

Mutually Exclusive Hole and Electron Transfer Coupling in Cross Stacked Acenes

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Section A: Materials and Methods

Computational Methods

All the calculations are carried out with ω B97XD functional and 6-311+G(d) basis set using Gaussian 16 program unless stated otherwise.¹ The acene monomers were optimized, and frequency calculations were carried out where no imaginary frequency was found. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of acenes are generated from the cube files of energy calculation. Two optimized monomers were placed at specific interplanar distances and twist angles for further charge transfer coupling and TDDFT calculations. The TrESP calculations were carried out with the basis set of 6-311G(d). Electron and hole transfer integral values were calculated by employing the CATNIP Tool version 1.9,² using the outputs of energy calculations of dimers and their monomers from Gaussian 16. The 3D surface plots were initially plotted in MATLAB, and the surface is exported as .stl format to Blender 2.9 for colouring and rendering (cycles).

Transition charge method utilizing the transition charge from electrostatic potential (TrESP)³

In order to obtain accurate Coulombic coupling (J_{Coul}) between chromophores, transition charge method is utilized in the current manuscript. The point atomic charges (q) for a monomer is obtained by the transition charge from electrostatic potential (TrESP), and the excitonic coupling corresponds to the Coulomb interaction of transition charges of two monomers:-

$$J_{\text{Coul}} = \frac{1}{4\pi\epsilon_0} \sum_i \sum_j \frac{q_i q_j}{|r_i - r_j|}$$

where q_i (q_j) represents the transition charge on atom i (atom j) of monomer 1 (monomer 2) in a dimer. Similarly, r_i (r_j) refers to the position vectors of atom i (atom j) of monomer 1 (monomer 2) in a dimer. The TrESP transition charges were obtained from Multiwfn program package.⁴

Charge Transport Mobility⁵

The charge transfer rate (k_i), which represents the rate of hole/electron hopping from a monomer to the i^{th} neighbour was obtained through the Marcus-Hush equation:

$$k_i = \frac{t^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{\frac{1}{2}} e^{\frac{-\lambda}{4k_B T}}$$

where t is the charge transfer coupling between the monomers of a dimer, λ is the reorganization energy for the hole (λ_h) or electron (λ_e) transport, k_B is the Boltzmann constant, and T is the temperature (300 K). The reorganization energy can be calculated using the following formula:

$$\lambda_{\pm} = (E_0^* - E_0) + (E_{\pm}^* - E_{\pm})$$

in which E_0 and E_{\pm} are the lowest energies of neutral and cationic/anionic species, respectively. For hole reorganization energy (λ_h), E_0^* is the energy of a neutral molecule with cation geometry, while for the electron reorganization energy (λ_e), E_0^* corresponds to the energy of the neutral molecule with anion geometry.

The 1-dimensional (1D) charge mobility from charge hopping is calculated using the following equation:

$$\mu = \frac{1}{2n} \frac{e}{k_B T} \sum_i r_i^2 W_i P_i$$

Where n is the special dimensionality, i corresponds to a specific hopping pathway along the hopping distance r_i , P is the hopping probability, and W_i is the charge hopping rate.

Section B: Tables

Table S1: HOMO-1, HOMO, LUMO, and LUMO+1 energy for Greek cross (+) stacked acene systems ($d_i = 4 \text{ \AA}$).

Linear Acene	Molecular Orbital	Energy (eV)	Non-linear acene	Molecular Orbital	Energy (eV)
${}^2N_{90^\circ}$	LUMO+1	0.6089	${}^2Py_{90^\circ}$	LUMO+1	0.1309
	LUMO	0.6089		LUMO	-0.0786
	HOMO	-7.6450		HOMO	-7.2009
	HOMO-1	-8.0322		HOMO-1	-7.2009
${}^2A_{90^\circ}$	LUMO+1	-0.1238	${}^2Pe_{90^\circ}$	LUMO+1	-0.4471
	LUMO	-0.1374		LUMO	-0.4471
	HOMO	-7.1941		HOMO	-6.7854
	HOMO-1	-7.1941		HOMO-1	-6.8335
${}^2T_{90^\circ}$	LUMO+1	-0.6482	${}^2Ov_{90^\circ}$	LUMO+1	-0.5858
	LUMO	-0.6482		LUMO	-0.7282
	HOMO	-6.6616		HOMO	-6.6164
	HOMO-1	-6.8599		HOMO-1	-6.6164
${}^2P_{90^\circ}$	LUMO+1	-1.0304	${}^2Nn_{90^\circ}$	LUMO+1	-0.7249
	LUMO	-1.0372		LUMO	-0.7573
	HOMO	-6.4619		HOMO	-6.5361
	HOMO-1	-6.4619		HOMO-1	-6.5372

