

First-Principles Study Of The Excited-State Properties Of Coumarin 6 Dye In Dye-Sensitized Solar Cells

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Abstract: Time dependent density functional theory (TDDFT) calculations have been carried out to study the electronic structure and the excited properties of coumarin 6 dye. The excited state properties have been investigated with inclusion of solvent effect. The B3LYP functional with a 6-31G(d,p) basis set have been used to compute transition energies. The solvent effects have been described within the polarizable continuum model. Ground-state geometries are optimized using density functional theory with B3LYP functional combined with 6-31G(d,p) basis sets. Vertical absorption energy calculations characterize the lower singlet excited states both in gas phase and in solvent. A large red-shift of the absorption maximum in the polar solvent suggests an intra-molecular charge transfer character of the excited state.

Keywords: DSSC; DFT; TDDFT; coumarin 6; Basis sets; HOMO-LUMO energy.

Introduction

Dye Sensitized Solar Cells (DSSC)¹⁻³ based on organic dyes have attracted considerable attention in recent years because of their high incident solar light-to-electricity conversion efficiency and low cost of production.⁴⁻⁷ The photochemical properties of different organic sensitizers have extensively been investigated in an attempt to design dyes with maximal visible light absorption coupled to long-lived excited states. However, major effort is still needed in both developing new sensitizers and finding optimal working conditions to improve the photon-to-current conversion efficiencies.

In DSSC only a monolayer of sensitizer is adsorbed on the semiconductor surface. Among the various proposed dyes, state-of-the-art ruthenium-based sensitizers have high energy conversion efficiencies exceeding 11%.⁸⁻¹⁰ However, the ruthenium based dyes are expensive and require very careful synthesis protocols and

purification procedures.¹¹ To reduce the manufacturing cost of the DSSCs various metal free, organic sensitizers are now being proposed and investigated. These organic dyes are advantageous due to their tunable light absorption, higher molar extinction coefficient and the electrochemical properties.^{4,11} An organic sensitizer usually is bestowed with a donor part (electron donating group), an acceptor part (electron accepting group) and a linker group. A number of donor groups have been investigated with varying success rates such as N, N-dimethylaniline,¹²⁻¹⁴ coumarins,¹⁵⁻²⁰ quinoxalines,^{21,22} triphenylamine,²³⁻²⁴ pyrrolidino,²⁷ and π -conjugated linker groups such as C-C double bonded chain,^{12,14} thiophene units.^{18,19,21,22,28,29} The electronic and optical properties of coumarin based dyes make them one of the most promising classes of organic sensitizers and they have been studied systematically.^{16,18,21,30-35} They are considered type-I dyes, in which electron injection

occurs through an indirect mechanism: there is a photo-excitation of the dye to an excited state, followed by the electron injection from this state to the semiconductor conduction band.

Theoretical methods are a powerful tool for molecular design, and conclusions drawn from calculations are valuable guidelines for synthesis of new efficient dyes. In recent years, coumarin based dyes have been extensively studied from experimental and theoretical methods.³⁶⁻⁴⁴ The Time-Dependent Density Functional Theory (TDDFT/B3LYP) has been used to simulate the electronic absorption spectra of free coumarin dyes.³⁶⁻⁴³ The obtained excitation energies that agree well with experimental data for coumarin dyes. Moreover, the inclusion of solvation effect *via* a PCM model tends to reduce the excitation energies, due to a stabilization of the LUMO orbital. Furthermore, TDDFT calculations have been used to establish a relationship between the electronic structure of free coumarin dyes and their efficiency as DSSC sensitizers.⁴⁴ Thus, the location of the first absorption band and the energy of the HOMO orbital were used as parameters to evaluate the electrochemical efficiency of coumarin dyes.³⁵

In this paper, we try to study the excited-state properties of coumarin 6 both in gas phase and in solvent using the TDDFT method.

Computational details

Coumarin 6 sensitizer was modeled using Avogadro.⁴⁵ The calculations were done using B3LYP hybrid functional and 6-31G(d,p) basis set. The effects of the solvent (water) was added using the polarizable continuum model (PCM)⁴⁶ of solvation as implemented in the GAMESS-US software suit.^{47,48} The optimized geometries are utilized to get the frontier orbitals and to carry out the time dependent density functional theory (TDDFT) studies. Transition energies are calculated at the level of TDDFT/6-31G(d,p). The functional used to calculate excited-state energies is same as that used in the geometry optimization. Molecular orbitals were plotted using wxMacMolPlt.⁴⁹ UV/Vis spectra were plotted using Gabedit.⁵⁰

Result and discussion

The optimized structure of the coumarin 6 sensitizer has planar geometries, as can be seen in Fig. 1. The highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) are shown in Fig. 2. This figure also show the computed isodensity surfaces for HOMO and LUMO. In both dyes, the HOMO and LUMO show π -character. While the HOMO is more or less delocalized over the entire dye molecule, LUMO is more localized on the coumarin and linker groups.

