Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for

Fragment-orbital tunneling currents and electronic couplings for analysis of molecular charge-transfer systems

Sang-Yeon Hwang, Jaewook Kim and Woo Youn Kim*

Department of Chemistry, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea

*E-mail: wooyoun@kaist.ac.kr

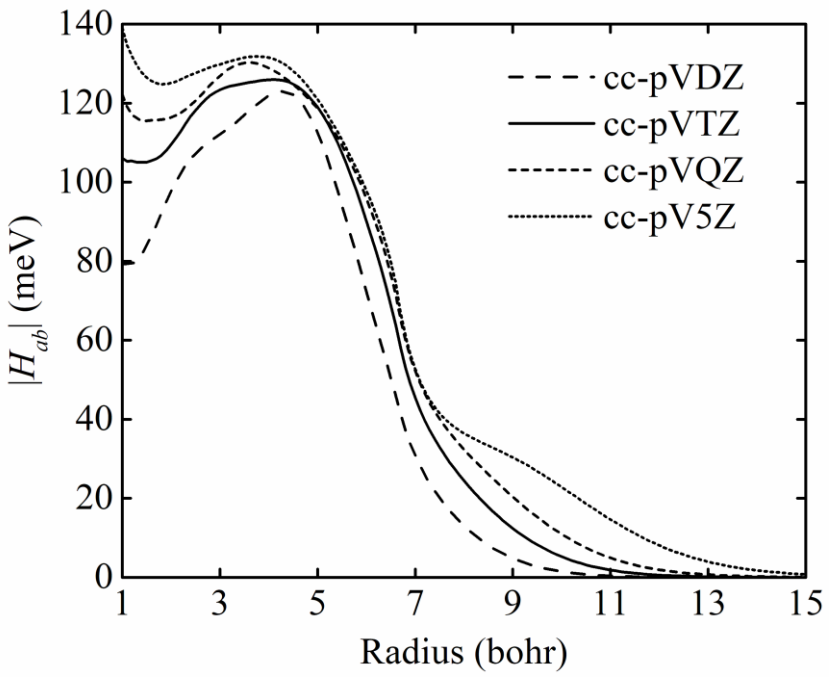

Fig. S1 Grid-radius test on a H-atom dimer with 3.5 Å separation. The grid spacing is 0.1 bohr. The incommensurability between the flux and the transferred population at large grids is gradually reduced as the basis-set size increases.

Table S1 Same as Table 3 in the text except the FOTC here used the neutral-fragment LUMOs instead of the anionic-fragment HOMOs. The reference values are from ref. [A. Kubas, F. Gajdos, A. Heck, H. Oberhofer, M. Elstner and J. Blumberger, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14342–14354]. All the coupling values are in meV.

Dimer	R	Ref.	FOTC
Anthracene	3.5 Å	421.1	387.4
	4.0 Å	212.3	210.9
	4.5 Å	106.1	103.5
	5.0 Å	52.3	47.4
Tetracene	3.5 Å	417.2	380.1
	4.0 Å	204.3	203.3
	4.5 Å	97.9	97.1
	5.0 Å	45.4	42.2
Pentacene	3.5 Å	411.0	377.2
	4.0 Å	198.0	199.8
	4.5 Å	92.4	93.8
	5.0 Å	41.0	39.6
Perfluoroanthracene	3.5 Å	310.9	266.4
	4.0 Å	139.1	132.3
	4.5 Å	59.9	60.3
	5.0 Å	24.0	20.5
Perylene	3.5 Å	423.7	388.5
	4.0 Å	220.7	221.4
	4.5 Å	116.6	107.4
	5.0 Å	62.8	54.2
Perylene diimide	3.5 Å	373.8	326.0
	4.0 Å	179.2	173.8
	4.5 Å	84.1	78.5
	5.0 Å	38.0	34.7

Porphin	3.5 Å	374.5	335.6
	4.0 Å	182.9	176.2
	4.5 Å	89.4	81.2
	5.0 Å	44.1	35.4
MSE			-12.4
MUE			12.7
MRSE/%			-6.6
MRUE/%			6.8

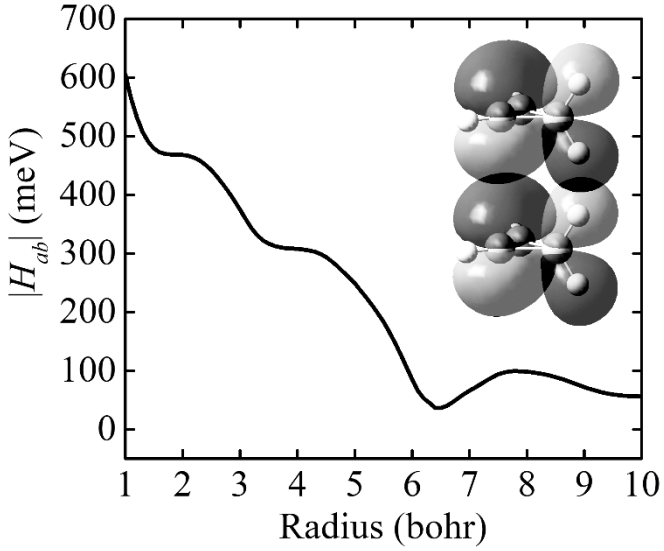

Fig. S2 Grid-radius test on the cyclopropene dimer with 3.5 Å separation. The grid spacing is 0.1 bohr. The structure and HOMO isosurfaces of the cyclopropene dimer are shown top right. The distance between the two inward hydrogens, or the shortest distance between the fragments, is 3.1 bohr.