Supporting Information for: "Charge Separation and Charge Transfer in the Low Lying Excited States of Pentacene"

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1 Density Functionals

RSH functionals used in this work follow the general form given in Eq. (9). Specific formulas are provided here, for definiteness:

$$E_{xc}^{\text{RSH-}\omega\text{PBE}} = E_{x,\text{LR}}^{\text{HF}} + E_{x,\text{SR}}^{\text{PBE}} + E_c^{\text{PBE}} \tag{S1}$$

$$E_{xc}^{\text{sRSH-}\omega\text{PBE}} = \epsilon^{-1} E_{x,\text{LR}}^{\text{HF}} + \epsilon^{-1} E_{x,\text{SR}}^{\omega\text{PBE}} + (1 - \epsilon^{-1}) E_x^{\text{PBE}} + E_c^{\text{PBE}} \tag{S2}$$

$$E_{xc}^{\text{RSH-}\mu\text{BLYP}} = E_{x,\text{LR}}^{\text{HF}} + E_{x,\text{SR}}^{\mu\text{B88}} + E_c^{\text{LYP}} \tag{S3}$$

$$E_{xc}^{\text{sRSH-}\mu\text{BLYP}} = \epsilon^{-1} E_{x,\text{LR}}^{\text{HF}} + \epsilon^{-1} E_{x,\text{SR}}^{\mu\text{B88}} + (1 - \epsilon^{-1}) E_x^{\text{B88}} + E_c^{\text{LYP}} \tag{S4}$$

$$E_{xc}^{\text{RSH-}\omega\text{PBEh}} = \alpha E_{x,\text{SR}}^{\text{HF}} + E_{x,\text{LR}}^{\text{HF}} + (1 - \alpha) E_{x,\text{SR}}^{\omega\text{PBE}} + E_c^{\text{PBE}} \tag{S5}$$

$$E_{xc}^{\text{sRSH-}\omega\text{PBEh}} = \alpha E_{x,\text{SR}}^{\text{HF}} + \epsilon^{-1} E_{x,\text{LR}}^{\text{HF}} + (\epsilon^{-1} - \alpha) E_{x,\text{SR}}^{\omega\text{PBE}} + (1 - \epsilon^{-1}) E_x^{\text{PBE}} + E_c^{\text{PBE}} \tag{S6}$$

By way of notation, $E_{x,\text{SR}}^{\text{PBE}}$ is called ωPBE, which is the short-range GGA exchange functional developed in Ref. 1 based on the original PBE functional. Similarly, $E_{x,\text{SR}}^{\mu\text{B88}}$ is called μBLYP as developed in Ref. 2. (The μB88 versus ωPBE nomenclature was introduced in Ref. 3.) In the present work, we use 20% short-range Hartree-Fock exchange ($\alpha = 0.2$) for the functionals in Eqs. (S5) and (S6), in combination with ωPBE exchange, as in the LRC-ωPBEh functional developed in Ref. 1. The "h" in ωPBEh indicates that the functional is a hybrid even at short range. The quantity ϵ that appears in the sRSH functionals is the dielectric constant, used to ensure that the asymptotic form of the electron–hole interaction is $\sim (\epsilon r)^{-1}$, and for pentacene we use $\epsilon = 3.6$.

For comparison to previous literature, Table S1 provides optimally-tuned range-separation parameters obtained for pentacene monomer using a variety of functionals and basis sets. However, the calculations reported here use the cluster-tuned values of ω that are provided in Table II.

2 TDDFT Results

The following additional TDDFT results are provided.

- Table S2: Excitation energies and dipole moments for the dimer and the two tetramers, computed using the OT-RSH-μBLYP and OT-sRSH-μBLYP functionals. These are analogous to the OT-(s)RSH-ωPBE results

- Table S3: Excited-state dipole moments for the low-lying states of pentacene hexamer. These data are analogous to those presented for the dimer in Table III and for the tetramer in Tables IV and V.

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- Figure S1: Electron–hole correlation plots (matrices $\boldsymbol{\Omega}$) computed for pentacene dimer with various functionals.

- Figure S2: Electron–hole correlation plots (matrices $\boldsymbol{\Omega}$) computed for the compact pentacene tetramer, with various functionals. These plots complement the ones provided in Fig. 6, providing results for some additional functionals.

- Figure S3: Electron–hole correlation plots (matrices $\boldsymbol{\Omega}$) computed for the compact pentacene tetramer, with various functionals. These plots complement the ones provided in Fig. 7, providing results for some additional functionals.

Table S1: Range separation parameters (ω) tuned for pentacene monomer.

