Exploring the excited-states of squaraine dyes with TD-DFT, SOS-CIS(D) and ADC(2)

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ABSTRACT

We investigate the electronic excited-states of a large panel of squaraine derivatives with first principles tools taking into account environmental effects, with a focus on 0-0 energies and band shapes. First we show that while TD-DFT yields significantly too large 0-0 energies, correcting the TD-DFT values with ADC(2) provides much more accurate estimates. Second, though the geometric relaxation after photon absorption is limited, this investigation also indicates that using theoretical vertical estimates to approximate the experimental 0-0 energies is not a very appealing approach. In contrast, for experimentally non-fluorescent compounds one can use the measured λ_{max} as an approximation of the 0-0 energy with a minimal loss of accuracy. The proposed computational approach delivers a ca. 0.125 eV accuracy for a large number of compounds and therefore stands as one of the first robust method to predict the optical spectra of this important class of dyes. We also investigate the band shapes of selected derivatives and show that TD-DFT vibronic couplings allow an accurate reproduction of the experimental topologies of both absorption and emission bands.

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1. Introduction

Squaraines (SQs) constitute an important class of organic dyes. They are known for their strong and intense absorption of light as well as their structural diversity, as various substituents can be added through organic synthesis in order to tune their optical properties [1—14]. These molecules are generally obtained by condensation of squaric acid with electron rich aromatic molecules, e.g., *N,N*-dialkylanilines, pyrroles, indoles, quinaldine, indolizine, benzothiazoles, azulenes, quinolones … and the resulting compounds typically show absorption at wavelengths going up to the near-infrared region. As their names imply, SQs present a core constituted of a four-member sp^2-carbon π-conjugated cycle often substituted by two oxygen atoms and two π-conjugated moieties. In one of the possible limit mesomeric forms, the SQ core is positively charged — the two oxygen atoms bearing the negative charge — and this positive charge can be viewed as delocalized over the odd number of carbon atoms constituting the π-conjugated

pathway. Therefore, SQ dyes present similarities with the traditional merocyanine dyes [15]. From another point of view, one can state that the electron-deficient square core acts as a strong acceptor whereas the electron-rich arms act as donors so that these dyes present a D—A—D quadrupolar charge-transfer (CT) structure. These very specific electronic features have made SQs valuable building blocks in numerous fields, e.g., bio-imaging [16—18], photodynamic therapy [19—25], electrophotography [26,27], organic light-emitting diodes [28,29], sensors [30,31], solar cells [32—34], and non-linear optical materials [35—37].

Unsurprisingly, SQs have also been the subject of several computational investigations. To the best of our knowledge, the first theoretical study, dating back from 1986, is due to Bigelow and Freund [38]. Using the MNDO and CNDO/S(S + DESCI) semi-empirical approaches, they characterized both the ground-state (GS) and the lowest excited-state (ES) of a prototypical SQ dye. These early calculations already demonstrated that the color of SQs is related to a state presenting a blend of cyanine and charge-transfer characters [38]. A decade later, the initial first principle calculations on SQs appeared. In 2009, Geiger and coworkers performed gas-phase Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) calculations of two SQ dyes used in solar cells [39]. They tested several exchange-correlation functionals (XCFs), i.e., B86,

BLYP, BPW91, PBE, B3LYP, PBE0, and X3LYP, and surprisingly found a better match with experiment when using pure XCFs rather than hybrid XCFs [39]. The same year, Russo's group considered the first significant panel of symmetric SQs dyes and used both TD-DFT and CC2 to explore their ES [40]. They found that the atomic basis set effects were small at both levels of theories and that the transition energies obtained with the two methods show quite large errors ($\sim$ 0.3 eV), with a significant overestimation of the transition energies for TD-DFT that yields too blueshifted λ_{max}. These outcomes are indicative of a significant cyanine-character of the excited-state [41], as the transition energies of CT ES are generally underestimated (and not overestimated) by TD-DFT [42,43]. More recently, the same group investigated the ES of six SQs using three functionals (PBE0, M06, and ωB97X-D) in a study focusing on the singlet-triplet splittings and spin-orbit couplings [44]. Besides a good agreement with experimental X-ray structures [45], the authors reported a good match between M06 and experimental optical data, though the above-mentioned blueshifts pertain [44]. In another recent work, TD-DFT transition energies determined with a large panel of functionals were compared to both SAC-CI values and experimental results for several SQs; the wavefunction method emerging as more accurate than the density-based one [46]. Eventually, the only investigation to date that went beyond the frozen GS geometry approach is due to Liu and coworkers [47]. They determined the ES geometries and vertical emission energies of four SQ dyes in four solvents using a continuum model to describe the environmental effects. One can also find other more specific TD-DFT investigations of SQs in the literature [48–51].

