



Research paper

A push-pull organic dye with a quinoidal thiophene linker: Photophysical properties and solvent effects

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ABSTRACT

In the present work we perform a computational study of the properties of a push-pull organic dye with a quinoidal thiophene unit as the conjugated linker between the electron donor and acceptor groups. We investigate the photophysical properties of the dye related to its potential use as a molecular sensitizer in dye-sensitized solar cells. We rationalize the solvation effects on the absorption band of the dye in protic and aprotic solvents, identifying the interaction of alcohol solvents with the amine in the donor group as the source for the blue shift of the absorption band with respect to aprotic solvents.

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1. Introduction

In the search of competitive and sustainable alternatives to well-established photovoltaic devices in the market, the optimization of the photoelectric conversion in dye-sensitized solar cells (DSSC) has been a major field of research in the past two decades [1–6]. To this end, synthetic chemists have contributed with a wide range of photosensitizers ranging from organometallic complexes such as the popular ‘black dye’ [7–9] to a plethora of organic molecules. In particular, donor- π -acceptor type organic dyes (D- π -A) have been widely employed due to their appealing properties as molecular sensitizers: large absorptivities in the visible and near IR region of the spectrum, necessary for a good light harvesting of solar photons [10–13] and strong charge-transfer (CT) character of the electronic transition to the lowest singlet state, favoring electron injection to the conduction band of the attached nanostructured semiconductor [14].

In a recent paper [15], the group of Segawa reported a D- π -A type organic dye, **QT1** (Fig. 1), with a quinoidal thiophene as π -bridge in order to efficiently extend π -conjugation without significant increase of the photosensitizer’s molecular size, which may be sometimes detrimental for efficient photo-conversion [16–20]. Their work was inspired by earlier reports in which efficient light harvesting of the visible spectrum was obtained using extended π -conjugated systems [13,21,22]. The photoelectric

conversion efficiency of 5.2% obtained with the quinoidal thiophene dye surely demonstrated its beneficial photophysical properties. In their work, the solvent dependence of the absorption maxima of the quinoidal thiophene dye was also studied and they found a linear relationship with the solvents polarity. This trend however was not followed in alcohol solvents, for which a blue shift of the absorption maxima was observed compared to aprotic solvents of similar polarity. The authors pointed to hydrogen bonding interactions being responsible of such observations.

In this work we investigate the atomic and electronic structural properties of **QT1** using different molecular and quantum mechanical models and a variety of computational tools. This study aims to characterize the main physical properties of the dye related with its potential use as a molecular sensitizer in DSSC, in particular to its light absorption ability. The identification of the principal hydrogen bonding interactions between methanol molecules and the quinoidal thiophene dye is one of the major goals of this work.

2. Computational details

Electronic structure calculations for ground and excited states were performed within the framework of density functional theory (DFT) and its time-dependent version (TDDFT), respectively. Ground state geometry optimizations of the molecular dye in solution with no explicit solvent molecules were carried out with the B3LYP functional [23,24]. Optimized structures with the M06-2X functional [25] are almost identical to the B3LYP geometries (see [Supporting Information](#)). Stationary geometry for the lowest

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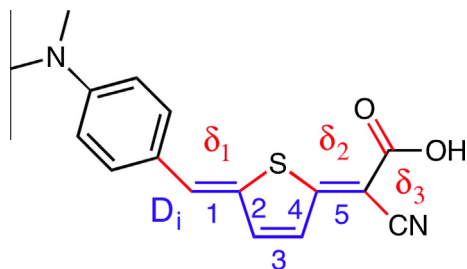


Fig. 1. Most stable conformation of **QT1** (CTT) with structural labels discussed in the text.

energy conformer (CTT as in Fig. 1) was confirmed to be a true minimum by evaluation of the hessian. Excited state calculations were performed with TDDFT and the CAM-B3LYP functional [26]. In all the calculations, the 6-31+G(d,p) basis set was used and the effects of the solvent were taken into account with the polarizable continuum model using the integral equation formalism variant (IEFPCM) [27,28]. The solvents considered in our calculations with the corresponding dielectric constants are: dioxane ($\epsilon = 2.21$), toluene ($\epsilon = 2.37$), chloroform ($\epsilon = 4.71$), propanol ($\epsilon = 19.26$), ethanol ($\epsilon = 24.85$), methanol ($\epsilon = 32.61$), acetonitrile ($\epsilon = 35.69$) and dimethylsulfoxide ($\epsilon = 46.83$). Geometry optimizations in methanol solution of model systems containing explicit solvent molecules were performed with the M06-2X functional, as it has been recommended in the presence of non-covalent interactions [25]. All electronic structure calculations were performed with the Gaussian 09 package [29]. In order to systematically scan over potentially relevant solvent-dye interactions, classical molecular dynamics simulations (Fig. S3) were performed for the most stable isomer (CTT) with 950 methanol molecules in a 40 Å cubic box, in accordance with the density of methanol in the experimental conditions, that is 0.792 g/cm³. The OPLS-AA force field [30] was used and reparametrized in order to reproduce DFT calculations (see Supporting Information for further details). A 100 ps simulation with 1 fs time step was run in the canonical (NVT) ensemble at 298 K using periodic boundary conditions with the Tinker program [31]. The principal solute-solvent interactions were identified from the molecular dynamics simulations and low energy structures were used as initial guesses in DFT geometry optimizations. From this procedure we identified up to five solvent molecules with significant interaction with the dye.

