

Theoretical Study of Intramolecular Singlet Fission in Xanthene-bonded Pentacene Dimers

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Abstract

Singlet fission is a spin-allowed process by which two non-interacting triplet excitons are generated from a singlet exciton. This type of multiexciton generation mechanism may have the potential to overcome the Shockley-Queisser limit and could enable the development of more efficient solar cells. In this contribution, we analyze intramolecular singlet fission in two modified pentacene dimers covalently bonded to a xanthene spacer employing density functional theory and multireference perturbation theory methods. The systems investigated differ in the electronic structure and bulkiness of the substituents used and in this work we analyze the impact that these aspects have in the relative contributions of the direct and mediated mechanisms to the intramolecular singlet fission.

Keywords: Intramolecular Singlet Fission, Multiexciton State, Direct Mechanism, Mediated Mechanism, Pentacene, Xanthene, XMCQDPT

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1. Introduction

The photophysical process of singlet fission (SF) in molecular materials has recently received significant attention[1–3] as a possible mechanism to increase the efficiency of solar cells, in particular dye-sensitized solar cells (also called Grätzel cells),[4–6]. SF is a multiexciton generation process whereby an optically excited singlet exciton (S_1) transforms into two triplet excitons (T_1) *via* a spin allowed process.[1, 7, 8] Since ionization of the T_1 states can provide two charge carriers, SF may facilitate the design of single junction dye sensitized solar cells surpassing the Shockley-Queisser efficiency limit.[9] This prospect has motivated an intense theoretical research directed to determine the mechanism of SF and also to identify the electronic and structural properties that SF-active dyes must exhibit.

Concerning the mechanism of SF, there is an ongoing controversy regarding different aspects of the SF process, which include the nature and role of the electronic states involved and the role of molecular vibrations.[1, 7, 8] In spite of this, there is general agreement that SF can proceed following two main reaction channels, the direct and the mediated, and virtually all mechanistic proposals discussed to date are built on these mechanisms, although introducing valuable new aspects for the understanding of SF. In the direct mechanism, the absorbing state (S_1) transforms into a correlated pair of triplet excited states $|^1(T_1T_1)\rangle$, also called multiexciton (ME) state, which ultimately dissociates into two (non-interacting) T_1 states. In the mediated mechanism, a charge transfer (CT) state virtually couples S_1 to the ME state, which then dissociates into two T_1 states. More recent proposals extend these mechanisms by invoking the possibility that the initial excitation prepares a coherent superposition of the lowest lying absorbing, CT, and ME states.[10, 11] Here, decoherence prompts the formation of the two independent T_1 states from the ME state. Furthermore, it has been suggested that the two non-interacting T_1 states are directly populated from S_1 without participation of additional electronic states.[12] Finally, recent works have identified a correlated triplet pair of quintet spin character ($|^5(T_1T_1)\rangle$) as

an intermediate state in the SF process.[13–15]

From the point of view of the structural and electronic properties of the dye, two energy matching relationships involving the absorbing state of the dye and the triplet manifold, namely (i) $E(S_1) \geq 2E(T_1)$ and (ii) $E(T_2) > 2E(T_1)$ have long been advocated as necessary conditions for a dye candidate to be SF-active, as they guarantee an exergonic SF process and ensure minimal quenching from triplet-triplet annihilation processes.[1] Aside from these energy relations, other electronic and structural parameters such as the diradical character of the dye, overlap of the electron density clouds, type of crystal packing in organic crystals or nature of the linker (conjugated, cross-conjugated or non-conjugated) and interference effects in covalently bonded dimeric dyes have also been identified as relevant factors for the design of SF-active dyes.[1, 7, 8, 16–20] In this respect, different families of compounds have been shown to fulfill these conditions and, therefore, have been considered as potential candidates to exhibit efficient SF.[1, 2] From all these families, acenes have been one of the most investigated compounds exhibiting SF and among them, pentacene derivatives have been thoroughly analyzed.[1, 7, 8]

