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Enhanced spin-orbit coupling driven by state mixing in organic molecules for OLED applications

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ABSTRACT

We investigate the energy gap variation as well as spin-orbit coupling (SOC) integrals between various low-lying singlet and triplet excited states for a series of fluorescein derivatives. We find that when the electron-donating property of the substituent group on the benzene moiety of fluorescein is gradually increased, the charge transfer states are lowered in energy and a mixing with nearby $\pi\pi^*$ or $n\pi^*$ states occurs, which causes a twisting in the *p* orbital on the carbonyl group and a non-zero SOC integral between the originally non-coupled $^1\pi\pi^*$ and $^3\pi\pi^*$ states. We also find an enhancement of about 3–4 times in the SOC integrals upon sulfur substitution for the oxygen in the carbonyl groups, and that with substantial energy lowering in $\pi\pi^*$ and especially in $n\pi^*$ states, the SOC between the S_1 state with energetically close triplet states is also increased significantly, signifying the possibility of enhanced phosphorescence or thermally-delayed fluorescence emission.

1. Introduction

The design and characterization of thermally activated delayed fluorescence (TADF) phenomenon represent a recently rising area of research for optoelectronic applications [1–7]. Instead of the usual "triplet harvesting" approach, some Cu-containing complexes [8–12] were found to exhibit small energy gap between S_1 and T_1 that allows the triplet excitons to be collected also at the S_1 state via fast reversed intersystem crossing (RISC) at ambient temperature. This alternative "singlet harvesting" approach circumvents the inherent problem of long phosphorescence radiative lifetimes and is expected to give rise to better quantum efficiency. In particular, metal-free organic TADF molecules [13–16] offer unique optical and electronic properties for low-cost optoelectronic devices ranging from light-emitting diodes (LED) [17] to oxygen or temperature sensors [18] with performances comparable to traditional heavy transition-metal complexes. Theoretically, the highest external quantum efficiency (EQE) for conventional OLED systems usually does not exceed 5%, based on the 25% singlet exciton population and a device light out-coupling efficiency of ~20% [19]. In comparison, organic TADF molecules with EQE as high as 19% (implying a >90% exciton utilization efficiency) have been reported [17].

In principle, two criteria are essential for efficient TADF to occur. The first (and often the most emphasized) requirement is a small energy gap between S_1 and T_1, ΔE_{ST}, in order to allow for efficient upconversion from T_1 to S_1 [20]. An energy gap within about 3000 cm^{-1} (0.37 eV) is required for effective thermal population [10]. The second (and the less discussed) requirement is a strong enough spin-orbit coupling between S_1 and T_1. In the Hartree-Fock framework, the energy splitting of the singlet and triplet spin states coming from the same electronic excitation (from ψ_i to ψ_f) is directly proportional to the exchange integral J_{if} (or more specifically, $\Delta E_{ST} = 2\ J_{if}$), which in turn is roughly proportional to the spatial overlap integral between the two orbitals [1,21–23]. Thus, a typical molecular design for efficient TADF involves a charge transfer excitation in a twisted donor-acceptor architecture to ensure minimal overlap between HOMO and LUMO [20,24–26], and therefore a minimal ΔE_{ST}. A successful approach to realize high-efficiency and short-lifetime TADF is to create a bipolar molecule with a large dihedral angle between an N-donor and a phenyl ring substituted with electron-withdrawing groups [27]. Systems with ΔE_{ST} as small as 0.083 eV [17] showing strong TADF have been reported. On the other hand, according to the El-Sayed's rule [28], the ISC rate for the organic systems may be dramatically enhanced if an orbital flipping is involved in the transition, i.e. $^1\pi\pi^* \rightarrow {}^3n\pi^*$ or $^1n\pi^* \rightarrow {}^3\pi\pi^*$ is significantly faster than $^1\pi\pi^* \rightarrow {}^3\pi\pi^*$ or $^1n\pi^* \rightarrow {}^3n\pi^*$. However, in typical TADF emitters, the RISC process is usually believed to proceed between charge-

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transfer (CT) excited states, which, in principle, belong to the $^3\pi\pi^* \rightarrow {}^1\pi\pi^*$ transition type. This implies that there is a possibility to further enhance the ISC or RISC process by minimizing the ΔE_{ST} if some extent of the $n\pi^*$ character might be introduced to CT excited states.

In this study, we compute the energy gaps and the SOC strength between various low-lying singlet and triplet excited states for selected fluorescein derivatives. The fluorescein molecule represents one of the stereotypical TADF systems [18]. Inspired by 2-Me-4-OMe Tokyo Green molecule, which exhibits a unique mixed charge transfer (CT)/$n\pi^*$ property in its S_2 (major transition HOMO-2 to LUMO) excited state (see Fig. 2 in Ref. [29]), we choose the fluorescein backbone as the prototypical model to investigate the substituent effect as we fine-tune the relative energy levels and the extent of mixing between the CT and $n\pi^*/\pi\pi^*$ states. Our goal is to clarify the ΔE_{ST} and the SOC strength dependence on the nature of the excited states, and in the process we hope that a few molecular design strategies for efficient TADF may be summarized.