Functional	Basis Set	ω (bohr^{-1})	Reference
RSH-ωPBE	6-31+G*	0.195	this work
RSH-ωPBEh	6-31+G*	0.160	this work
RSH-μBLYP	6-31+G*	0.200	this work
RSH-ωPBE	cc-PVTZ	0.195	4
RSH-ωPBEh	cc-PVTZ	0.157	4
RSH-ωPBEh	cc-PVTZ	0.160	5
RSH-ωPBE	6-31G**	0.20	6
RSH-μBLYP	6-31G**	0.21	6
RSH-ωB97X	6-31G**	0.18	6
RSH-ωB97X-D	6-31G**	0.17	6
RSH-ωB97X-D	6-31G**	0.165	7
RSH-ωPBEh	6-311+G**	0.155	8

Table S2: Excitation energies and dipole moments obtained with the OT-RSH-μBLYP and OT-sRSH-μBLYP functionals.

State	OT-RSH-μBLYP		OT-sRSH-μBLYP	
	ΔE (eV)	μ (D)	ΔE (eV)	μ (D)
Dimer				
0		1.16		1.11
1	2.08	14.27	2.12	14.65
2	2.47	1.42	2.49	1.31
3	2.49	1.53	2.51	1.45
4	2.87	15.81	2.88	16.23
5	3.29	5.35	3.31	1.24
Compact Tetramer				
0		0.05		0.05
1	1.83	0.58	1.86	0.95
2	1.85	0.43	1.88	0.78
3	1.89	0.34	1.92	0.59
4	1.92	0.20	1.94	0.42
5	1.95	0.08	1.97	0.11
Linear Tetramer				
0		3.67		3.50
1	1.96	10.27	1.99	11.05
2	2.00	13.10	2.03	12.78
3	2.05	10.77	2.07	11.07
4	2.21	11.72	2.23	12.04
5	2.28	11.28	2.30	11.41

Table S3: Excitation energies (ΔE, in eV) and dipole moments (μ, in D) of pentacene hexamer.

State	ωB97X-V		CAM-B3LYP		OT-RSH-ωPBE		OT-sRSH-ωPBE	
	ΔE	μ	ΔE	μ	ΔE	μ	ΔE	μ
0		2.73		2.69		2.70		2.66
1	2.60	2.04	2.26	7.90	1.70	16.11	1.70	16.15
2	2.62	2.79	2.26	4.43	1.70	15.70	1.71	15.74
3	2.67	2.35	2.35	3.22	1.80	17.26	1.80	17.45
4	2.71	3.13	2.38	8.42	1.81	16.71	1.81	16.71
5	2.74	2.14	2.43	3.69	1.89	15.07	1.89	15.12

(a) dimer, ωB97X-V

(b) dimer, CAM-B3LYP

(c) dimer, OT-RSH-ωPBE

(d) dimer, OT-sRSH-ωPBE

(e) dimer, OT-RSH-µBLYP

(f) dimer, OT-sRSH-µBLYP

(g) dimer, OT-RSH-ωPBEh

(h) dimer, OT-sRSH-ωPBEh
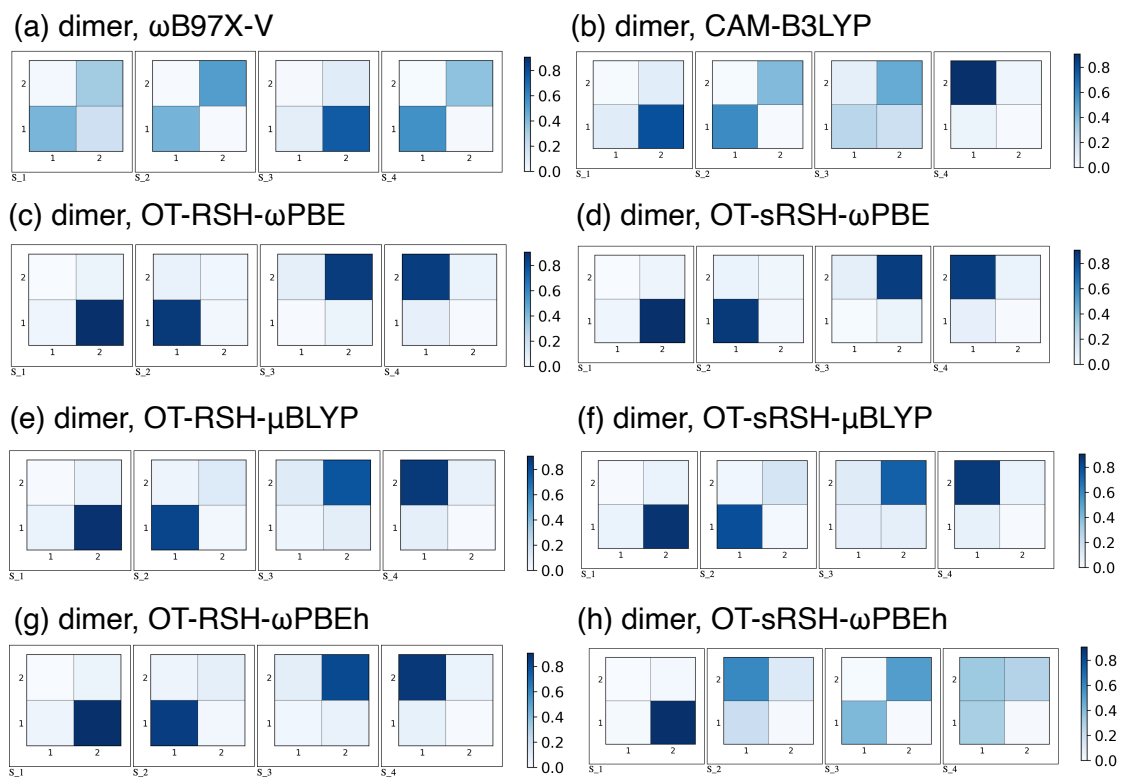
Figure S1: Electron–hole correlation plots for the first four excited states of pentacene dimer, obtained using four different functionals and presented in the form of matrices $\mathbf{\Omega}$, where Ω_{AB} is defined in eq. 14.

