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Introduction

Singlet fission generates two electron-hole pairs from the absorption of a single photon. This process has been target in solar cells to improve the efficiency of solar energy conversion. Recently, mechanistic studies of singlet fission in tetracene and pentacene provided the first experimental evidence of an intermediate state that consists of a pair of correlated triplet states, known as a multiexciton (ME).¹ It is proposed that the ME state is populated through a coherent superposition of the initially excited singlet state (S_1) and the ME state, which then decouples to give two separate triplet states (Fig. 1).¹

Objective

Identify the mechanism for populating the ME state during singlet fission in pentacene by calculating the electronic coupling of S_1 and ME states for two possible mechanisms: direct coupling and indirect coupling mediated by a charge transfer (CT) state as shown in Fig. 2.

Methods

Multistate density functional theory (MSDFT)^{2,3}

Each electronic state is defined by localizing Kohn-Sham (KS) orbitals to one monomer within a given monomer pair (Fig. 3). Thus, Coulomb and exchange interactions within a monomer pair are explicitly treated by DFT. For monomers u and v ,

$$\Phi_{uv}(S_1) = \hat{A}\{\Omega_u(S_1)\Omega_v(S_0)\} \prod_{k \neq u,v}^N \Psi_k(S_0)$$

$$\Phi_{uv}(ME) = \hat{A}\{\Omega_u(T_1^{\uparrow\uparrow})\Omega_v(T_1^{\downarrow\downarrow})\} \prod_{k \neq u,v}^N \Psi_k(S_0)$$

$$\Phi_{uv}(CT) = \hat{A}\{\Omega_u(D^{\bullet+})\Omega_v(A^{\bullet-})\} \prod_{k \neq u,v}^N \Psi_k(S_0)$$

Computational Details

- PBE0/6-31G(d) as implemented in GAMESS
- MSI Calhoun (SGI Altix XE 1300 Linux cluster)