2. Computational details

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations of all compounds are carried out by using the Gaussian 09 program [30] and the Amsterdam Density Functional (ADF) program [31–33], respectively. Geometry optimizations are performed for the singlet ground states using the DFT with the hybrid exchange-correlation functional B3LYP [34,35] with 6-31 + G (d, p) basis set [36,37] by Gaussian 09 or with TZP basis set by ADF. Solvation corrections for the solvent used in most experiments, water (ε = 78.39), were calculated using the polarizable continuum model (PCM) method [38] with the default UFF radii. TDDFT [39–43] calculations based on the optimized structures at ground states are performed using the B3LYP functional with TZP basis by ADF. The relativistic effect, is included by applying the zeroth-order regular approximation (ZORA) [44] to the full relativistic effect treated in Dirac equation. The scalar relativistic ZORA method [45] is applied and 10 lowest triplet and singlet roots of the non-hermitian eigenvalue equations were obtained to determine the vertical excitation energies. The oscillator strengths were then deduced from dipole transition matrix elements (for singlet states only). The SOC integrals are computed based on the "configuration-interaction-singles" analogy in TDDFT under the Tamm-Dancoff approximation [46]. The one-electron SOC integral between the S_i and T_j states are evaluated based on the following expression

$$\langle S_i|H_{so}|T_j\rangle = \sum_{l}^{N_{S_i}} \sum_{m}^{N_{T_j}} c_{il}^{S} c_{jm}^{T} \left\langle \Psi_{il}^{s}|H_{so}|\Psi_{jm}^{T} \right\rangle$$

where H_{so} is the Breit-Pauli operator in the effective nuclear charge one-electron form, Ψ_{il}^{S} and Ψ_{jm}^{T} re the l-th singlet and m-th triplet state transitions generated from one-electron vertical excitation over the ground state electronic configurations for the S_i and T_j states, respectively. The weighted coefficients c_{il}^{S} and c_{jm}^{T} are taken from time-dependent density functional (TDDFT) calculations. The $^1n\pi^*-{}^3\pi\pi^*$, or $^3n\pi^*-{}^1\pi\pi^*$ contribution to the SOC in fluorescein is estimated by the one-center contributions in the one-electron SOC integrals based on the following form analogous to the case of transition metal complexes [47,48].

$$\langle S_n|H_{so}|T_m\rangle = \sum_{k} a_i a_j' c_k c_k' \xi_c \langle {}^1p_k\pi^*|\hat{l}\cdot\hat{s}|{}^3p_k'\pi^{*'}\rangle$$

Where a_i and a_j' are the normalized configuration interaction coefficients of the excitation in S_n and T_m states, respectively, and c_k and c_k' are the atomic orbital coefficients of p_k and p_k', the p orbitals on different atoms in the molecular orbitals involved in S_n and T_m states, respectively. Here the one-electron spin-orbit coupling constant for main-group elements C, O, and N are comparable and are considered on an equal footing. Model calculations on the benzaldehyde and thiobenzaldehyde shows that the one-center one-electron estimation tends to over-estimate the SOC integrals, but overall the results are on the same order of magnitude with the full two-electron Breit-Pauli integral calculated by MolSOC [49], as shown in Fig. S2. For the twisted $\pi\pi^*$ system, e.g. the non-coplanar helicene molecule, the one-center one-electron estimation also gives qualitative agreement with the INDO/CIS results [50], as shown in Fig. S7.

3. Results and discussions

3.1. Relative energies of $n\pi^*$, $\pi\pi^*$, and CT states

Fluorescein (R = COOH, **1**) along with four other derivatives **2**–**5** with increasingly electron-donating substituents are investigated, as shown in Fig. 1. The anionic (basic) forms are studied as it is well known that the quantum yields of fluorescein derivatives are higher in alkaline solvents and are decreased in acidic media [29,51]. Relative energies and shapes of selected frontier molecular orbitals in the ground state geometry for **1**–**5** are shown in Fig. 2. The energies and the excitation nature of the selected low-lying singlet excited states are shown in Fig. 3, with detailed excitation composition shown in Table S1. As Fig. 2 shows, for fluorescein, LUMO, HOMO, HOMO-1 and HOMO-4 are all π orbitals localized on the xanthene moiety, HOMO-2 and HOMO-3 are mainly the nonbonding p orbitals of the oxygen atoms on the carbonyl groups (MOs enclosed by square boxes in Fig. 2), while HOMO-5 and LUMO+1 are the π orbitals localized on the benzene moiety. Therefore, as shown in Fig. 3, the lowest singlet excited state of fluorescein, S_1 (HOMO to LUMO), is a locally excited (LE) $\pi\pi^*$ state and remains at around 2.5 eV above the ground state for **1** to **5** since both the energy levels and the electron density distribution of the HOMO and LUMO remain roughly the same with different substituents. The S_2 state (HOMO to LUMO+1) corresponds to a charge transfer state (denoted as CT′) from the xanthene to the benzene moiety, so do S_6 and S_7. The S_3 (HOMO-1 to LUMO) and S_4 (HOMO-2 to LUMO) are $\pi\pi^*$ and $n\pi^*$ states, respectively, and are slightly affected with substituent variation (vide infra). And finally the S_9 (HOMO-5 to LUMO) corresponds to the charge transfer state in the opposite direction (denoted as CT) from benzene to xanthene and is the most strongly affected by the substituent groups. As can be expected, the stronger the electron donating ability the substituent, the higher the energy level of the molecular orbitals that are localized on the benzene moiety (MOs enclosed by red circles in Fig. 2). The HOMO-6 in **1**, when R = COOH, is gradually shifted upward to HOMO-2 for **5**, when R = $N(CH_3)_2$. As xanthene-centered

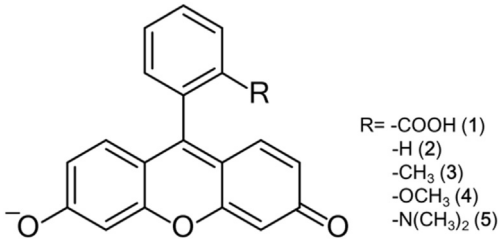

Fig. 1. Fluorescein (**1**) and its derivatives (**2**–**5**) in the basic form investigated in this study.