Table S2: Hole and electron reorganization energies of linear and non-linear acenes.

Chromophore	λ_h (eV)	λ_e (eV)
Naphthalene	0.188	0.247
Anthracene	0.143	0.202
Tetracene	0.116	0.164
Pentacene	0.096	0.134
Pyrene	0.153	0.216
Perylene	0.151	0.171
Ovalene	0.093	0.122
Nanographene	0.080	0.103

Table S3: Coulombic coupling (J_{Coul}) for the eclipsed dimers of the selected acene candidates.

Dimer	Transition	d_i (Å)	J_{Coul} (eV)
${}^2\text{N}_0$	$S_2 \leftarrow S_0$	8	0.005
${}^2\text{A}_0$	$S_1 \leftarrow S_0$	8	0.007
${}^2\text{T}_0$	$S_1 \leftarrow S_0$	8	0.008
${}^2\text{P}_0$	$S_1 \leftarrow S_0$	8	0.009
${}^2\text{Py}_0$	$S_2 \leftarrow S_0$	8	0.016
${}^2\text{Pe}_0$	$S_1 \leftarrow S_0$	8	0.025
${}^2\text{Ov}_0$	$S_1 \leftarrow S_0$	8	0.013
${}^2\text{Nn}_0$	$S_1 \leftarrow S_0$	8	0.015

