

Supplementary Information

Electronic couplings for molecular charge transfer: benchmarking CDFT, FODFT and FODFTB against high-level ab initio calculations. II.

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Table S1. Electronic coupling matrix elements (meV) and the decay constants β (\AA^{-1}) for some additional molecules that were initially considered as candidates to be included in the HAB7- database.

Dimer		CDFT/PBE %HFX			CDFT/ HSE06	FODFT	FODFTB*	AOM	Ref.	
		0	25	50						
C ₂₀	$ H_{ab} $	3.5 \AA	–	–	–	69.0	81.3	23.6	159.6	
		4.0 \AA	–	–	–	33.4	35.3	16.1	99.9	
		4.5 \AA	–	–	–	16.3	14.6	10.1	64.6	
		5.0 \AA	–	–	–	7.9	5.7	5.9	45.6	
	β	–	–	–	–	2.88	3.53	1.84	1.68	
Coronene	$ H_{ab} $	3.5 \AA	589.1	514.7	431.1	535.5	300.5	215.6	214.3	–
		4.0 \AA	288.1	239.3	195.4	252.4	137.1	87.1	118.0	–
		4.5 \AA	146.1	116.2	93.5	124.2	63.2	33.7	61.0	–
		5.0 \AA	73.2	57.2	46.0	60.9	29.7	12.5	30.0	–
	β	2.77	2.93	2.98	2.89	3.09	3.80	2.62	–	
Triphenylene	$ H_{ab} $	3.5 \AA	618.8	539.5	457.6	558.1	304.0	216.0	214.9	–
		4.0 \AA	318.6	266.2	221.3	279.1	143.4	87.2	119.6	–
		4.5 \AA	171.4	139.1	114.7	147.5	67.8	33.8	62.7	–
		5.0 \AA	94.0	76.0	62.7	81.5	31.3	12.5	31.4	–
	β	2.51	2.61	2.65	2.56	3.03	3.80	2.56	–	

*For coronene, triphenylene and C₂₀ molecules there are several (quasi)degenerate orbitals. Such orbitals that are very close in energy can be relevant for the charge transfer processes. In case of the FODFTB calculations, averaged effective couplings were derived. The square of these effective couplings should describe the hopping probability of an electron from molecule A to molecule B without considering explicitly which one of the degenerate orbitals is carrying the charge. According to Fermi's golden rule the transition rate from initial (i) to final (f) state is proportional to $|H_{if}|^2 \cdot \rho(E_f)$ where in the initial state the electron is located on the donor and in the final state on the acceptor and $\rho(E_f)$ is the density of final states. In the non-degenerate case H_{if} would be the matrix element between the LUMOs on each molecule and the density of states on the acceptor $\rho(E_f)$. In case of degeneracy $|H_{if}|^2$ is given as mean square average of all possible coupling elements between the degenerate orbitals whereas $\rho(E_f)$ is equal to degeneracy of the acceptor. Following these considerations we derive an effective coupling $H_{ab} = \sqrt{|H_{if}|^2 \cdot \rho(E_f)}$ that can be directly plugged in rate equations like Marcus Theory and reduces the multi-orbital description to a transition probability from one molecule to other. For coronene and triphenylene the two degenerate LUMOs were considered and for C₂₀ the three lowest unoccupied orbitals.