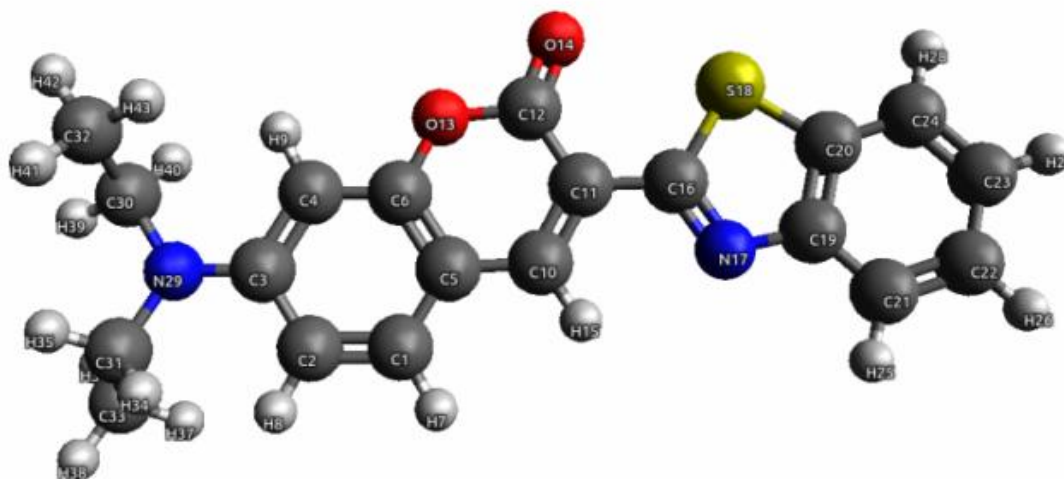


Fig. 1. Optimized structure of coumarin 6 dye.

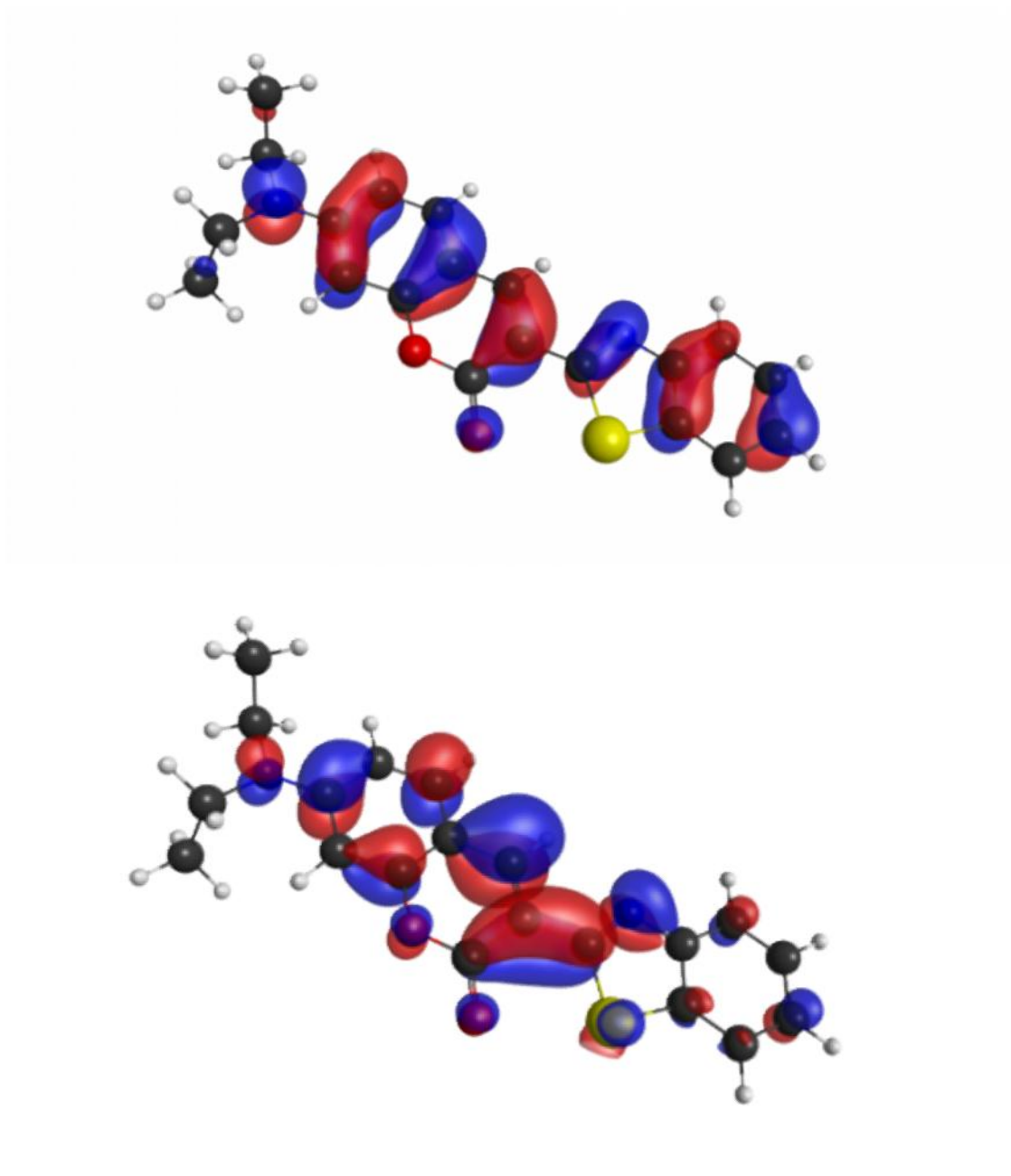


Fig. 2. Molecular orbitals of coumarin 6 during photo-excitation. HOMO (top) and LUMO (bottom).