Section C: Figures

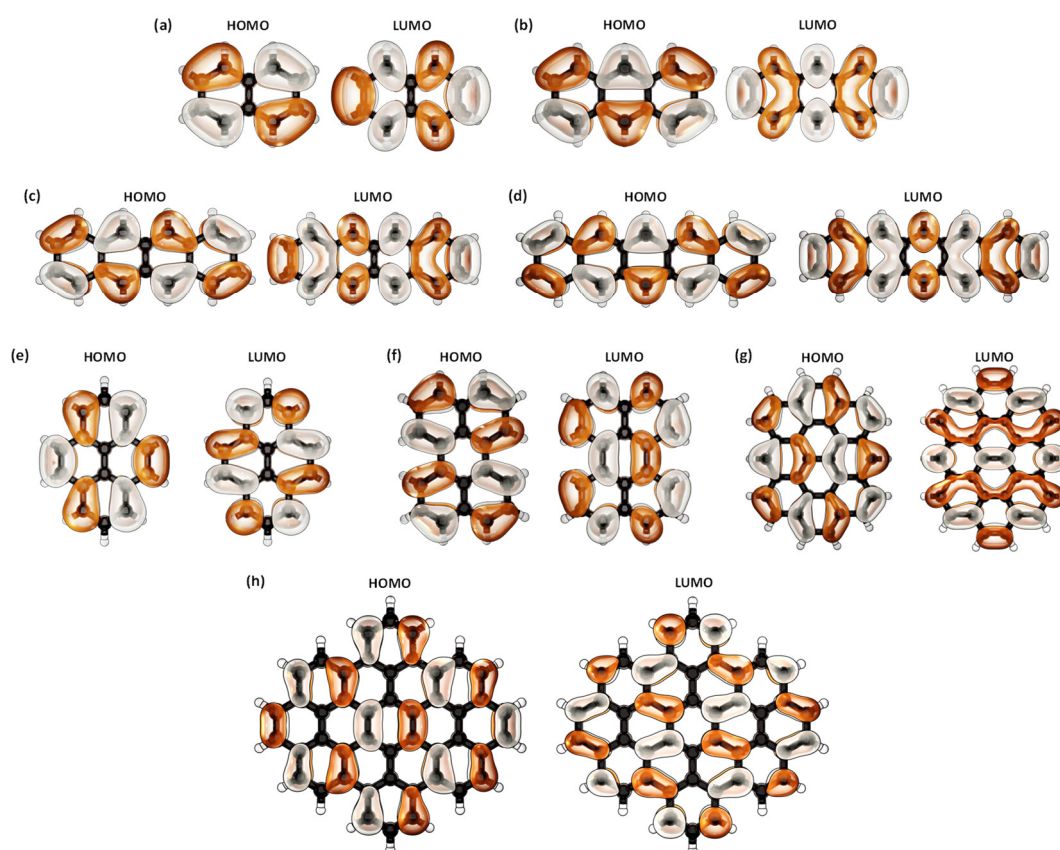


Fig. S1: Frontier Molecular Orbitals of (a) naphthalene, (b) anthracene, (c) tetracene, (d) pentacene, (e) pyrene, (f) perylene (g) ovalene and (h) nanographene.

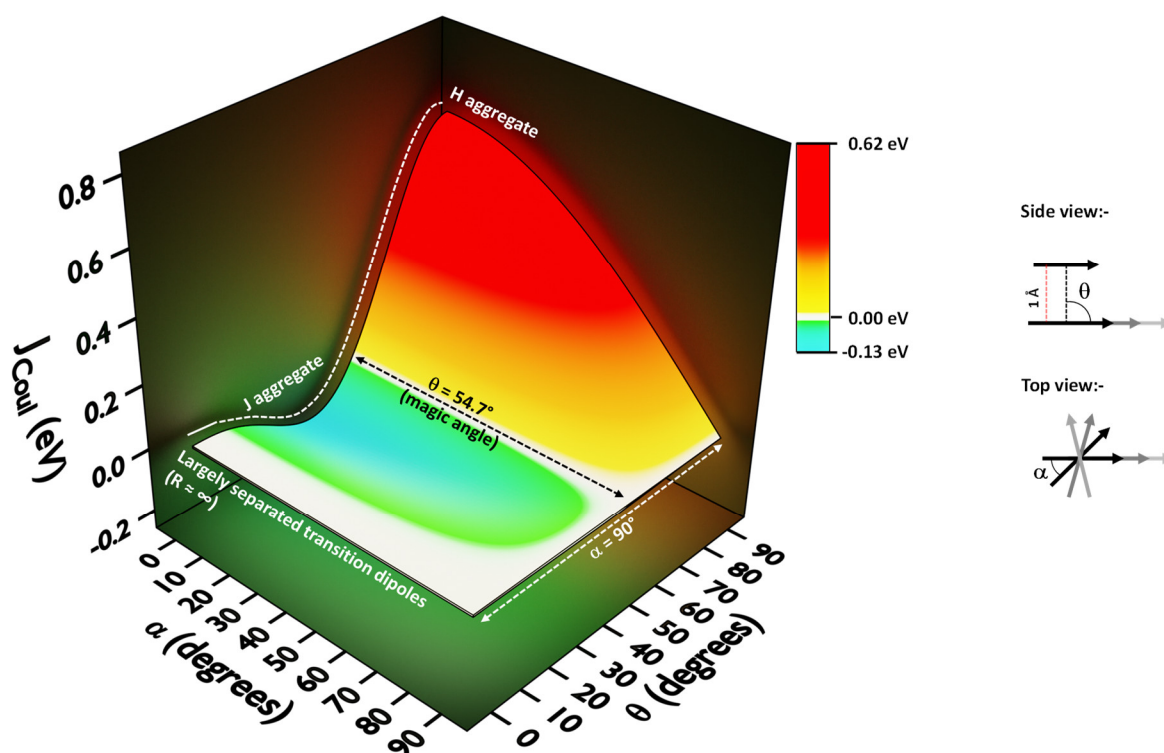


Fig. S2: J_{Coul} of two transition dipoles (with magnitude of 1 Debye each) placed at an interplanar distance of 1 Å at varying slip angle (θ) and rotational angle (α). The orientation factor (κ) = $\cos\alpha(1 - 3\cos^2\theta)$.