We have recently investigated different aspects of the mechanism of intramolecular SF (iSF) in dimers of pentacene derivatives that are covalently bonded to conjugated, cross-conjugated and non-conjugated spacers[15, 18, 19, 21]. Following these works, we investigate here theoretically iSF in two pentacene based dimers covalently bonded to a xanthene spacer at the 4 and 5 positions (see Fig. 1). These systems were recently studied experimentally.[22] They have been chosen mainly to maximize the through space coupling *via* large cofacial overlap of the π -orbitals of the pentacene moities. In addition, it has recently been shown in related systems that the through bond contribution can also be very relevant,[23, 24] which make these systems good candidates to exhibit efficient iSF. The functionalized pentacenes considered differ in the type of substituent used, *tri-isopropylsilylethynyl* and *phenylethynyl*, respectively. These groups differ in their electronic properties and bulkiness and here we analyze the effects that these different characteristics have in the iSF process in

these systems.

FIGURE 1

2. Electronic structure methods

To elucidate the mechanism of iSF we have used an approach that combines density functional theory (DFT) and multireference perturbation theory methods. Specifically, the ground state equilibrium structures of the systems investigated have been obtained at the DFT level of theory using the B3LYP hybrid exchange-correlation functional[25–28] and the def2-TZVP basis set.[29] Dispersion interactions were incorporated using Grimmes empirical dispersion correction.[30] All the calculations were carried out using Turbomole.[31]

At the equilibrium geometries, we have calculated the eight lowest-lying singlet electronic states in the adiabatic representation and used them to build the diabatic states[32, 33] typically considered to play a role in SF.[1] For this, we have used the extended multi-configuration quasi-degenerate perturbation theory (XMCQDPT) level,[34], employing a double- ζ (DZV) basis set[35] and making use of Nakamura and Truhlar’s fourfold diabatization scheme.[36, 37] The XMCQDPT calculations employed state averaged complete active space self-consistent field (SA-CASSCF)[38] wavefunctions as reference, calculated using an active space of 4 electrons in 4 orbitals (4e/4o) (HOMO and LUMO of each pentacene moiety), and an intruder state avoidance shift of 0.02 au². [39] In the diabatization process, all configuration state functions (CSFs) whose coefficients are more than 0.20 in any of the adiabatic electronic states have been considered. All these calculations were carried out using GAMESS.[40, 41] To estimate the relative contributions of the direct and mediated mechanisms, we follow the approach of Berkelbach *et al.*[42] and evaluate the effective SF coupling as

$$V_{eff} \approx \langle {}^1(S_1S_0) | V | {}^1(T_1T_1) \rangle - 2 \frac{\langle {}^1(S_1S_0) | V | {}^1(CA) \rangle \langle {}^1(CA) | V | {}^1(T_1T_1) \rangle + \langle {}^1(S_1S_0) | V | {}^1(CA) \rangle \langle {}^1(CA) | V | {}^1(T_1T_1) \rangle}{[E(CT) - E({}^1(T_1T_1))] + [E(CT) - E({}^1(S_1S_0))]} \quad (1)$$

where $E(CT)$ stands for the average of the energies of both CT states. In this expression, the first term of the right hand side accounts for the contribution of the direct channel to the overall SF coupling and the second term for that of the mediated channel. Using V_{eff} , the rate constant for the transformation of the locally excited (LE) state into the ME state can be calculated as

$$k_{SF} \approx \frac{2\pi}{\sqrt{4\pi\hbar^2\lambda k_B T}} |V_{eff}|^2 \times \exp\left(-\frac{[E(|^1(S_1S_0)\rangle) - E(|^1(T_1T_1)\rangle) + \lambda]^2}{4\lambda k_B T}\right), \quad (2)$$

where λ is the reorganization energy.[43]

3. Results and discussion

The equilibrium structures of **X1** and **X2** are depicted in Fig. 1. Despite the different bulkiness of the substituent groups of the pentacene moieties both systems are characterized by having very similar bond lengths and bond angles. The most relevant exception is the different relative orientation of the pentacene-derived moieties with respect to the xanthene linker, with **X1** showing a nearly perpendicular arrangement of the pentacene moieties with respect to the xanthene while in **X2** they are slightly slanted. This result is in line with previous results where these two conformations were found in the crystal structure of a similar system.[23] The pentacene moieties are in a stacked arrangement with distances ~ 3.4 Å and are slightly staggered, with **X2** showing the largest distortion.