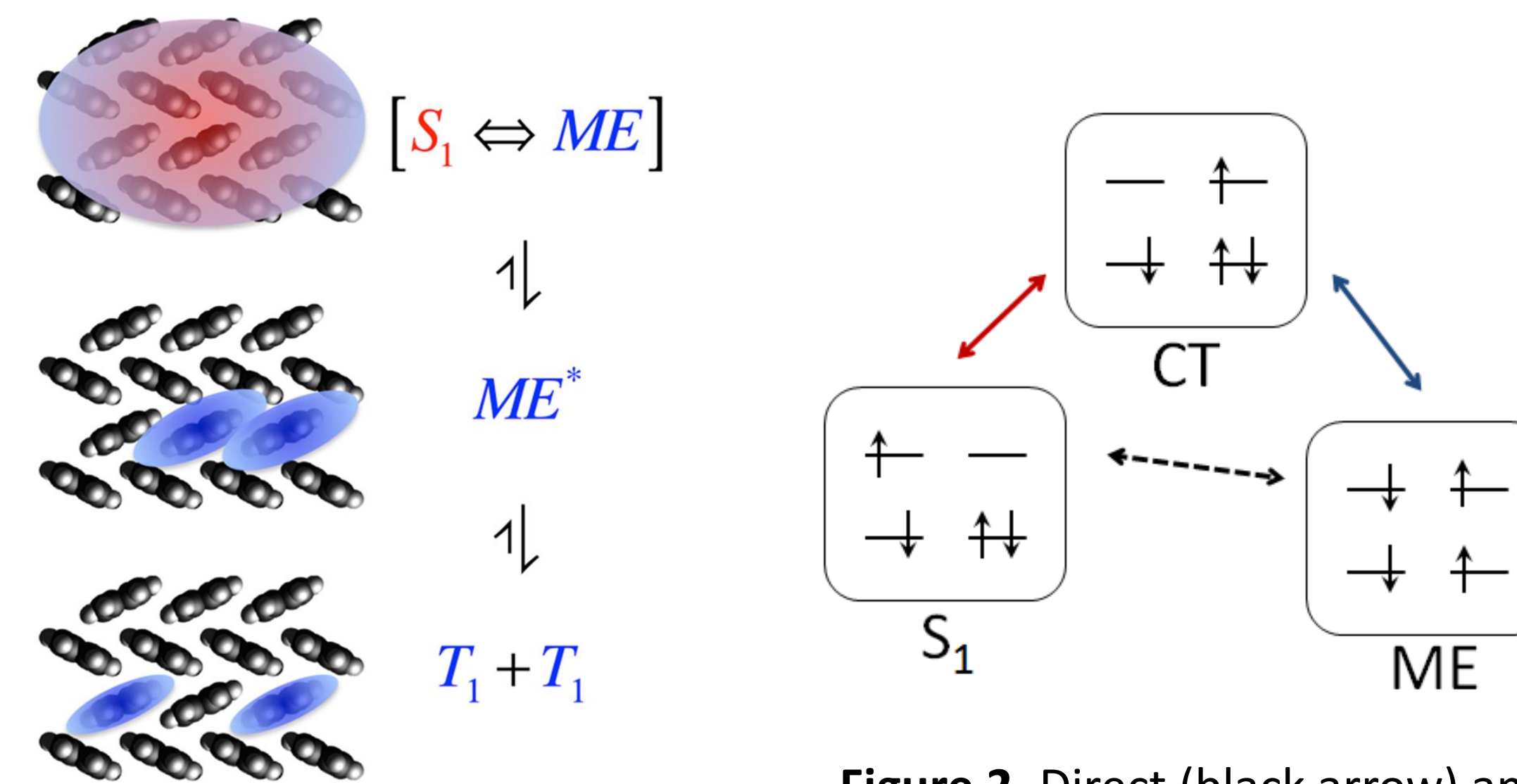


Figure 1. Mechanism of singlet fission, where ME* indicates an ME state decoupled from S_1 .

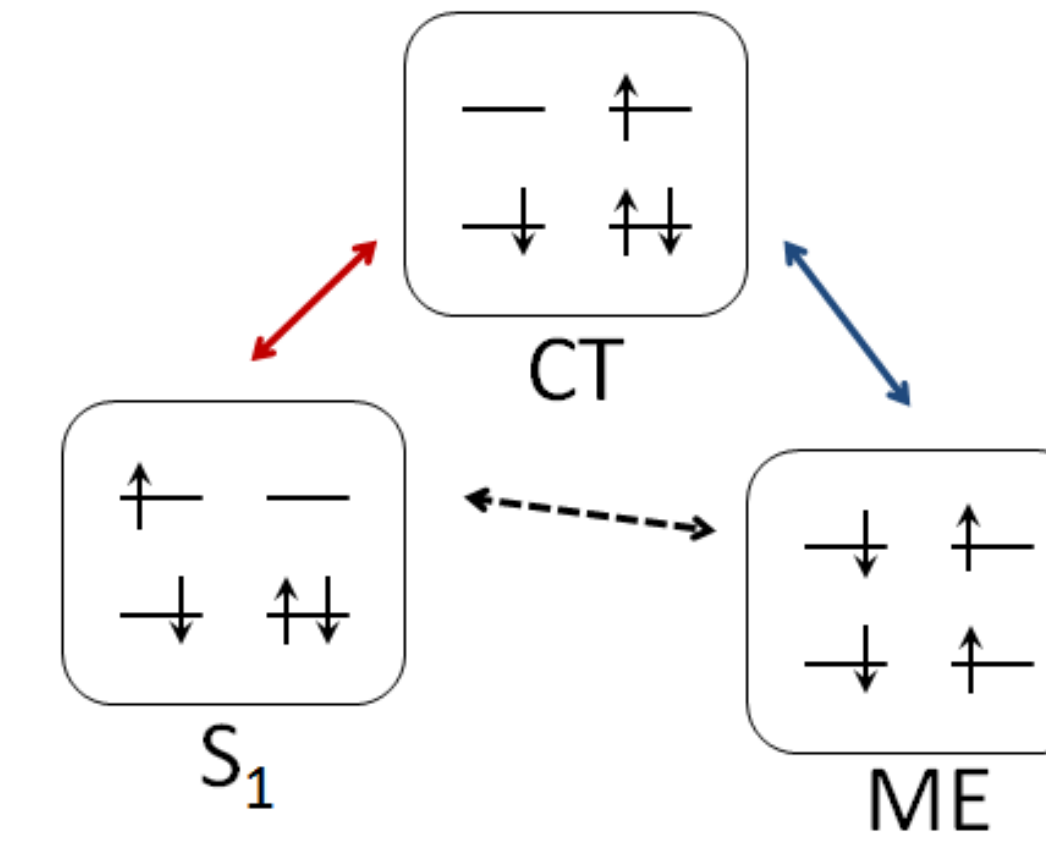


Figure 2. Direct (black arrow) and indirect (red and blue arrows) coupling of S_1 and ME.

