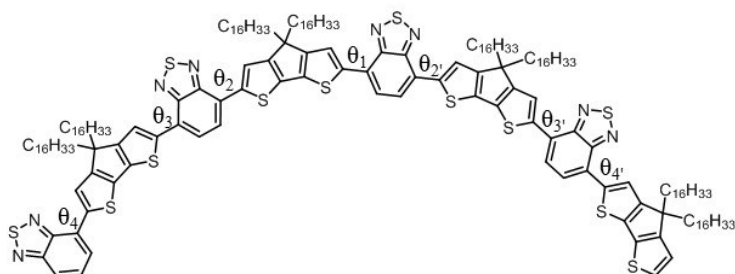


Figure S9: Chemical structure of the PCPDTBT tetramer.

Table S5: Dihedral angles of the neat PCPDTBT tetramer, its radical cation, the protonated tetramer and its radical.

	θ_1	θ_2	$\theta_{2'}$	θ_3	$\theta_{3'}$	θ_4	$\theta_{4'}$
PCPDTBT	18	17	16	19	20	21	18
(PCPDTBT)⁺·	18	17	16	19	20	21	18
(PCPDTBT-H)⁺	6	21	10	19	53	20	17
(PCPDTBT-H)[·]	6	18	0	19	160	21	19

Table S6: Computed electronic enthalpy ΔH_{elec}^0 values for the reactions presented in Scheme 1 and Scheme 2 in the main text, either by modelling species based on a PCPDTBT tetramer or those based on a PCPDTBT octamer.

ΔH_{elec}^0	w/ PCPDTBT tetramer		w/ PCPDTBT octamer	
	Protonation	Electron transfer	Protonation	Electron transfer
Scheme 1	+22.9	+18.2	+23.5	+17.5
Scheme 2	+36.9		+37.0	

To check whether the PCPDTBT polaron and the “protonated radical” could in principle be distinguished in the same way, we computed the g-tensor values of the two PCPDTBT radical species. It turns out that the isotropic average g value, g_{iso} , of the radical (PCPDTBT) $^{\cdot+}$ cation and the protonated radical (PCPDTBT-H) $^{\cdot}$ species are very different. Namely, for the former, we obtained $g_{\text{iso}} = 2.0019$, while for the latter $g_{\text{iso}} = 2.0031$. We note that such a difference in g-tensor relates to different spin density distributions being delocalized over the entire molecular backbone in the radical (PCPDTBT) $^{\cdot+}$ cation but more spatially confined in the protonated radical (PCPDTBT-H) $^{\cdot}$.

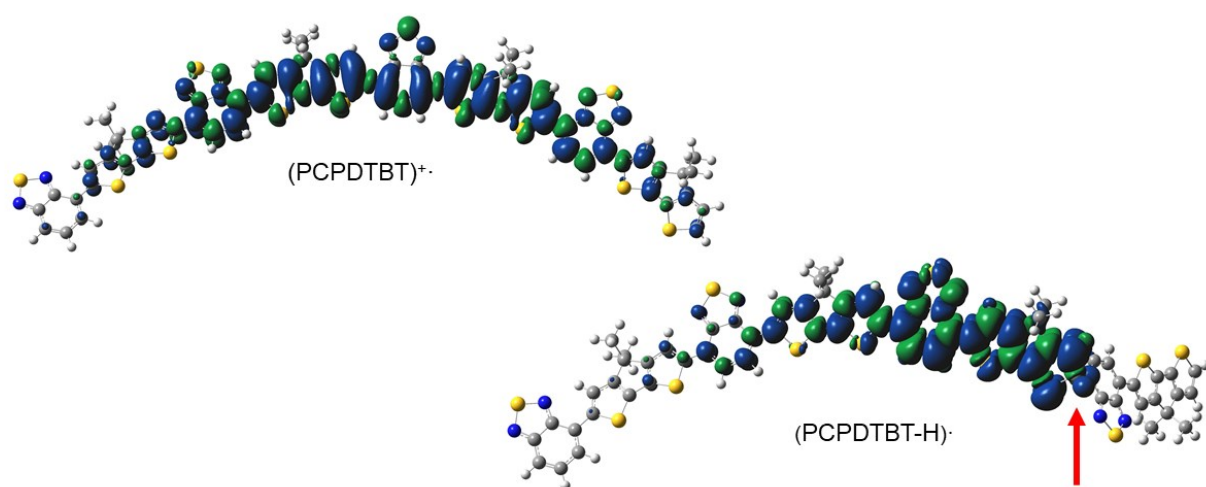


Figure S10: Spin density distribution of the two radical species. The red arrow point to the position in which the hydrogen atom was added, i.e. an α -carbon atom in the CPDT group.