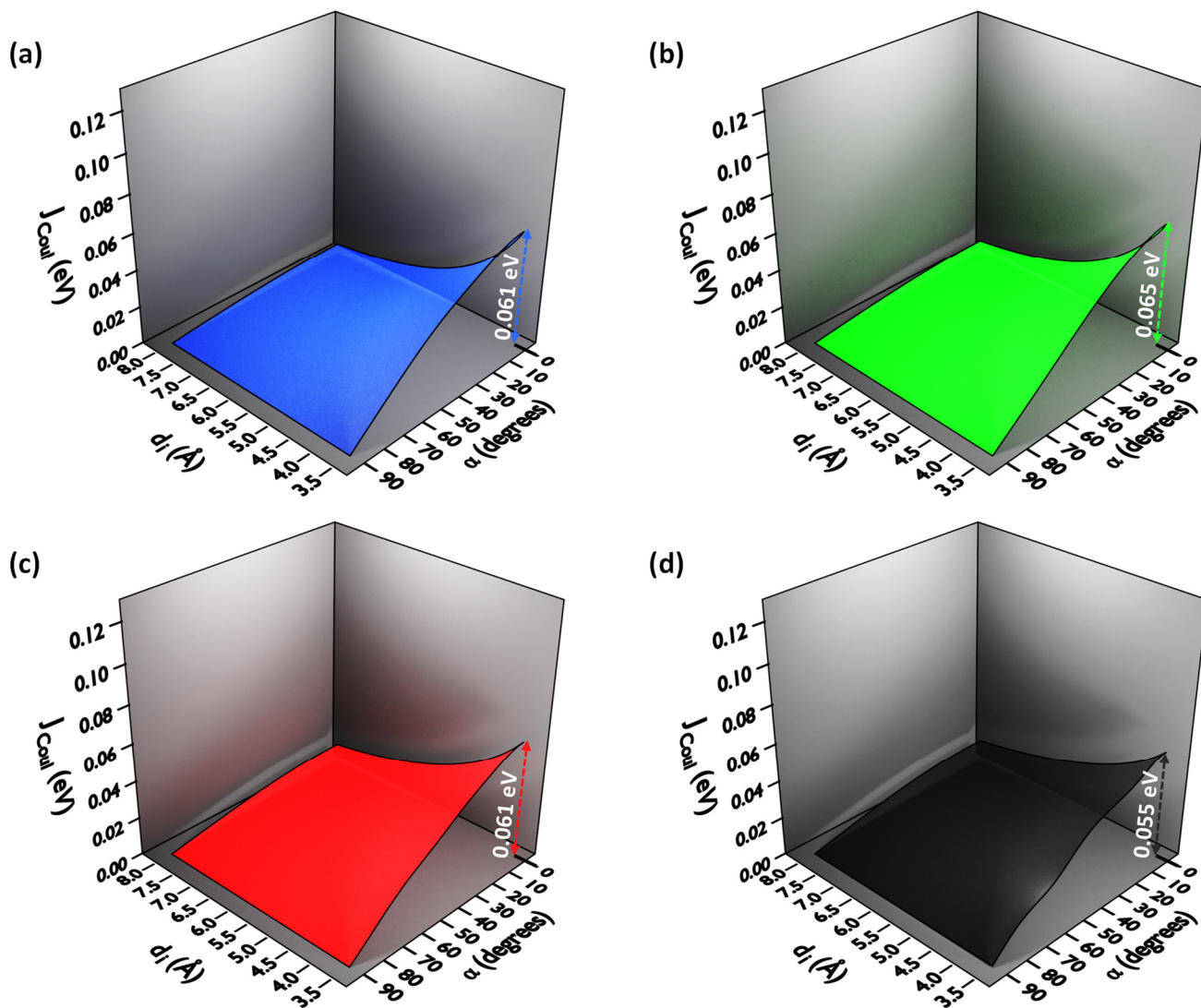


Fig. S3: J_{Coul} of dimers of (a) anthracene, (b) pentacene, (c) ovalene and (d) nanographene at various interplanar spacing (d_i) and rotational angles (α).