(a) compact tetramer, OT-RSH-μBLYP

(b) compact tetramer, OT-sRSH-μBLYP

(c) compact tetramer, OT-RSH-ωPBEh

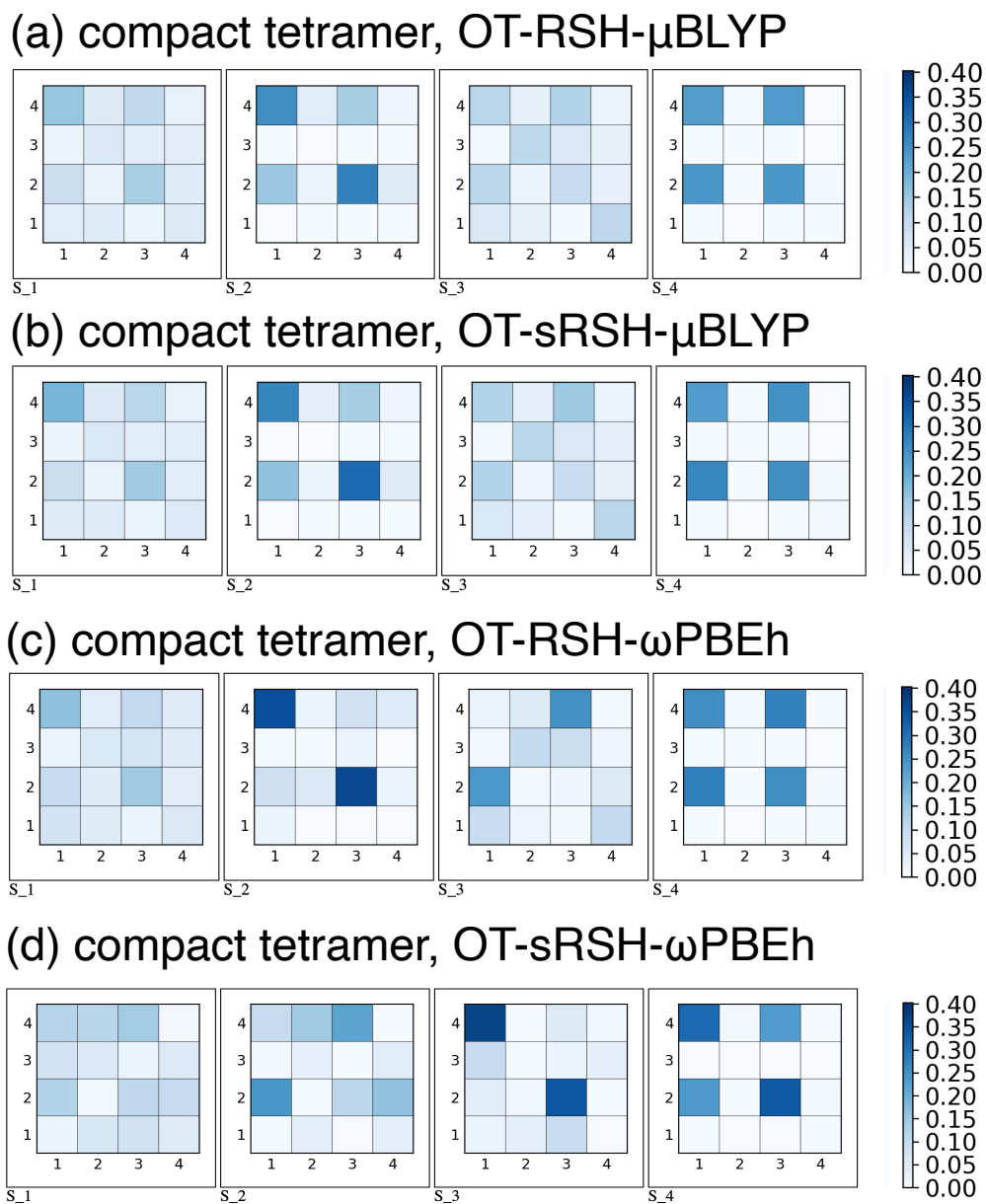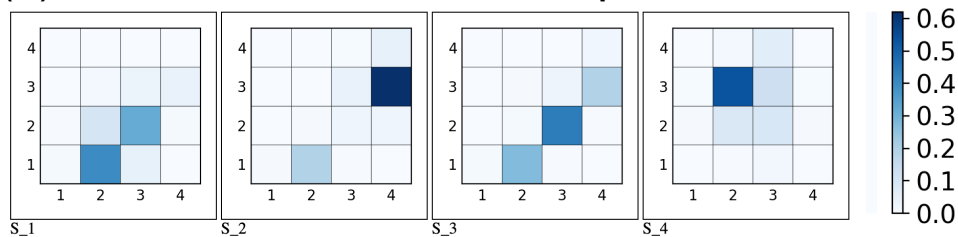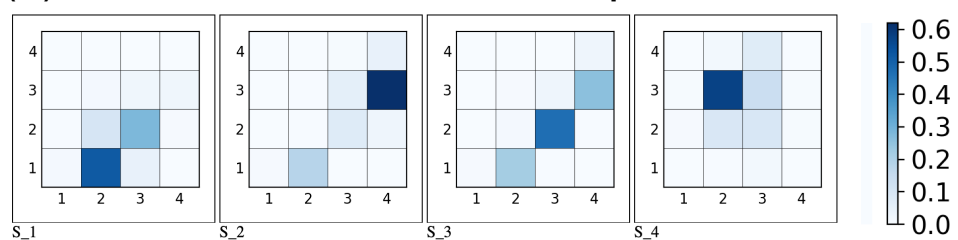## (d) compact tetramer, OT-sRSH-ωPBEh

