Supporting Information

"Electrochemical and spectrophotometrical investigation of the electron-accepting strength of organic superélectrophiles : X-Ray structure of their charge transfer complexes with tetrathiafulvalene."

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Experimental Part:

The EA_{CT} of **1-17** were determined from the energies of the *in situ* generated Charge Transfer Complexes (CTC) resulting from the interaction between the heterocycles **1-17**, used as acceptors and five donors of known Ionization Potential (IP) [Hexamethylbenzene (IP = 7.85 eV), Pyrene (IP =7.41 eV), Anthracene (IP = 7.33 eV), 9-Chloroanthracene (IP = 7.39 eV), 9-Methylanthracene (IP = 7.17 eV) and 9,10-Dimethyl-anthracene (IP = 7.04 eV)]. The two equations 1 and 2 describe the relation between the energy of the CTCs and the electron affinity of the acceptor for an unknown acceptor and the energy of a CTC for a known acceptor such as DNBF or TCNQ, respectively. Assuming that P is constant and insensitive to the structure of the donor, the difference between the two equations 1 and 2 (for a same donor) leads to the equation 3 and allows the determination of the EA_{CT} of heterocycles.

$$E_{CT} = IP - EA_{CT} - P \qquad \text{eq. 1}$$

$$E^{0}_{CT} = IP - EA^{0}_{CT} - P \qquad \text{eq. 2}$$

$$EA_{CT}(\mathbf{1\text{-}17}) = EA^{0}_{CT}(\text{DNBF}, \mathbf{10}) + E^{0}_{CT}(\text{DNBF } \mathbf{10}) - E_{CT}(\mathbf{1\text{-}17}) \qquad \text{eq. 3}$$

In the table are collected, the wavelengths of the CTC in nm, their corresponding energies (in eV) and the EA_{CT} values of each acceptor. Finally, in the last line are reported the average EA_{CT} for each heterocycle with an accuracy of $\pm$ 0.05 eV .

Energies E_{CT} (eV) for each CT complexes

donors	IP	DNBZ **6**	NBZ **5**	NBDF **12**	ClDNBF **11**	TCNQ **1**	DNBS **15**	BTF **13**	NBDS **16**	NBF **8**	6CN4NBF **9**	DNBF **10**	**7**
9,10-dimethylanthracene	7.04	1.854	2.347	1.942	1.739	1.316	2.073	2.473	2.265	2.144	1.870	1.777	1.910
9-methylanthracene	7.17	1.960	2.439	2.073	1.856	1.446	2.201	2.538	2.392	2.269	1.990	1.913	2.039
Anthracene	7.33	2.022	2.618	2.241	1.990	1.574	2.347	2.704	2.580	2.392	2.126	2.020	2.148
9-chloroanthracene	7.39	2.155	2.704	2.347	2.022	1.615	2.415	2.733	2.647	2.434	2.182	2.073	2.233
Pyrene	7.41	2.152	2.745	2.333	2.022	1.636	2.392	2.795	2.644	2.510	2.201	2.070	2.211
Hexamethylbenzene	7.85	2.439	3.109	2.675	2.453	2.073	2.795	3.189	2.997	2.850	2.590	2.492	2.635

λ^{CT} (nm) for each CT complexes

donors	IP	DNBZ **6**	NBZ **5**	NBDF **12**	ClDNBF **11**	TCNQ **1**	DNBS **15**	BTF **13**	NBDS **16**	NBF **8**	6CN4NBF **9**	DNBF **10**	**7**
9,10-dimethylanthracene	7.04	671	530	640	715	945	600	503	549	580	665	700	651
9-methylanthracene	7.17	635	510	600	670	860	565	490	520	548	625	650	610
Anthracene	7.33	615	475	555	625	790	530	460	482	520	585	616	579
9-chloroanthracene	7.39	577	460	530	615	770	515	455	470	511	570	600	557
Pyrene	7.41	578	453	533	615	760	520	445	470	495	565	601	562
Hexamethylbenzene	7.85	510	400	465	507	600	445	390	415	436	480	499	472

EA_{CT} (eV)for each CT complexes

donors	IP	DNBZ **6**	NBZ **5**	NBDF **12**	ClDNBF **11**	TCNQ **1**	DNBS **15**	BTF **13**	NBDS **16**	NBF **8**	6CN4NBF **9**	DNBF **10**	**7**
9,10-dimethylanthracene	7.04	2.57	2.08	2.48	2.69	3.10	2.35	1.95	2.16	2.28	2.56	2.65	2.52
9-methylanthracene	7.17	2.60	2.12	2.49	2.71	3.10	2.36	2.02	2.17	2.29	2.57	2.65	2.52
Anthracene	7.33	2.65	2.05	2.43	2.68	3.10	2.32	1.97	2.09	2.28	2.54	2.65	2.52
9-chloroanthracene	7.39	2.57	2.02	2.38	2.70	3.10	2.31	1.99	2.08	2.29	2.54	2.65	2.49
Pyrene	7.41	2.57	1.97	2.39	2.70	3.10	2.33	1.93	2.08	2.21	2.52	2.65	2.51
Hexamethylbenzene	7.85	2.70	2.03	2.47	2.69	3.10	2.35	1.95	2.15	2.29	2.55	2.65	2.51
		2.61	2.05	2.44	2.69	3.10	2.34	1.97	2.12	2.27	2.55	2.65	2.51
EA_{CT} (± 0.05 eV)		2.60	2.05	2.45	2.70	3.10	2.35	1.95	2.10	2.25	2.55	2.65	2.50