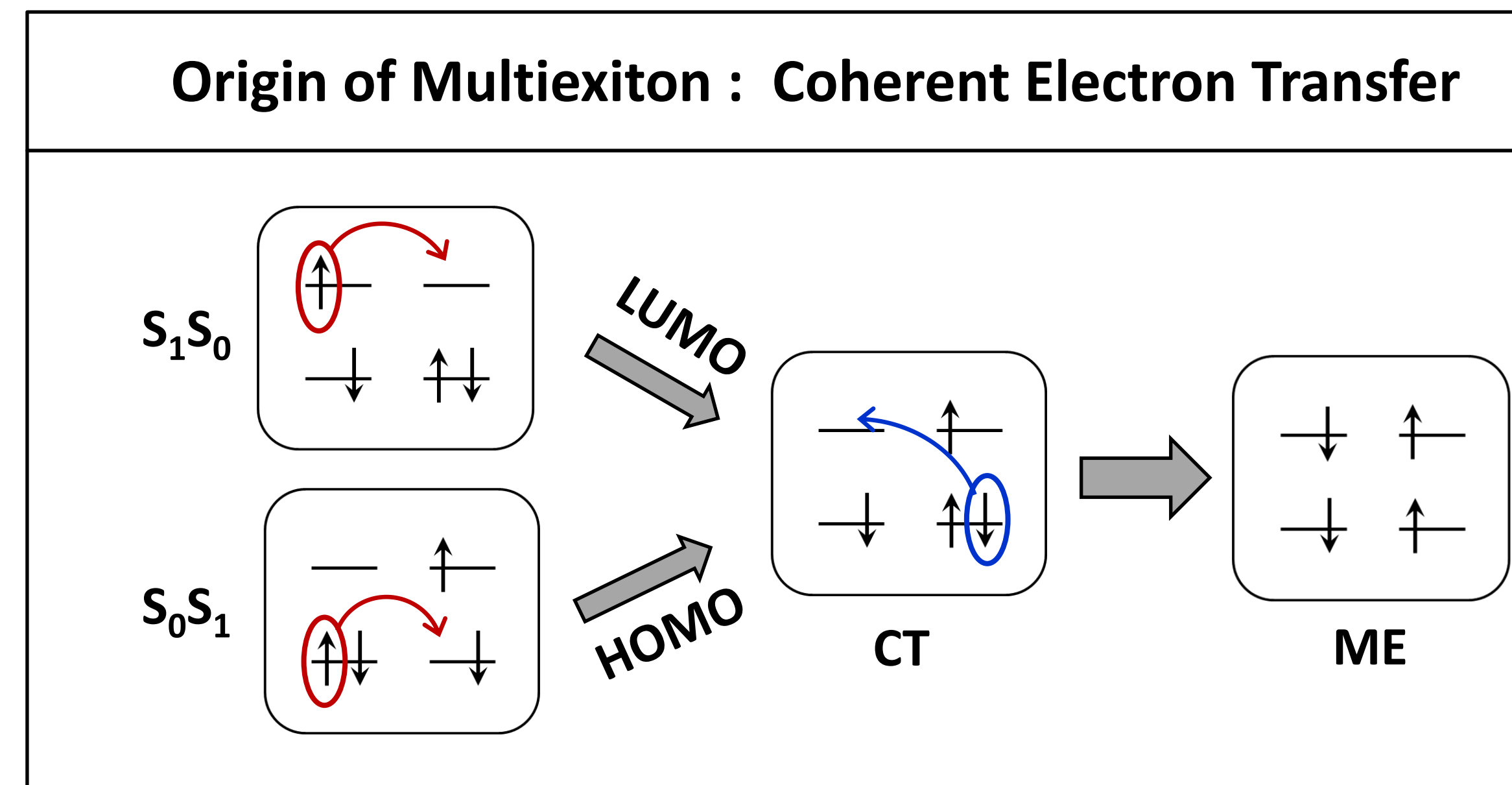


Figure 4. Schematic of indirect electronic coupling. Electron transfer may occur in the opposite direction (right monomer to left monomer).

Conclusions

- Singlet fission in crystalline pentacene proceeds through a quantum coherent mechanism in which S_1 and ME states are coupled indirectly through a CT intermediate state.
- The relative orientation of correlated monomers dictates the direction of electron transfer, which may occur through HOMO to HOMO or LUMO to LUMO transitions.
- KS orbitals calculated using MSDFT may be used in future density matrix calculations for comparison to experiment.

Results

The model system consisted of a monolayer of 56 pentacene monomers fixed in a 7x8 lattice based on the unit cell of vapor-phase-grown pentacene crystal.⁴

Electronic coupling values (W_{el}) are negligible for direct coupling (Table 1); thus, singlet fission is not likely to proceed through this incoherent process.

Indirect coupling produces large W_{el} values (Table 2) for specific CT intermediate states, i.e. excited electron localized on the left or right monomer. The favored CT state depends on the orientation of the monomers within a given monomer pair. As shown in Fig. 4, indirect coupling may occur through HOMO or LUMO electron transfer, but this electronic coupling constants do not vary significantly on this distinction.