Table 1 contains the adiabatic vertical excitation energies, modulus of the dipole moments, oscillator strengths, and character of the seven lowest-lying singlet excited states of **X1** and **X2**. The latter have been assigned on the basis of the dominant excitations between localized CASSCF orbitals (see Figs. 2 and 3). For both systems, the states of interest lie within an energy window of ~ 0.8 eV and in both cases the state ordering is similar, with the lowest-lying state (S_1) having dominant ME character. S_2 and S_3 are two states with the dominant CSFs showing LE character. The energy gap between these states is ~ 0.2 eV for both **X1** and **X2**. In addition, the energy gap between S_1 and S_2 is very small,

resulting in near degeneracy of these states for both systems, while S_3 always shows a larger energy gap with respect to S_1 (~ 0.3 eV). Furthermore, while the oscillator strengths of S_2 and S_3 are very similar for **X1** they strongly differ for **X2**, with S_2 having a bright state character while S_3 shows weak absorption properties. The remaining states in the window of energies investigated are of CT and doubly excited (DE) type and their energies and order are similar for both structures, with the CT states showing energy gaps of $\sim 0.5 - 0.7$ eV with respect to the ME-like state in both systems.

TABLE 1

FIGURE 2

FIGURE 3

As it is advantageous to describe the iSF process in terms of diabatic states,[1] we have used the adiabatic states discussed above to build those diabatic states considered to play a relevant role in SF. These comprise the ground state ($|^1(S_0S_0)\rangle$), the ME state ($|^1(T_1T_1)\rangle$), two LE states where excitation is localized in one of the pentacene moieties ($|^1(S_1S_0)\rangle$ and $|^1(S_0S_1)\rangle$) and two CT states ($|^1(CA)\rangle$ and $|^1(AC)\rangle$) where one of the pentacene moieties is formally a radical cation ($C^{\bullet+}$) and the other is a radical anion ($A^{\bullet-}$). In addition, and because of energy considerations and the existence of non-negligible electronic couplings with the rest of states, two DE states ($|^1(DE_1)\rangle$ and $|^1(DE_2)\rangle$) corresponding to double excitations in one pentacene moiety have also been included in the diabatic basis. Among the different diabatization procedures available [33], we have employed the configuration uniformity [44] based fourfold way diabatization technique of Nakamura and Truhlar.[36, 37] In this approach, the diabatic wavefunctions are expressed in terms of diabatic molecular orbitals (DMOs), which are obtained from the adiabatic molecular orbitals using the three-fold density criterion and the maximum overlap reference molecular orbitals (MORMO) condition.[36, 37] Diabatic prototypes are defined using dominant configuration state functions (CSFs) whose coefficients are more than a certain threshold (a value of 0.20 was used in this work) in any of the adiabatic

electronic states considered. The adiabatic states are represented using these CSFs expressed in the DMOs basis and transformed to diabatic states using an orthogonal transformation consistent with the configuration uniformity concept.

Eqs. (3) and (4) contain the diabatic to adiabatic matrix transformation for **X1** and **X2**, respectively. As can be noted, the adiabatic states of both systems show an important mixing of the different diabatic states included in the basis except for the DE states, which are rather decoupled from the rest. In particular, the lowest-lying singlet excited state of ME character of **X1** (S_1), despite having a dominant contribution of the $|^1(T_1T_1)\rangle$ state, also shows significant contributions from both the LE and CT states. The same happens for the lowest-lying bright state (S_2), while the other bright-state, S_3 , exhibits much smaller CT contributions. On the other hand, the S_1 state of **X2** differs from the corresponding one of **X1** in the smaller contribution of the LE states, while showing a significant mixing of the CT diabats. The mixing pattern of the CT diabats in S_2 and S_3 is reversed to that of **X1**, i.e., S_2 shows smaller CT contributions than S_3 .