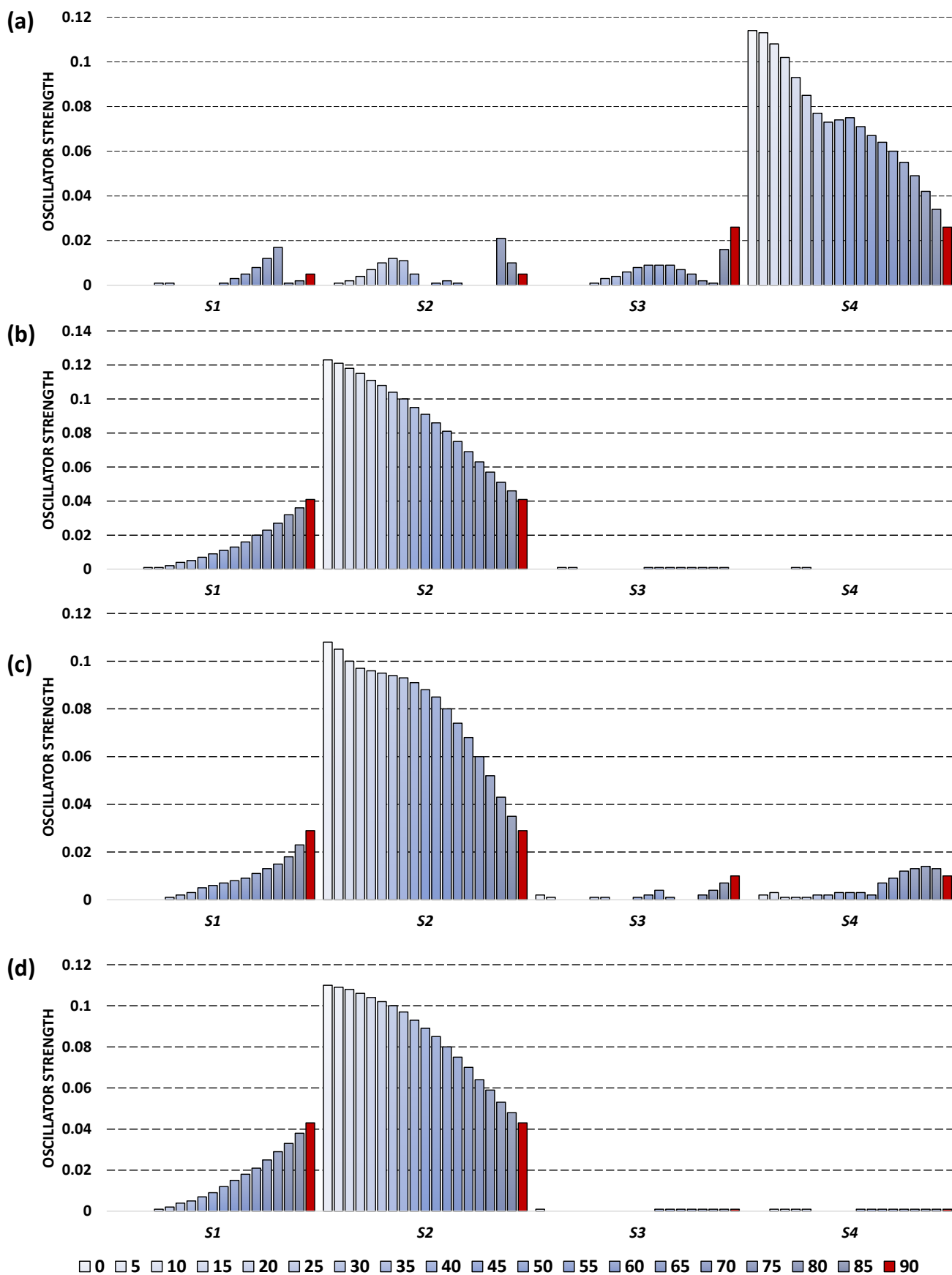


Fig. S4: Oscillator strengths (f) for first four electronic states of (a) naphthalene, (b) anthracene, (c) tetracene and (d) pentacene dimers at various rotational angles. Equal f is observed at $\alpha = 90^\circ$ for S_1 and S_2 (S_3 and S_4) electronic states.