3. Results and discussion

3.1. Molecular structure

In order to investigate the photophysical properties of **QT1** we first look at its ground state structure in solution. The **QT1** molecule presents several structural conformers, each one of them corresponding to a local minimum on the ground state potential energy surface (PES). These forms can be mostly described in terms of three dihedral angles corresponding to the relative disposition between the different moieties of the dye (Fig. 1). Note that different dispositions of H atoms within the methyl and carboxylic acid groups also result in different conformations, but since they represent only slight variations of the structure with a very small effect on the photophysical properties of the molecule, they have not been considered in our study.

Electronic conjugation of the **QT1** dye imposes molecular planarity along the entire molecule only broken by the hydrogen atoms on the methyl groups of the dimethylaniline fragment. Mono dimensional energy profiles along each of the three dihedral angles defined in Fig. 1 exhibit two energy minima corresponding

to *cis* ($\delta \sim 0^\circ$) and *trans* ($\delta \sim 180^\circ$) conformations. The *cis* conformation is preferred for the δ_1 angle in order to avoid steric hindrance between hydrogen atoms in the two rings, while electronic interactions favor the *trans* disposition between sulfur and cyano groups (δ_2) and between the cyano and carbonyl groups (δ_3). Therefore, the energetically most stable conformer can be labeled in terms of δ_1 , δ_2 and δ_3 as CTT (*cis-trans-trans*). The *cis/trans* energy differences in solution for δ_1 , δ_2 and δ_3 obtained as the relative energies between the CTT form and the conformers TTT, CCT and CTC respectively, averaged over all studied solvents, are computed as 2.4, 1.7 and 2.4 kcal/mol, respectively. These values dictate the relative stability between conformers (Fig. 2 and Table S1). It is worth noticing that molecular planarity is preserved in all conformers except for the ones with δ_1 in *trans* (TXX forms), which exhibit torsion angles of the order of $\delta_1 \sim 155^\circ$ to minimize interactions between hydrogen atoms on the two rings. Potential energy profiles computed along the δ_1 , δ_2 and δ_3 torsion angles can be found as Supporting Information.

Interatomic C–C distances confirm the quinoidal form of the thiophene unit in all conformations and solvents (Fig. 3). The larger bond length obtained for D₅ with respect to the D₁ and D₃ C–C bonds can be attributed to the electron withdrawing power of the cyanoacrylic acid group, which diminishes its double bond character.

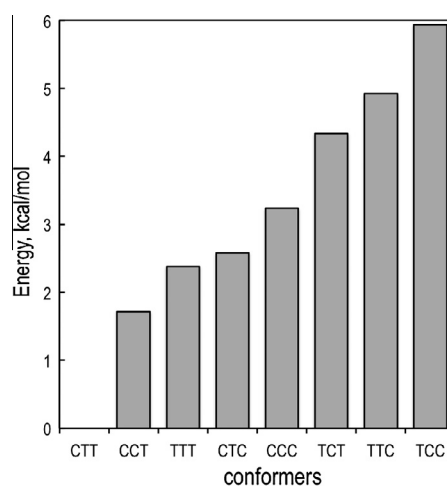


Fig. 2. Computed relative stability of **QT1** conformers with respect to the most stable conformer (CTT) in solution averaged over all studied solvents.

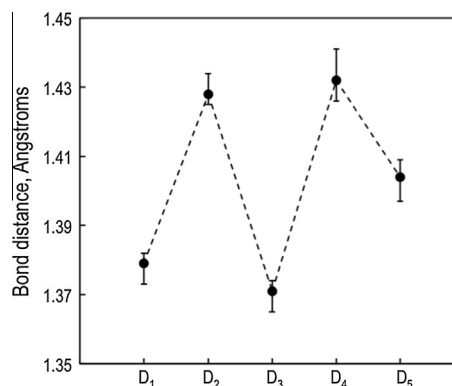


Fig. 3. Average interatomic distances of **QT1** for all conformers and solvents. Vertical bars indicate maximum and minimum values. Labels correspond to Fig. 1.

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