

Supporting information for: “First principles study of fluorescence quenching in rhodamine B dimers: How can fluorescence occur in dimeric species?”

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Simple model of lowest excited states of dimeric species

Let us consider a dimer made of two monomeric species with two orbitals: the doubly occupied HOMO, h_i , and the empty LUMO, l_i , where $i = 1, 2$ labels the monomer unit (see Figure 1). In the dimer, the 4 frontier orbitals can be represented as linear combinations of the HOMO and the LUMO of the monomer units 1 and 2 (Eq. (S-1)). In Eq. (S-1), the two doubly occupied orbitals of the dimer are denoted as h_a and h_b and the two empty orbitals are l_a and l_b .

$$\begin{aligned} h_a &= \frac{1}{\sqrt{2}}(h_1 + h_2); & l_a &= \frac{1}{\sqrt{2}}(l_1 + l_2) \\ h_b &= \frac{1}{\sqrt{2}}(h_1 - h_2); & l_b &= \frac{1}{\sqrt{2}}(l_1 - l_2), \end{aligned} \quad (\text{S-1})$$

Using these frontier orbitals, the ground state Slater determinant of the dimer is $|h_a\bar{h}_a h_b\bar{h}_b\rangle$, where the bar over the orbital symbol denotes population with the β -spin electron. The singly excited Slater determinants which can be formed within the space of the 4 frontier orbitals are combined to eight spin-symmetry adapted configuration state functions (CSFs) as given in Eq. (A-2).

$$\begin{aligned} |1^{S,T}\rangle &= \frac{1}{\sqrt{2}}(|h_a\bar{l}_a h_b\bar{h}_b\rangle \pm |l_a\bar{h}_a h_b\bar{h}_b\rangle) \\ |2^{S,T}\rangle &= \frac{1}{\sqrt{2}}(|h_a\bar{l}_b h_b\bar{h}_b\rangle \pm |l_b\bar{h}_a h_b\bar{h}_b\rangle) \\ |3^{S,T}\rangle &= \frac{1}{\sqrt{2}}(|h_a\bar{h}_a h_b\bar{l}_a\rangle \pm |h_a\bar{h}_a l_a\bar{h}_b\rangle) \\ |4^{S,T}\rangle &= \frac{1}{\sqrt{2}}(|h_a\bar{h}_a h_b\bar{l}_b\rangle \pm |h_a\bar{h}_a l_b\bar{h}_b\rangle) \end{aligned} \quad (\text{S-2})$$

Using these CSFs the lowest excited states of the dimer can be found from diagonalization of the Hamiltonian matrix, $H_{i,j}^{S,T} = \langle i^{S,T} | H | j^{S,T} \rangle$, $i, j = 1, 2, 3, 4$ in the CSF basis.

The matrix elements of the Hamiltonian are derived under the assumption of a negligible overlap between the frontier orbitals of the monomer units, which leads to the following condition:

$$(h_i h_j | h_k h_l) = (h_i l_j | h_k h_l) = (l_i l_j | h_k h_l) = 0, \quad i \neq j, \quad \forall k, l = 1, 2$$

Furthermore, it is assumed that the splitting between the two HOMOs of the dimer and between the two LUMOs of the dimer is negligibly small compared to the HOMO–LUMO gap of the monomer, ε_0 . Under these assumptions, the Hamiltonian matrices for the singlet and the triplet excited states are given in Eqs. (S-3) and (S-4),

$$H^S = \begin{pmatrix} \varepsilon_0 + \frac{K_1}{2} + \frac{K_2}{2} & 0 & 0 & -D + K_1 + K_2 \\ 0 & \varepsilon_0 + \frac{K_1}{2} - \frac{K_2}{2} & -D + K_1 - K_2 & 0 \\ 0 & -D + K_1 - K_2 & \varepsilon_0 + \frac{K_1}{2} - \frac{K_2}{2} & 0 \\ -D + K_1 + K_2 & 0 & 0 & \varepsilon_0 + \frac{K_1}{2} + \frac{K_2}{2} \end{pmatrix} \quad (\text{S-3})$$