Figure S2: Electron–hole correlation plots for the first four excited states of the compact pentacene tetramer, obtained using four different functionals and presented in the form of matrices $\mathbf{\Omega}$, where Ω_{AB} is defined in eq. 14.
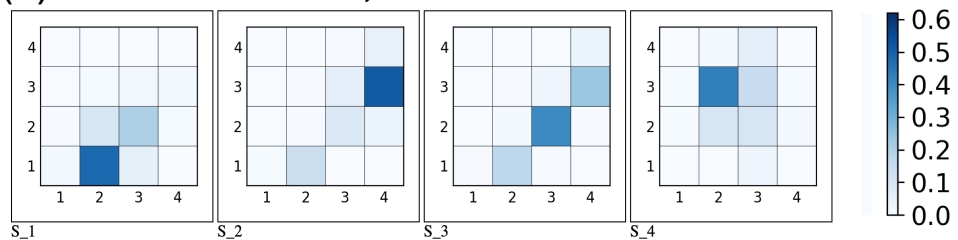
(a) linear tetramer , OT-RSH-µBLYP

(b) linear tetramer, OT-sRSH-µBLYP

(c) linear tetramer, OT-RSH-ωPBEh
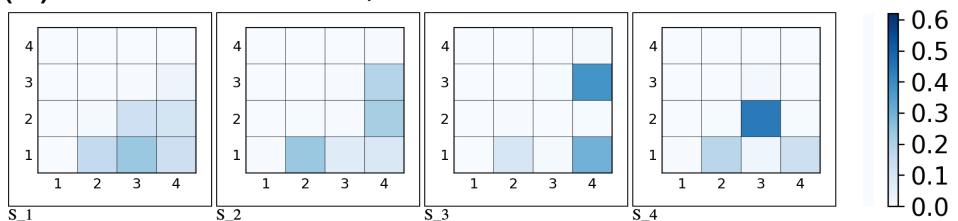
(d) linear tetramer, OT-sRSH-ωPBEh

Figure S3: Electron–hole correlation plots for the first four excited states of the compact pentacene tetramer, obtained using four different functionals and presented in the form of matrices $\mathbf{\Omega}$, where Ω_{AB} is defined in eq. 14.

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