Despite these earlier useful theoretical works, there is, to the best of our knowledge, no investigation of the band shapes nor 0-0 energies of SQ derivatives. In contrast to the vertical estimates determined up to now (see above), these two properties allow direct and physically meaningful comparisons with experiment [52]. Indeed, the former can be straightfowardly compared to the measured absorption and fluorescence spectra if proper normalization is carried out [53], whereas the 0-0 energies correspond to the experimental absorption-fluorescence crossing point (AFCP) [54,55]. However, the determination of these two properties require the calculation of the ES Hessian, which remains computationally expensive, as well as of the vibronic couplings for the band shapes. We perform such task in this paper. Indeed we treat a very large number of SQs and determine 0-0 transition energies and compare them to available experimental data. The solvent effects are taken into account at all calculations steps by a refined continuum model [56,57], whereas several first principle methods are used. Indeed, we applied TD-DFT but also the second-order Algebraic-Diagrammatic Construction approach, ADC(2) [58], as well as the Scaled Opposite Spin version of Configuration Interaction Singles with a Double correction, namely SOS-CIS(D) [59].

2. Computational details

The general computational approach followed here has been detailed elsewhere [41,60], so that we only briefly outline it here. In this protocol, the structures and vibrational spectra are determined with TD-DFT, the solvent effects with the Polarizable Continuum Model (PCM) whereas the total and transition energies are computed with TD-DFT as well as electron-correlated wavefunction approaches. This protocol that allows to access accurate 0-0 energies at a reasonable computational cost even for rather large compounds was shown to be successful for several cyanine-like compounds (see Ref. [41] and references therein).

All the DFT and TD-DFT calculations were performed using the Gaussian09 program package [61], using a tightened self-consistent field convergence criterion (at least 10^{-8} a.u.) and an improved DFT

integration grid (so-called *ultrafine* grid). We applied the Berny-GEDIIS algorithm during the force-minimization process imposing a threshold of 10^{-5} a.u. on the residual mean forces. Point group symmetry was used when possible in order to lighten the computational burden that can be important for the computation of the TD-DFT Hessian. The GS equilibrium geometry of all investigated dyes was fully optimized at the DFT level using the M06-2X hybrid exchange-correlation functional [62,63] and the 6-31G(d) atomic basis set. It was checked by vibrational frequency calculations performed at the same level of theory that all structures are true minima of the potential energy surfaces. This choice of M06-2X is justified by numerous previous benchmarks [55,64–66], demonstrating the ability of this XCF to reproduce the ES trends in a wide range of organic compounds. The ES structures have been optimized at the same level of theory, using TD-DFT, and the numerical ES Hessian was systematically computed to ascertain the nature of the stationary point, as well as to obtain the zero-point vibrational energies (ZPVE) of the ES. The total and transition energies were computed on these GS and ES structures using the same XCF but selecting a much more extended atomic basis set, namely 6-311+G(2d,p).

Solvent effects have been included in the DFT and TD-DFT calculations by using the well-known Polarizable Continuum Model (PCM) [56] as implemented in Gaussian09. For both the ES geometry optimizations and Hessian calculations, we applied the linear-response (LR) PCM approach [67,68], whereas the ES total and transition energies have been determined within the corrected LR scheme (cLR) [57]. We applied the equilibrium PCM limit during the structural and vibrational calculations. We have determined both the absorption and emission energies in both the non-equilibrium and equilibrium limits. The differences between these two limits were found to be trifling ($\sim$ 0.001 eV) for the SQ dyes treated here. Default PCM radii and cavities were used.

In a second step, two wavefunction approaches have been employed to improve the TD-DFT transition energies. The first is the second-order ADC method, ADC(2) [58], that employs a diagrammatic perturbation expansion of the polarization propagator based on the Møller-Plesset partition of the Hamiltonian. The second is the more computationally effective SOS-CIS(D) approach [59], that was shown particularly successful for BODIPY derivatives [69]. The ADC(2) and SOS-CIS(D) calculations were performed with the Turbomole [70] and Q-Chem [71] packages, respectively, applying the resolution-of-identity (RI) technique to speed-up the calculations. The SOS-CIS(D) calculations were performed with the 6-311+G(2d,p) atomic basis set whereas the ADC(2) calculations used the *aug*-cc-pVDZ atomic basis sets. These choices are justified by previous works [40,72].

Vibrationally resolved absorption and emission spectra within the harmonic approximation were computed using the FCclasses program and the Franck-Condon (FC) approximation using the TD-DFT vibrational signatures of the two states (so-called adiabatic Hessian approach) [53,73–75]. The reported spectra were simulated using a convoluting Gaussian function presenting a half width at half maximum (HWHM) that was adjusted to allow straightforward comparisons with experiments (0.04 eV). A maximal number of 25 overtones for each mode and 20 combination bands on each pair of modes were included in the calculation. The maximum number of integrals to be computed for each class (ca. 10^6) was set so to obtain a sufficiently large FC factor ($>$ 0.95).

3. Results and discussion

3.1. Excited-state geometries and electronic reorganization

Fig. 1 provides density difference plots for two typical SQs. In