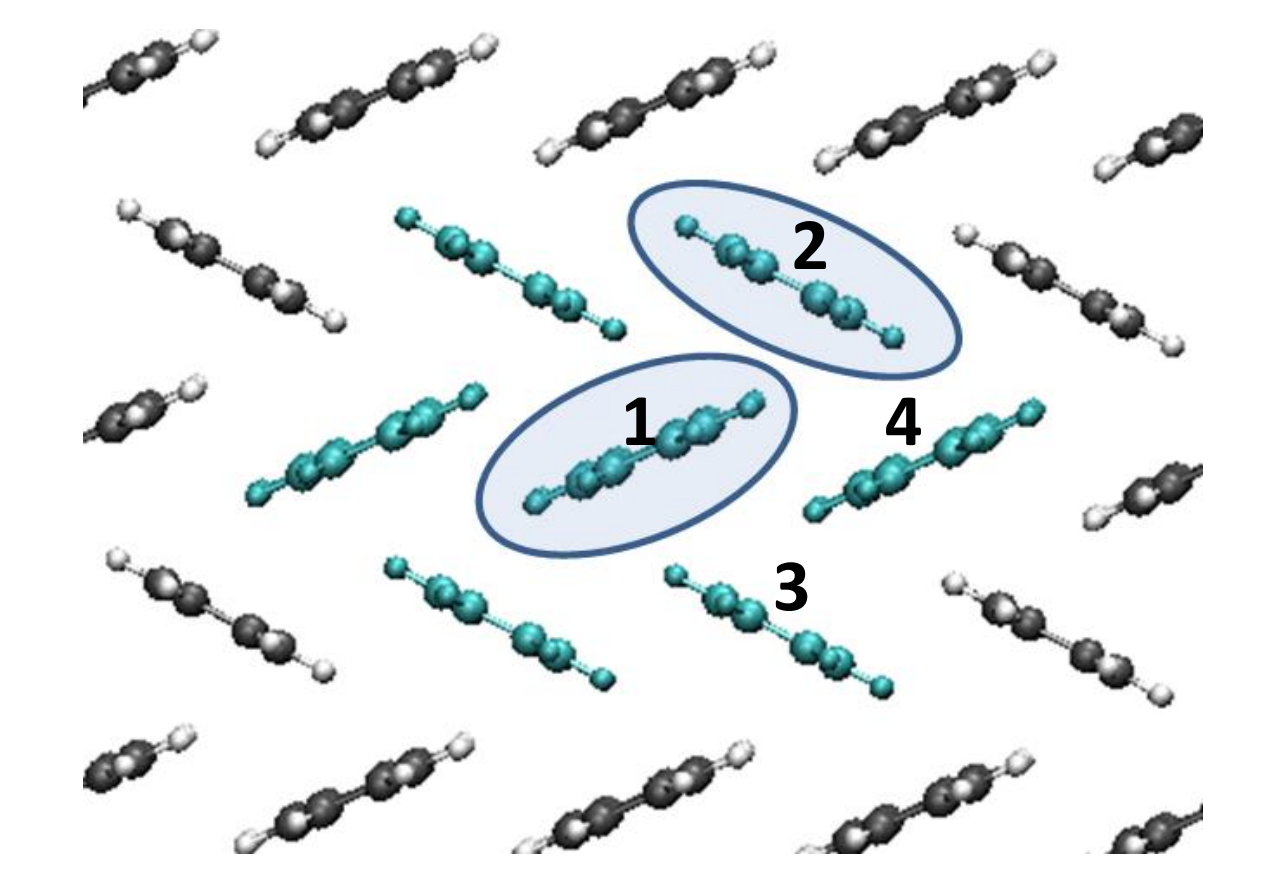


Figure 3. Segment of the model system. Monomers highlighted in cyan were treated with MSDFT. Shaded circles represent localization of KS orbitals on monomers 1 and 2.

Table 1. Direct Coupling

	$\langle S_1 W_{el} ME \rangle$	
	$S_1 S_0$	$S_0 S_1$
1, 2	-1.14	0.96
1, 3	-1.48	1.53
1, 4	-0.42	-0.51

Note: W_{el} values in meV for spin-adapted S_1 and CT states and appropriate ME spin state of each pathway.

Table 2. Indirect Coupling via CT State

	$\langle S_1 W_{el} CT \rangle$		$\langle CT W_{el} ME \rangle$
	$S_1 S_0$	$S_0 S_1$	
1 → 2	-0.10	0.14	-37.0
2 → 1	58.1	-83.6	45.2
1 → 3	85.8	-93.3	-41.5
3 → 1	0.48	-0.14	-49.8
1 → 4	-0.06	0.01	-30.5
4 → 1	-38.3	-48.6	-30.5

References

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- 3) Mo, Y. et al. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6760.
- 4) Siegrist, T. et al. *Angew. Chem. Int. Ed.* **2001**, *40*, 1732.