$$H^T = \begin{pmatrix} \varepsilon_0 - \frac{K_1}{2} - \frac{K_2}{2} & 0 & 0 & -D \\ 0 & \varepsilon_0 - \frac{K_1}{2} + \frac{K_2}{2} & -D & 0 \\ 0 & -D & \varepsilon_0 - \frac{K_1}{2} + \frac{K_2}{2} & 0 \\ -D & 0 & 0 & \varepsilon_0 - \frac{K_1}{2} - \frac{K_2}{2} \end{pmatrix} \quad (\text{S-4})$$

where $D = \frac{1}{2}(J_1 - J_2)$, with $J_1 = (l_1 l_1 | h_1 h_1)$, $J_2 = (l_1 l_1 | h_2 h_2)$, and $K^1 = (h_1 l_1 | h_1 l_1)$, $K_2 = (h_1 l_1 | h_2 l_2)$ are the usual Coulomb and exchange two-electron integrals.

The eigenvalues and eigenvectors for the singlet excited states are

$$\begin{aligned} E_1^S &= \varepsilon_0 + D - \frac{1}{2}K^1 - \frac{1}{2}K_2; & (-1, 0, 0, 1) \\ E_2^S &= \varepsilon_0 + D - \frac{1}{2}K^1 + \frac{1}{2}K_2; & (0, -1, 1, 0) \\ E_3^S &= \varepsilon_0 - D + \frac{3}{2}K^1 - \frac{3}{2}K_2; & (0, 1, 1, 0) \\ E_4^S &= \varepsilon_0 - D + \frac{3}{2}K^1 + \frac{3}{2}K_2; & (1, 0, 0, 1) \end{aligned} \quad (\text{S-5})$$

and for the triplets are

$$\begin{aligned} E_1^T &= \varepsilon_0 - D - \frac{1}{2}K^1 + \frac{1}{2}K_2; & (0, 1, 1, 0) \\ E_2^T &= \varepsilon_0 - D - \frac{1}{2}K^1 - \frac{1}{2}K_2; & (1, 0, 0, 1) \\ E_3^T &= \varepsilon_0 + D - \frac{1}{2}K^1 - \frac{1}{2}K_2; & (-1, 0, 0, 1) \\ E_4^T &= \varepsilon_0 + D - \frac{1}{2}K^1 + \frac{1}{2}K_2; & (0, -1, 1, 0) \end{aligned} \quad (\text{S-6})$$

Analysis of the eigenvectors shows that the states $\Psi_{3,4}^S$ and $\Psi_{1,2}^T$ correspond to the in-phase and out-of-phase combinations of the intramolecular single excitations, whereas the $\Psi_{1,2}^S$ and $\Psi_{3,4}^T$ are the excited states with charge transfer character.

Introducing $\Delta = \frac{1}{2}(J_1 - J_2 - K^1)$, the energies can be written:

$$\begin{aligned}
E_{3,4}^S &= \varepsilon_0 - \Delta + K_1 \pm \frac{3}{2}K_2 \\
E_{1,2}^S &= \varepsilon_0 + \Delta \pm \frac{1}{2}K_2 \\
E_{3,4}^T &= \varepsilon_0 + \Delta \pm \frac{1}{2}K_2 \\
E_{1,2}^T &= \varepsilon_0 - \Delta - K_1 \pm \frac{1}{2}K_2,
\end{aligned} \tag{S-7}$$

From general considerations, it can be expected that $K_1 \geq K_2$ and $J_1 \geq J_2$. Assuming that $\Delta \approx 0$ leads to Eq. (1) which is illustrated in Figure 4 of the accompanying article where the ordering of the excited states is schematically shown. The described simple model predicts the degeneracy between the singlet and the triplet excited states with charge transfer character. Depending on the parameters used in Eqs. (S-7) and (1) the intramolecular excited singlet states of the dimer and the charge transfer states may occur in a narrow energy region.