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## Electronic structure of fullerene-squaraine complexes for photovoltaic devices

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## ABSTRACT

Squaraine dyes are promising materials to be used as electron donors in photodevices. We applied quantum chemical methods to investigate the electronic spectrum of three different squaraine dyes and of their complexes with fullerene C<sub>60</sub> in the gas phase. Based on the excited-state densities, the electronic states were characterized as localized, delocalized and charge transfer, allowing an understanding of the basic photophysics of these compounds. Comparison with experimental data showed that the measured short-circuit voltage is correlated not only to the energy of the charge-transfer state, but also to the energy of the lowest excited state, localized at the squaraine dyes. We discuss whether this may imply a non-Marcus regime for the charge-pair dissociation at the interface.

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## 1. Introduction

Donor–acceptor (D–A) organic heterojunctions are promising materials for the development of photovoltaic devices. Even though their power-conversion efficiency is bound to be lower than that of inorganic and dye-sensitized devices, this can be compensated by their low production costs and high plasticity [1–8]. In recent years, the field of organic photovoltaics (OPV) has seen a major thrust towards development of new materials, morphological control, and device architecture [9–13]. In particular, monomeric donors gain increasing importance as photovoltaic materials, as they can be easily purified and self-assembled into ordered domains compared to polymeric materials [7,14].

Squaraine (SQ) dyes form a notable class of monomeric donors with high optical density [15–18]. They absorb in the green to the near infrared region, have very high absorption coefficients of  $\sim 3 \times 10^5 \text{ cm}^{-1}$  and hence are excellent candidates for OPVs [16]. The power conversion efficiency can be greater than 5% with SQ/C<sub>60</sub> heterojunctions [16]. This efficiency is, however, found to be highly dependent on architecture and morphology: for the same composition of SQ/C<sub>60</sub> heterojunction, it can vary from 1.8% to 4.6% depending specificities of the device processing [15,18]. There

is also evidence in the literature that changing the amino substituents from alkyl to aryl groups improves the charge and exciton properties due to increased  $\pi$ – $\pi$  overlap [19,20]. The crystal structure of such compounds, showing molecular stacking of the donors, supports this observation [15].

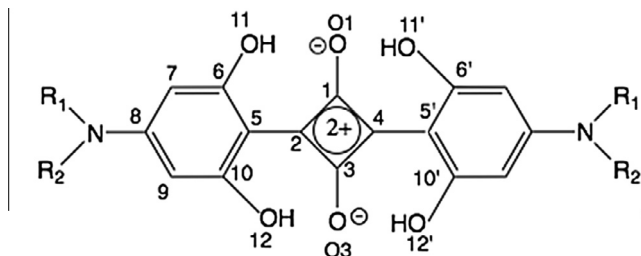
OPVs constructed with few different substituted SQ dyes and C<sub>60</sub>, using the same device architecture and the same spin-cast technique for preparing SQ films, are reported in literature [15]. From a computational perspective, this homogenous set of experimental data is especially valuable, as it allows gauging the quality of the theoretical predictions, while avoiding complications arising from the architecture and morphology. In this report, we use time-dependent density functional theory (TDDFT) to characterize and understand the electronic structure of this set of SQ/C<sub>60</sub> heterojunctions. The three SQ dyes investigated are indicated in Scheme 1. We show that their lowest excited states, corresponding to a local excitation at the donor and to a charge-transfer (CT) transition from donor to acceptor, are correlated to the measured open-circuit voltage ( $V_{OC}$ ). We also address the question whether this correlation may imply non-Marcus behavior in the photophysics of these devices.

## 2. Computational details

Ground-state geometries of the monomers and complexes were optimized with density functional theory (DFT) using the  $\omega$ B97X-D

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- 1 R1 =R2 = isobutyl
- 2 R1 =R2 = phenyl
- 3 R1 = 1-naphthyl, R2 = phenyl

Scheme 1. Investigated squaraine dyes.

functional [21,22]. Cartesian coordinates are provided in the Supplementary Data. Excited-states were computed with TDDFT mostly using this functional. In addition, TDDFT calculations were performed with B3LYP [23,24], CAM-B3LYP [25], and M06-2X [26] to assess the dependence of the electronic structures on the functionals. The 6-31G(d) basis set [27] was adopted for the computations. The 6-31+G(d), 6-311++G(d,p) and TZVP [28] basis sets were used for comparison. All TDDFT calculations were performed with Gaussian 09 [29].