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \end{pmatrix} = \begin{pmatrix} 0.95 & -0.01 & 0.00 & 0.00 & 0.22 & -0.00 & -0.22 & 0.00 \\ -0.04 & 0.65 & -0.34 & -0.35 & 0.11 & -0.38 & -0.10 & 0.40 \\ 0.00 & 0.43 & 0.62 & 0.61 & 0.01 & -0.38 & -0.10 & 0.40 \\ 0.00 & 0.00 & -0.70 & 0.71 & -0.06 & 0.01 & -0.05 & 0.04 \\ -0.30 & -0.29 & 0.06 & 0.06 & 0.64 & -0.17 & -0.60 & 0.05 \\ -0.03 & 0.00 & 0.06 & -0.01 & -0.05 & 0.70 & -0.17 & 0.68 \\ 0.00 & 0.00 & -0.04 & 0.05 & 0.68 & 0.12 & 0.71 & 0.11 \\ 0.08 & -0.54 & 0.05 & 0.03 & -0.21 & -0.53 & 0.20 & 0.57 \end{pmatrix} \begin{pmatrix} |^1(S_0S_0)\rangle \\ |^1(T_1T_1)\rangle \\ |^1(S_1S_0)\rangle \\ |^1(S_0S_1)\rangle \\ |^1(DE_1)\rangle \\ |^1(CA)\rangle \\ |^1(DE_2)\rangle \\ |^1(AC)\rangle \end{pmatrix} \quad (3)$$

$$\begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \end{pmatrix} = \begin{pmatrix} 0.95 & -0.03 & -0.01 & 0.00 & -0.22 & 0.00 & 0.21 & 0.00 \\ -0.03 & 0.67 & 0.17 & 0.16 & -0.11 & 0.48 & 0.10 & -0.48 \\ 0.00 & -0.19 & 0.71 & 0.65 & 0.00 & -0.05 & 0.00 & 0.15 \\ 0.00 & -0.01 & -0.60 & 0.69 & 0.04 & -0.28 & 0.03 & -0.29 \\ 0.29 & 0.37 & 0.02 & 0.04 & 0.65 & -0.09 & -0.56 & 0.15 \\ -0.01 & 0.00 & -0.32 & 0.26 & -0.04 & 0.65 & 0.02 & 0.64 \\ -0.01 & -0.02 & 0.03 & -0.03 & 0.66 & 0.04 & 0.74 & 0.01 \\ -0.10 & 0.60 & 0.01 & 0.02 & -0.26 & -0.50 & 0.26 & 0.48 \end{pmatrix} \begin{pmatrix} |^1(S_0S_0)\rangle \\ |^1(T_1T_1)\rangle \\ |^1(S_1S_0)\rangle \\ |^1(S_0S_1)\rangle \\ |^1(DE_1)\rangle \\ |^1(CA)\rangle \\ |^1(DE_2)\rangle \\ |^1(AC)\rangle \end{pmatrix} \quad (4)$$

