

Theoretical studies on the electronic structures and absorption spectra of Cu-based dye sensitizer

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We studied the description of charge-transfer excitations in $[\text{CuL}_2]^+$ (L=6,6'-dimethyl-2,2'-bipyridine-4,4'-bis(propenoic acid))dye sensitizer. This dye was studied using density functional theory (DFT), and the electronic absorption spectrum was investigated via time-dependent DFT (TD-DFT) with several hybrid functional, both in the gas phase and in acetonitrile solution. We also have investigated HOMO and LUMO levels in gas and solvent phases for this dyes. The HOMO LUMO transition describes all lowest singlet excited states. We performed TDDFT calculations at the B3LYP/6-31G(d) level of theory. Solvation effects were included by the conductor-like polarizable continuum model (CPCM). The excitation in the range 500-800 nm of absorption spectra confirms metal-to-ligand charge-transfer (MLCT) transitions. The results of this work suggest that the copper complexes are effective as sensitizers for DSSCs and they can replace ruthenium (II) complexes.

Keywords: DFT; TD-DFT; Dye Sensitizer Solar Cell; Absorption spectra

1. Introduction

Over the past decade, dye-sensitized solar cells (DSSCs) have been extensively investigated both experimental and theoretically as to silicon-based photovoltaic devices for solar energy utilization because of their low cost and high performance [1]. In these devices, dye sensitizers are used to absorb the solar radiation and transfer the photoexcited electron into nanostructured semiconductor electrodes. In the commonest type of DSSC,

the semiconductor is anatase-like TiO_2 and the charge-transfer sensitizers are polyridyl ruthenium (II) complexes with carboxylic acid, dihydroxy, and phosphonic acid groups used to link the dyes to the surfaces of oxide nanoparticles [2].]. Instead of Ru, transition metals such as Os, Fe, Re, Cu, and Pt have been employed in the metal complexes for the sensitizers [3-7].

It was early recognized that carboxylate-derivatised copper (I) bis (2,2'-bipyridine) complexes might be good substitutes to meet the requirements for next-generation DSSC devices due to similar photophysical properties to archetypal $[\text{Ru}(\text{bpy})_3]^{2+}$ salts (bpy = 2,2'-bipyridine) [8]. Although initial results are not comparable with state of the art ruthenium dyes, they indicate that with iterative chemical optimization, sensitizers comparable to ruthenium complexes might be prepared. However, the “Techno-Economic” analyses of the two sensitizers clearly show that even though the efficiency of the copper complex is 4 times lower than that of the ruthenium sensitizer, the cost is an order of magnitude lower [9]. Theoretical calculations are useful in the description of these properties and the design of new sensitizers. Therefore, these studies support an important step toward the optimization of DSSC dyes. In this work, we analyzed the electronic structures and optical properties of the copper-based complexes $[\text{CuL}_2]^+$ (L=6,6'-dimethyl-2,2'-bipyridine-4,4'-bis(propenoic acid)), both in the gas phase and in solution by means of DFT/TD-DFT calculations.

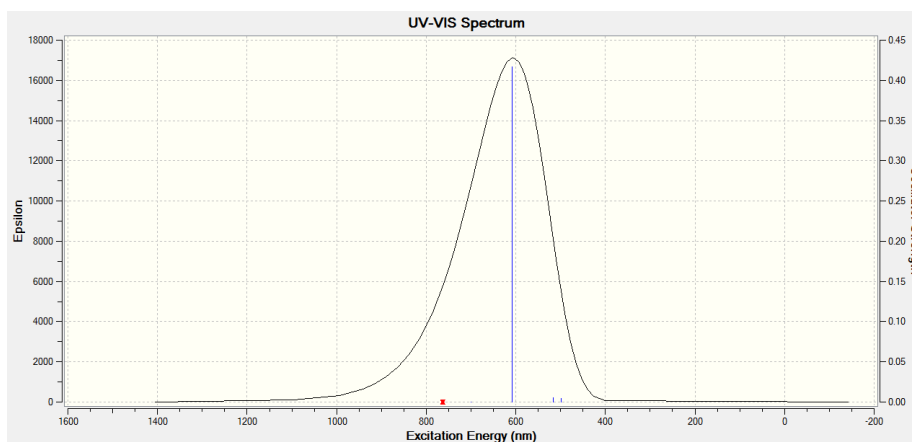
2. Computational method

All calculations were performed with density functional theory (DFT) in the Gaussian 98 program [4]. The B3LYP exchange correlation functional in conjunction with the 6-31G(d) basis sets were employed in the geometrical optimizations of the copper-based dye sensitizer, both in the

gas phase and in acetonitrile solution. The solvent effects were evaluated using the polarizable continuum model (C-PCM). We also made use of the natural bond orbital (NBO) theory to characterize interactions between the copper atom and the bipyridine ligands in the dyes. These calculations were performed using the program packages of NBO5.0 [5].