To understand the character of the excited states, we employed a classification scheme based on the partition of the excited-state electron densities between two arbitrary molecular fragments, A and B [30,31]. This method classifies the states using two quantities,  $\Sigma P$  and  $\Delta P$ , which measure the degree of charge localization and charge transfer respectively. Adopting a threshold of 0.5 electron [30,31], electronic transitions are classified as localized in A or B (LOC(A) or LOC(B)), as delocalized over A and B (DELOC), or as charge transfer from A to B (CT(A  $\rightarrow$  B)) or from B to A (CT(B  $\rightarrow$  A)). The definitions of the A and B subunits are discussed later. Quantitative information about the charge distribution, including values of  $\Sigma P$  and  $\Delta P$ , are provided in the Supplementary Data.

### 3. Results and discussion

#### 3.1. Isolated SQ

Three SQ dyes (Scheme 1) were investigated in the gas phase. Two configurations of each dye are used in this comparison. In the first one,  $C_2$  symmetry is kept and the dye has two intramolecular hydrogen bonds. In the other one, the dye loses its symmetry and forms four intramolecular hydrogen bonds. The structures of

Table 1

Computed vertical excitation energies [TD- $\omega$ B97X-D/6-31G(d)] and experimental absorption maxima in solvent and film. Configurations with 2 or 4 hydrogen bonds are denoted by 2HB and 4HB respectively.

SQ	Calculated (eV)		Experimental (eV), Ref.[15]		
	2HB	4HB	CH <sub>2</sub> Cl <sub>2</sub>	Toluene	Film
1	2.46	2.52	1.90	1.91	1.79
2	2.36	2.42	1.84	1.83	1.73
3	2.42	2.41	1.86	1.85	1.79

all three molecules in their two configurations are shown in Fig. 1. A noticeable difference between the structures with 2 and 4 hydrogen bonds is the planarity around the central 4-membered ring. With 2 hydrogen bonds, the average twisting angle around C2–C5/C4–C5' (Scheme 1) is 13°, 15° and 14° for **1A**, **2A** and **3A** respectively. On the other hand, with 4 hydrogen bonds, the central 4-membered ring and the 2,6-dihydroxyphenyl groups are almost co-planar in **1B**, **2B** and **3B**. The geometric parameters associated with these structures are given in Table S1 of the Supplementary Data.

Next, we calculated the vertical excitation energies for all six configurations. The energy of the first excited state (which is also the first bright state) for the three molecules is given in Table 1 along with the experimentally observed absorption maximum in CH<sub>2</sub>Cl<sub>2</sub>, in toluene, and in neat films. There is a substantial blue shift of the computed energies in comparison to the experiments, which is discussed below. Despite the shifts, the computed vertical excitations (especially for the configurations with 2 hydrogen bonds) and experimental absorption maxima in either solution or film follow the same trends. For instance, there is a reduction of  $\sim 0.1$  eV in the energies when comparing **1–2** for all computational and experimental situations.

The impact of the choice of functional, of the long-range separation parameter  $\omega$ , of the basis set, and of the dielectric constant in the polarizable continuum model (PCM [32]) on the first excited state was examined for SQ **1A** (Table 2). When varying  $\omega$  between 0.10 and 0.35  $a_0^{-1}$ , the lowest excitation energy increases monotonically by only 0.1 eV. The energy variation with the choice of functional is also about 0.1 eV. The extension of the basis set to include a triple- $\zeta$  partition, more polarization and diffuse functions reduces the energy of the first excited state by about 0.2 eV. The change in the dielectric constant from 1.000 (gas phase) to 2.374 (toluene) reduces the energy from 2.46 to 2.31 eV.

As mentioned above, the calculated vertical excitations are blue shifted in comparison to the corresponding experimental absorption peaks (Table 1). The main reason for this shift are (i) the difference between the vertical excitation and the band maximum, which is about  $\sim 0.2$  eV [31], (ii) the small basis set, and (iii) the influence of the environment. As already discussed, basis set

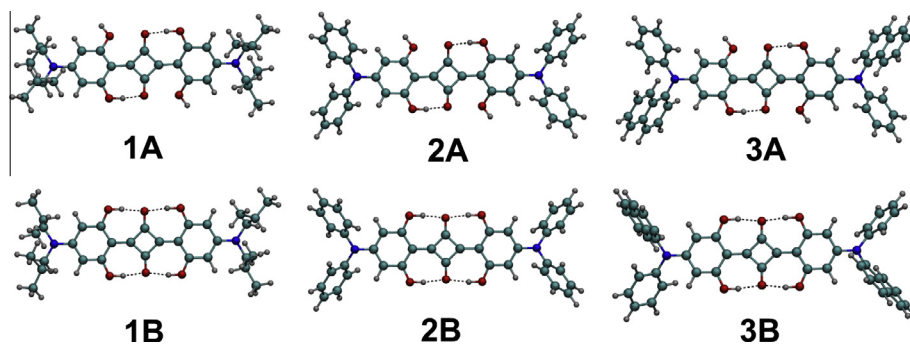


Fig. 1. Structures of the donors. Top: 2 hydrogen bonds. Bottom: 4 hydrogen bonds.

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