To assess the relative contributions of the direct and the mediated mechanisms to the iSF mechanism, we have calculated the diabatic Hamiltonian in the diabatic basis described above and used Eq. (1) to obtain a quantitative estimate

of the effective electronic coupling. Tables 2 and 3 contain the diabatic energies and the electronic couplings between the different diabatic states considered and Table 4 contains the effective coupling and the relative contribution of the direct and mediated channels. The results indicate a minor contribution of the direct coupling to the overall process, with the electronic coupling of $|^1(\text{T}_1\text{T}_1)\rangle$ to both $|^1(\text{S}_1\text{S}_0)\rangle$ and $|^1(\text{S}_0\text{S}_1)\rangle$ being small (~ 10 meV or less) for both **X1** and **X2**. The contribution of the mediated mechanism is, on other hand, dominant as a result of the slightly larger couplings of both $|^1(\text{S}_1\text{S}_0)\rangle$ and $|^1(\text{S}_0\text{S}_1)\rangle$ to the CT states and mainly due to that of $|^1(\text{T}_1\text{T}_1)\rangle$, which is one order of magnitude larger (~ 0.23 eV and ~ 0.28 eV for **X1** and **X2**, respectively, see Tables 2 and 3).

TABLE 2

TABLE 3

Although a more staggered arrangement of the pentacene moieties leads to lower lying CT states possibly due to an increase of the charge localized at the pentacene fragments, this fact does not have a significant impact on the contribution of the mediated mechanism and as a result in the effective iSF electronic effective coupling. In fact, the latter is moderate for both systems (~ 0.07 eV). This is a result of the opposite signs of the different coupling terms, which lead to cancellation (destructive interference) in the mediated channel contribution (see Table 4). A possible role of the DE states in the process is ruled out on the basis of their negligible mediated contribution.

TABLE 4

To assess the possibility of using these molecules as potential SF-dyes in a solar conversion device we have calculated an estimate of the rate of formation of the ME state (k_{SF}) using Eq. 2. For this, and taking into account that the reorganization energy of pentacene is estimated to be in the range 50 - 150 meV[45], we have used a value of 100 meV as an educated guess of λ for the systems investigated in this work. Using this value, we obtain rate

constants of $2.44 \times 10^{14} \text{ s}^{-1}$ and $2.02 \times 10^{14} \text{ s}^{-1}$ for **X1** and **X2**, respectively. These values are significantly larger than those recently reported for several prototypical systems (see Table 5) exhibiting SF, which suggests that these systems could be potential candidates for efficient iSF.

TABLE 5

4. Conclusions

We have analyzed intramolecular singlet fission in two modified pentacene dimers covalently bonded to a xanthene spacer employing density functional theory and multireference perturbation theory methods. The systems investigated differ in the electronic structure and bulkiness of the substituents groups functionalizing the pentacene cores and in the geometrical arrangement of the pentacene moieties both with respect to the xanthene linker and between themselves. The results obtained show that iSF in these systems mainly proceeds via a superexchange-like mediated mechanism with higher-lying CT states acting as virtual states. Other high-lying states of DE character seem not to play a relevant role for the process. Although a more staggered conformation of the pentacenes moieties seems to facilitate the mixing of the ME state with the CT states, other interference effects counterbalance the impact of conformation. The results obtained for the rate constants suggest that these systems could be potential candidates for efficient iSF.

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Table 1: Adiabatic vertical excitation energy (ΔE , in eV),^a modulus of the dipole moment (μ , in Debye),^b oscillator strength (f)^b and character (char.)^c of the lowest lying singlet excited states of **X1** and **X2** calculated at the ground state equilibrium structure.

State	X1				X2			
	ΔE	μ	f	Char.	ΔE	μ	f	Char.
S ₁	1.53	2.99	< 0.001	ME	1.40	2.17	0.002	ME
S ₂	1.62	2.86	0.581	LE	1.55	3.01	1.180	LE
S ₃	1.83	3.10	0.466	LE	1.72	2.36	0.160	LE
S ₄	1.99	3.87	0.039	DE	1.93	2.54	< 0.001	DE
S ₅	2.04	1.97	0.074	CT	1.94	3.30	0.096	CT
S ₆	2.13	2.61	< 0.001	DE	2.07	2.33	< 0.001	DE
S ₇	2.28	2.18	< 0.001	CT	2.28	2.89	0.012	CT

^a Calculated at the XMCQDPT/DZV level of theory (8 roots with equal weights and a 4e/4o active space were used in the CASSCF calculation). ^b Calculated at the CASSCF/DZV level of theory (8 roots with equal weights and a 4e/4o active space were used). ^c ME = multiexciton state, LE = absorbing states that correlate with the plus and minus combinations of locally excited states of both pentacene monomers, CT = charge transfer states, DE = doubly excited states.