IV. BCF complexes with H₂O

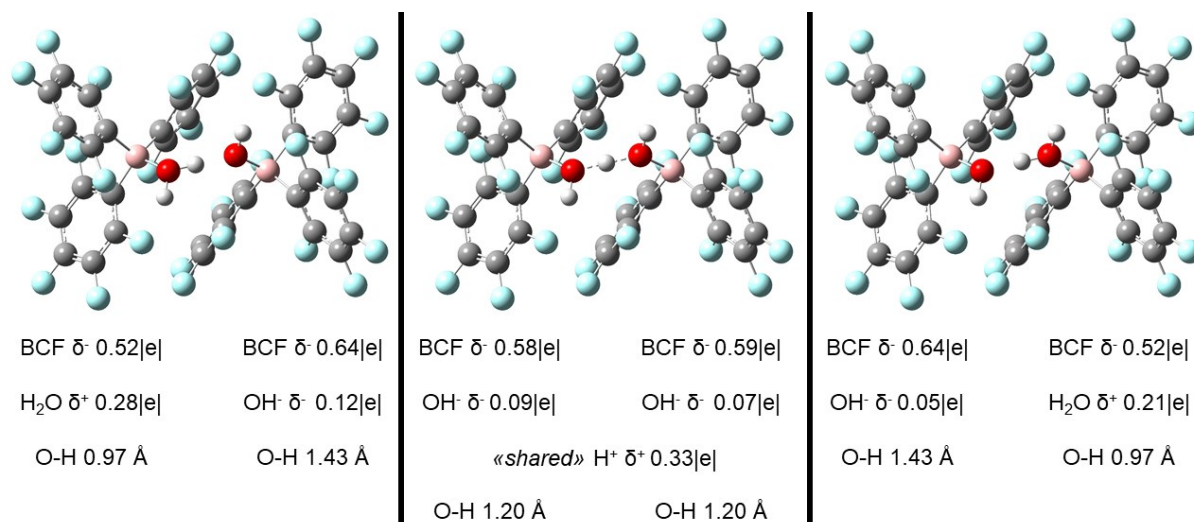


Figure S11: CM5 charge distributions of the anionic $[BCF(OH)(OH_2)BCF]^-$ complex. Here, we changed the interatomic O-H distance, moving the hydrogen atom from the left oxygen to the right one. Note that none of the three cases corresponds to the global minimum, where the H atom is distant 1.10 Å from the O atom (on the left) and 1.30 Å from the other O atom (on the right). The relative energy of the three scenarios with respect to the global minimum is: +0.14 eV (case on the left), +0.02 eV (case in the middle), +0.26 eV (case on the right).

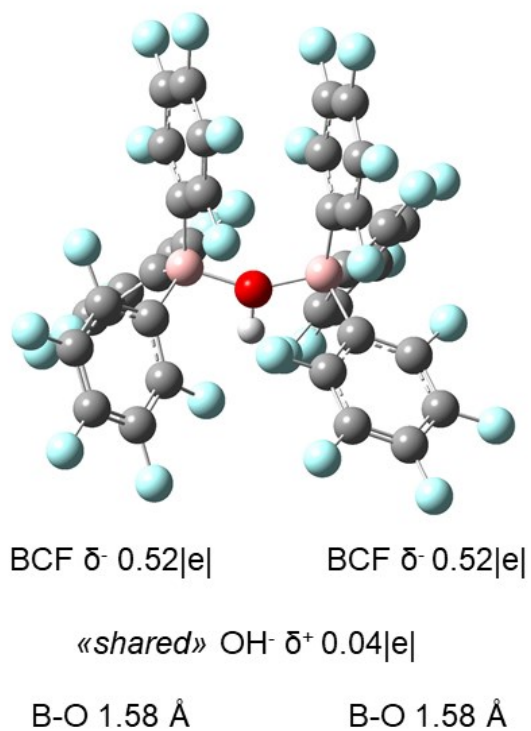


Figure S12: CM5 charge distributions of the anionic $[BCF(OH)BCF]^-$ complex.

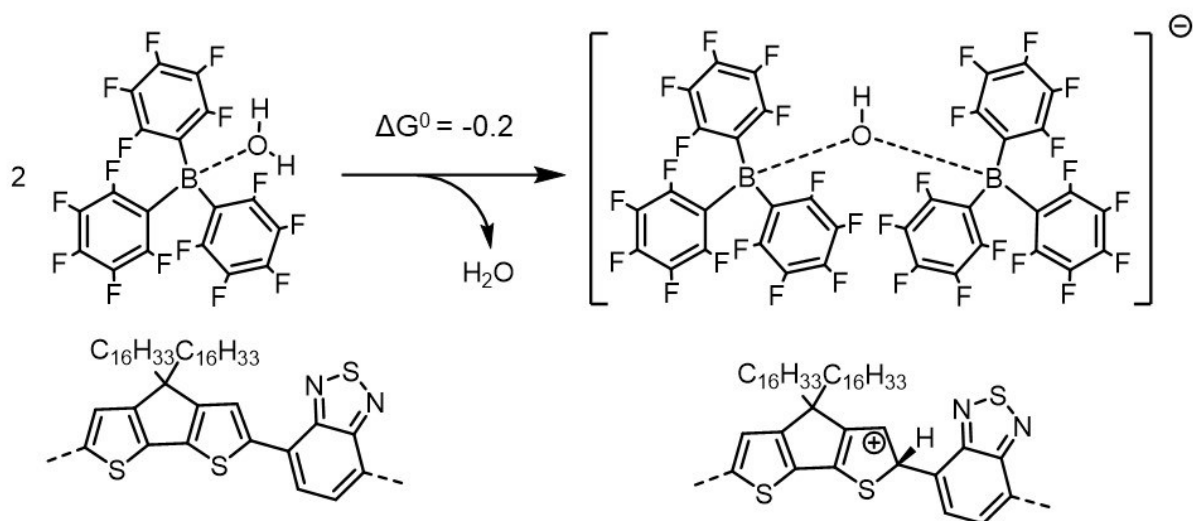


Figure S13: Formation of the $[BCF(OH)BCF]^-$ anion and protonation of the neat PCPDTBT tetramer, when two $BCF:OH_2$ complexes react together and an H_2O molecule is eliminated. DFT calculations yield $\Delta G^0 = -0.2 \text{ kcal mol}^{-1}$ (or -9 meV) for this reaction.