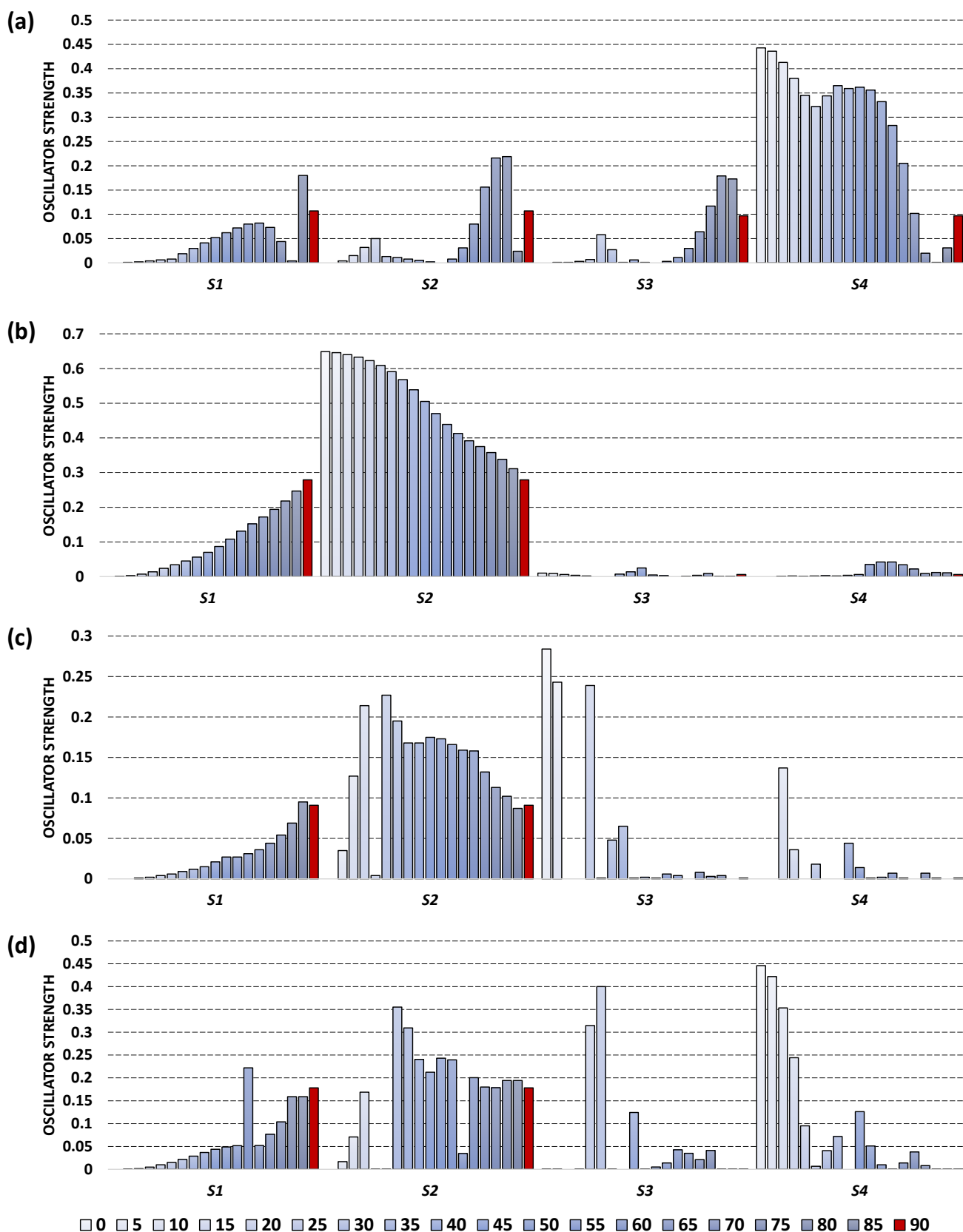


Fig. S5: Oscillator strengths (f) for different electronic states of (a) pyrene, (b) perylene (c) ovalene and (d) nanographene dimers at various rotational angles. Equal f is observed at $\alpha = 90^\circ$ for S_1 and S_2 (S_3 and S_4) electronic states.