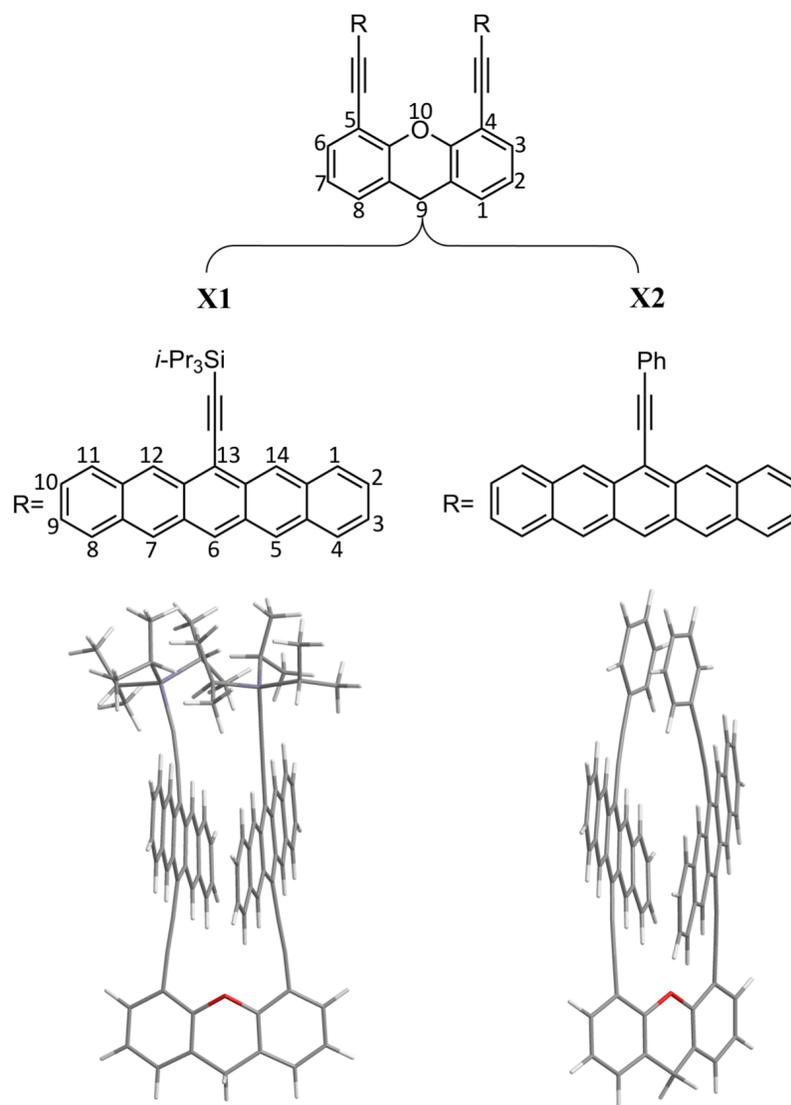
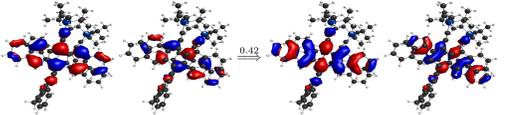
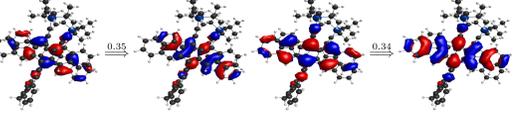
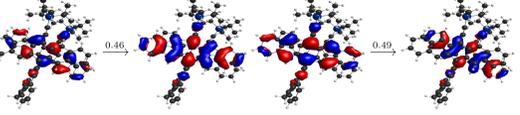
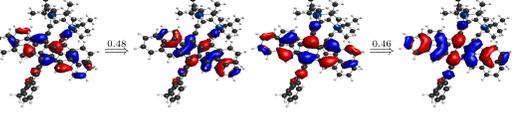
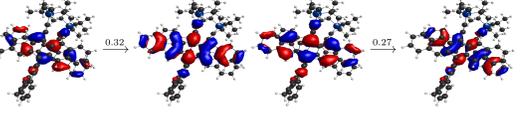