This is desirable and leads to the intra-molecular charge separation upon excitation (push-pull effect). The change in electronic distribution between HOMO and LUMO is also indicative of a large dipole moment in the first excited state (as compared to the ground state)²⁵ and is the possible reason for the large oscillator strength for the HOMO → LUMO transition as seen in Fig. 3. The

computational UV/Vis absorption spectrum for coumarin 6 in gas phase and in solvent (water) shows transition energies of high intensities, corresponding to the λ_{max} of 378 nm and 426 nm at 3.284 eV and 2.914 eV (Table 1) respectively, as shown in Fig. 3(a) and Fig. 3(b).

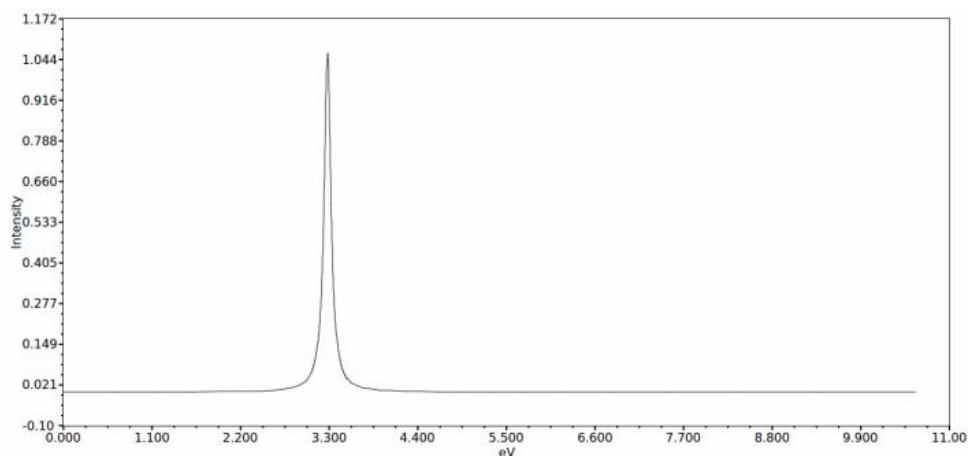


Fig. 3(a). Calculated UV/Vis absorption spectra of coumarin 6 in vacuum.

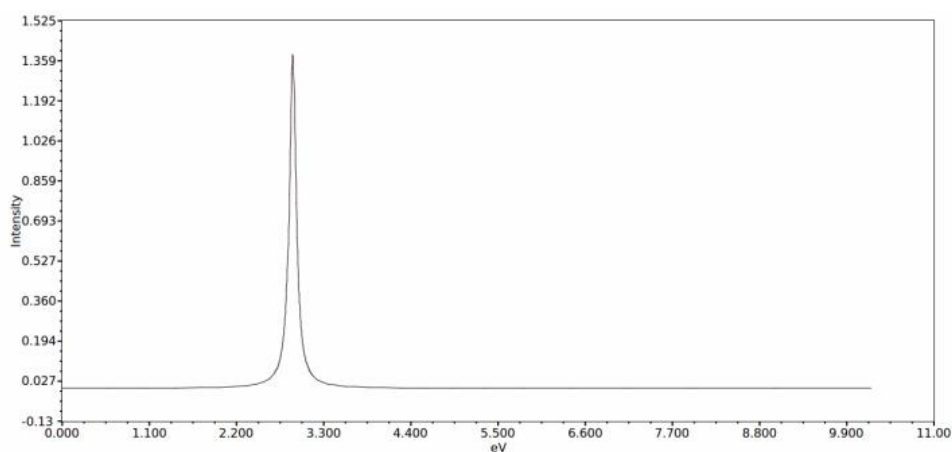


Fig. 3(b). Calculated UV/Vis absorption spectra of coumarin 6 in solvent (water)

Table 1. TDDFT absorption energy (E) at λ_{\max} corresponding HOMO (H), LUMO (L) energies, HOMO-LUMO gap ($H - L = U_{HL}$), oscillator strength (f) and dipole moment (D).

System	E (eV)	H (eV)	L (eV)	U_{HL} (eV)	f	D (Debye)
Free dye	3.284	-5.225	-1.679	3.546	1.066	7.355
In solvent (water)	2.914	-5.255	-1.875	3.380	1.387	9.895

Conclusions

In this study we carried out a detailed DFT/TDDFT calculation for coumarin 6 sensitizer in isolated state and in solvent (water) via the PCM model. Vertical excitation energy

calculations shows red-shift of the absorption maximum in the presence of a polar solvent and it suggests an intra-molecular charge transfer feature of the excited state.

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