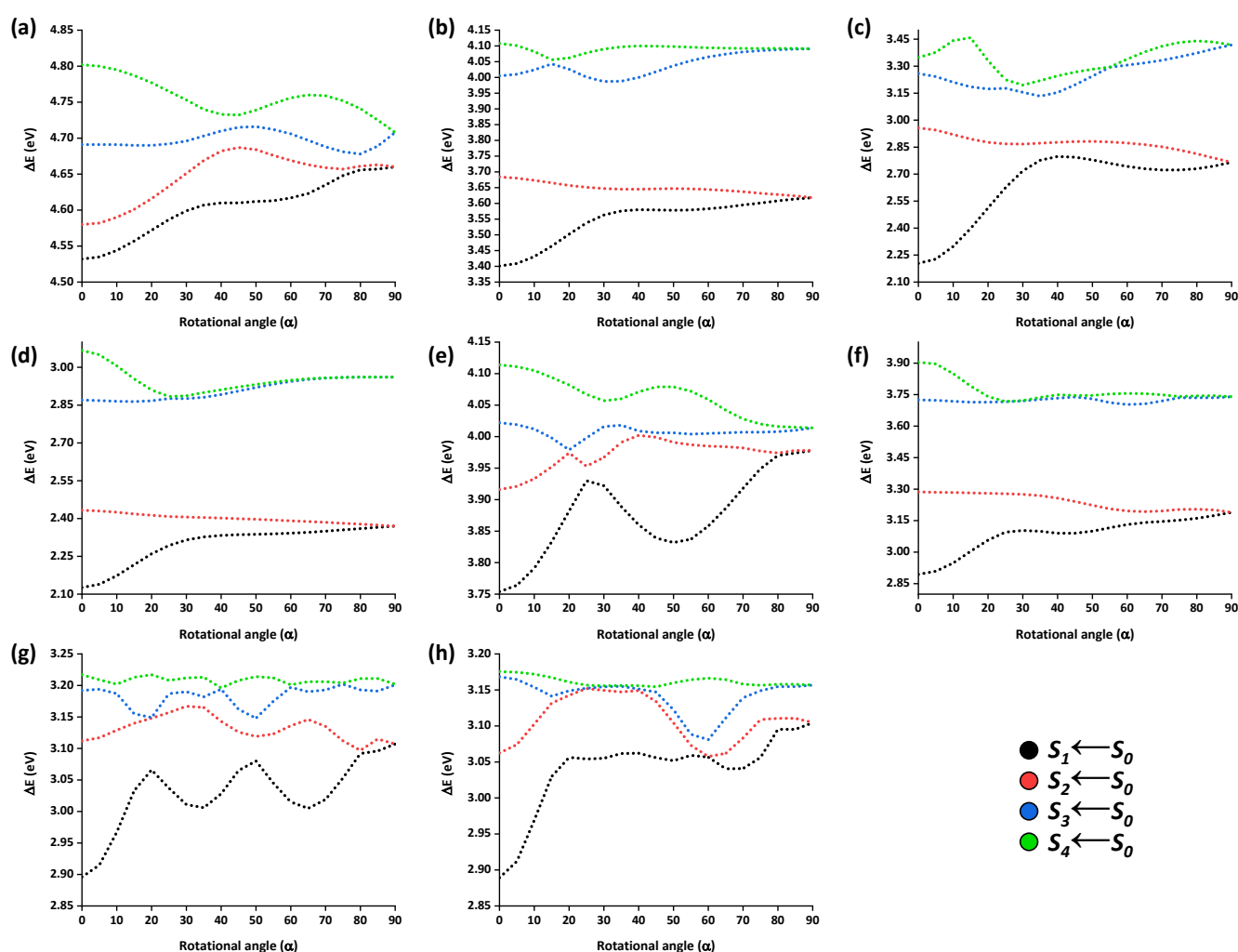


Fig. S6: Electronic excitation energies (ΔE) to first four excited states in (a) naphthalene, (b) anthracene, (c) tetracene, (d) pentacene, (e) pyrene, (f) perylene, (g) ovalene and (h) nanographene dimers at various rotational angles. ΔE for $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ ($S_3 \leftarrow S_0$ and $S_4 \leftarrow S_0$) transitions is degenerate at $\alpha = 90^\circ$.

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