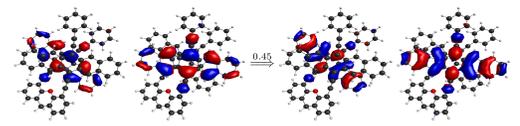
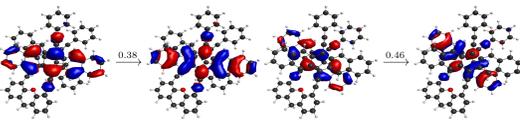
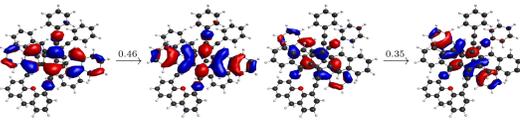
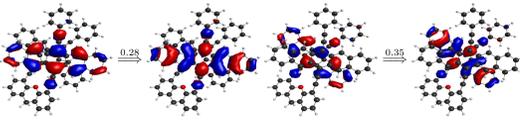
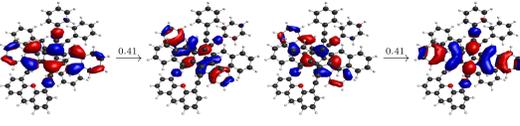
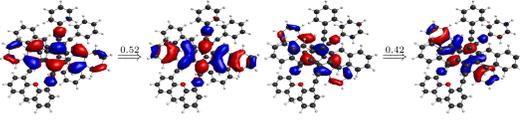
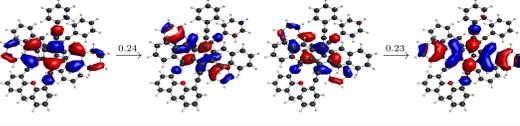
Figure 1: Xanthene linked pentacene based dimers investigated in this work. Left: 4,5-bis(13-(tri-*isopropylsilyl*ethynyl)pentacen-6-yl)ethynyl)-9*H*-xanthene (**X1**). Right: 4,5-bis(13-(phenylethynyl)pentacen-6-yl)ethynyl)-9*H*-xanthene (**X2**).

Figure 2: Characterization of the adiabatic excited electronic states of **X1** in terms of the electron excitations involving localized CASSCF molecular orbitals.^{a,b,c}

State	Orbital transition	Weight	Character
S ₁		0.42	ME
S ₂		0.69	LE
S ₃		0.97	LE
S ₄		0.69	DE
S ₅		0.95	CT
S ₆		0.94	DE
S ₇		0.59	CT

^a Double arrows represent double excitations and single arrows represent single excitations. ^b The number on each arrow is the weight of the particular excitation in the wavefunction of the adiabatic state. ^c Character of excited state: ME = multi-excitonic state, LE = excited states that correlate with the plus and minus combinations of locally excited states of both pentacene monomers, CT = charge transfer states, DE = doubly excited states.

Figure 3: Characterization of the adiabatic excited electronic states of **X2** in terms of the electron excitations involving localized CASSCF molecular orbitals.^{a,b,c}

State	Orbital transition	Weight	Character
S ₁		0.45	ME
S ₂		0.84	LE
S ₃		0.81	LE
S ₄		0.63	DE
S ₅		0.82	CT
S ₆		0.94	DE
S ₇		0.47	CT

^a Double arrows represent double excitations and single arrows represent single excitations. ^b The number on each arrow is the weight of the particular excitation in the wavefunction of the adiabatic state. ^c Character of excited state: ME = multi-excitonic state, LE = excited states that correlate with the plus and minus combinations of locally excited states of both pentacene monomers, CT = charge transfer states, DE = doubly excited states.