3. Results and discussion

The TD-DFT-simulated absorption spectra of the Cu-based complexes are shown in Figure 1. The top panel shows the spectra calculated in the gas phase, and the lower panel shows the spectra obtained in acetonitrile solution. The simulated spectrum of the gas-phase $[\text{CuL}_2]^+$ shows one peak at 607.58 nm with the oscillator strength of 0.4167. This peak corresponds to $\text{HOMO} \rightarrow \text{LUMO}$ and $\text{HOMO}-1 \rightarrow \text{LUMO} + 1$. For the $[\text{CuL}_2]^+$ complex in acetonitrile solution calculated using the C-PCM model, the peak of the spectrum appears at 609.16 nm, a 1.58 nm red shift from the gas-phase spectrum. The oscillator strength of the lowest-energy excitation increases from 0.4167 to 0.4203 involving the mixed transitions of $\text{HOMO} \rightarrow \text{LUMO}$ and $\text{HOMO}-1 \rightarrow \text{LUMO}+1$.



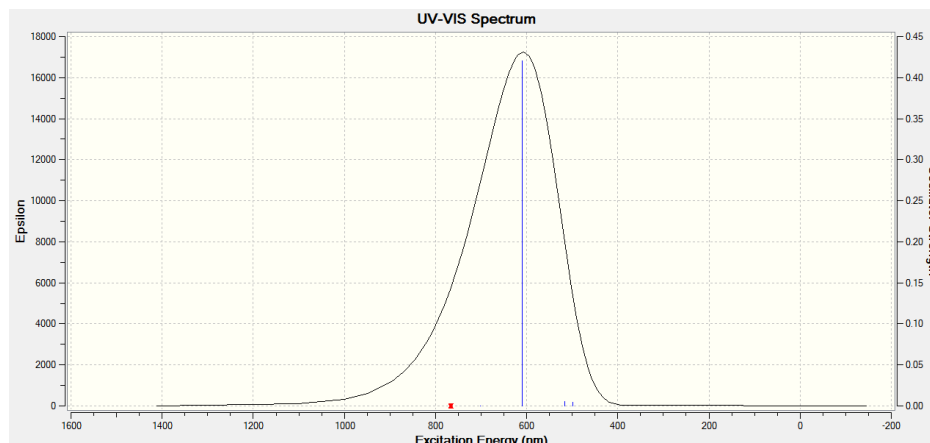


Fig 1. Simulated absorption spectra of $[\text{CuL}_2]^+$ in the gas phase (top) and acetonitrile solution (bottom) at the B3LYP/6-31G(d) levels.

Note that the HOMO-LUMO gap was calculated to be 2.74 eV for the $[\text{CuL}_2]^+$ dye complex in the gas phase. When the water solvent is considered, all of the energies of the MOs in the $[\text{CuL}_2]^+$ dye are shifted upward. Using the form of C-PCM model, the HOMO was calculated to shift from -8.13 to -8.25 eV.

Even though switching from the gas phase to water solution does not change the composition of the Cu 3d orbital contributions. Similarly, the solution also destabilizes the six LUMOs (LUMO to LUMO + 5) of dye .

Conclusions

The molecular geometries, electronic structures, and optical absorption spectra of $[\text{CuL}_2]^+$ dye both in the gas phase and in water solution have been investigated by mean of combined DFT/TD-DFT calculations. The spectra in the range of 350-600 nm originate from metal-to-ligand charge-transfer (MLCT) transitions, whereas the spectra in the range of 350-400

nm are excitations mainly from the metal Cu 3d orbitals to the carboxyl group π^* orbitals. The solvent effect strengthens the short-range interaction by dispersing the repulsive interaction and weakens the long-range interaction by coupling the respective dipole moments of different moieties.

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