Table 2: Energies and coupling matrix elements in meV of the low-lying diabatic electronic states of **X1** calculated at the XMCQDPT/DZV level of theory ^a.

	$ ^1(S_0S_0)\rangle$	$ ^1(S_1S_0)\rangle$	$ ^1(S_0S_1)\rangle$	$ ^1(T_1T_1)\rangle$	$ ^1(DE_1)\rangle$	$ ^1(DE_2)\rangle$	$ ^1(CA)\rangle$	$ ^1(AC)\rangle$
$ ^1(S_0S_0)\rangle$	0	-6	-2	29	-430	420	-14	13
$ ^1(S_1S_0)\rangle$		1523	-110	11	26	-3	-27	36
$ ^1(S_0S_1)\rangle$			1525	2	3	-23	-22	47
$ ^1(T_1T_1)\rangle$				1606	4	-5	231	-237
$ ^1(DE_1)\rangle$					1760	154	63	-49
$ ^1(DE_2)\rangle$						1770	-46	60
$ ^1(CA)\rangle$							1815	26
$ ^1(AC)\rangle$								1825

^a Calculated at the XMCQDPT/DZV level of theory (8 roots with equal weights and a 4e/4o active space were used in the CASSCF calculation).

Table 3: Energies and coupling matrix elements in meV of the low-lying diabatic electronic states of **X2** calculated at the XMCQDPT/DZV level of theory ^a.

	$ ^1(S_0S_0)\rangle$	$ ^1(S_1S_0)\rangle$	$ ^1(S_0S_1)\rangle$	$ ^1(T_1T_1)\rangle$	$ ^1(CA)\rangle$	$ ^1(AC)\rangle$	$ ^1(DE_1)\rangle$	$ ^1(DE_2)\rangle$
$ ^1(S_0S_0)\rangle$	0	13	11	42	-24	24	405	-397
$ ^1(S_1S_0)\rangle$		1460	-97	-10	-39	-78	14	4
$ ^1(S_0S_1)\rangle$			1463	-7	58	18	-4	-11
$ ^1(T_1T_1)\rangle$				1608	286	-289	-29	31
$ ^1(CA)\rangle$					1690	36	-73	76
$ ^1(AC)\rangle$						1701	82	-68
$ ^1(DE_1)\rangle$							1719	142
$ ^1(DE_2)\rangle$								1743

^a Calculated at the XMCQDPT/DZV level of theory (8 roots with equal weights and a 4e/4o active space were used in the CASSCF calculation).

Table 4: Direct, mediated, and effective electronic iSF coupling (meV) for **X1** and **X2** calculated at the XMCQDPT/DZV level of theory.^a

System	State	Direct	Mediated		Effective
			CT	DE	
X1	$ ^1(S_1S_0)\rangle$	11	58	-0.6	68
	$ ^1(S_0S_1)\rangle$	2	64	-0.6	65
X2	$ ^1(S_1S_0)\rangle$	-10	-58	-1.4	-69
	$ ^1(S_0S_1)\rangle$	-7	-58	1.1	-64

^a The effective channel does not include the contribution of the mediated DE channel.

Table 5: Rate constants (s^{-1}) of **X1** and **X2** and comparison to other relevant SF active systems.

System	rate	Reference
X1	2.44×10^{14}	This work
X2	2.02×10^{14}	This work
Pentacene solids	$1.0 \times 10^{12} - 1.5 \times 10^{13}$	[46]
Orthogonal	2.5×10^{12}	[47]
Conjugated	$6.1 \times 10^{10} - 2.0 \times 10^{12}$	[18]
Cross-conjugated	0.7×10^{12}	[19]
Bent	1.8×10^9	[48]
Non-conjugated	2.4×10^9	[15]