

Research Article

Theoretical Study of Copper Complexes: Molecular Structure, Properties, and Its Application to Solar Cells

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We present a theoretical investigation of copper complexes with potential applications as sensitizers for solar cells. The density functional theory (DFT) and time-dependent DFT were utilized, using the M06 hybrid meta-GGA functional with the LANL2DZ (D95V on first row) and DZVP basis sets. This level of calculation was used to find the optimized molecular structure, the absorption spectra, the molecular orbitals energies, and the chemical reactivity parameters that arise from conceptual DFT. Solvent effects have been taken into account by an implicit approach, namely, the polarizable continuum model (PCM), using the nonequilibrium version of the IEF-PCM model.

1. Introduction

A survey of our energy supply options reveals that the sun is the only clean energy source in sufficiently abundant supply to meet global demand, yet less than 0.1% of our energy needs are met through the direct conversion of sunlight [1]. For this reason, considerable attention and extensive research efforts have been devoted over the last years to dye-sensitized solar cells (DSSCs) as valuable and low-cost alternatives to silicon and other inorganic semiconductor-based photovoltaic devices [2–4]. The DSSC devices are composed of a nanocrystalline TiO₂ film adsorbed by organic or inorganic dyes as the sensitizer. When the dye molecule is excited by the absorption of sunlight, an electron is readily injected into the conduction band of TiO₂. The electron is then transported to the external circuit, and the dye molecule is regenerated by redox reaction coupled to ion pair in electrolyte [5].

One of the key components of a DSSC is the sensitizer [6], which is responsible for light absorption and the generation of electric charges [7], thus exerting a significant

influence on the power conversion efficiency (η) [8]. The most common sensitizers are Ru(II) complexes based on 2,2'-bipyridine (bpy) ligands, such as cis-di(thiocyanato) bis(bpy-4,4'-dicarboxylate)ruthenium(II) (N3 [9] and N719 [10]). These complexes have reached over 11% power conversion efficiency [11]; but the rarity and high cost of the Ru may limit their practical usage. Alonso-Vante and coworkers [12] discovered that copper(I) complexes have similar photophysical properties with Ru complexes, indicating that the iterative chemical optimization of common metal complexes sensitizers can be comparable to that of Ru complexes [13]. Copper(I) complexes display a wide variety of excited states and especially photophysical and photochemical processes; particularly, copper(I)-polypyridine complexes exhibit low-lying MLCT transitions that can participate, among others, in electron transfer processes [14]. Copper-based dye sensitizers might be good substitutes to meet the requirements for next-generation DSSC devices. However, only a few studies have reported work on DSSCs coupled with copper-based dye sensitizers [15–18]. In this research, we propose the study of five molecular systems of the type [CuL₂]⁺ with bipyridine

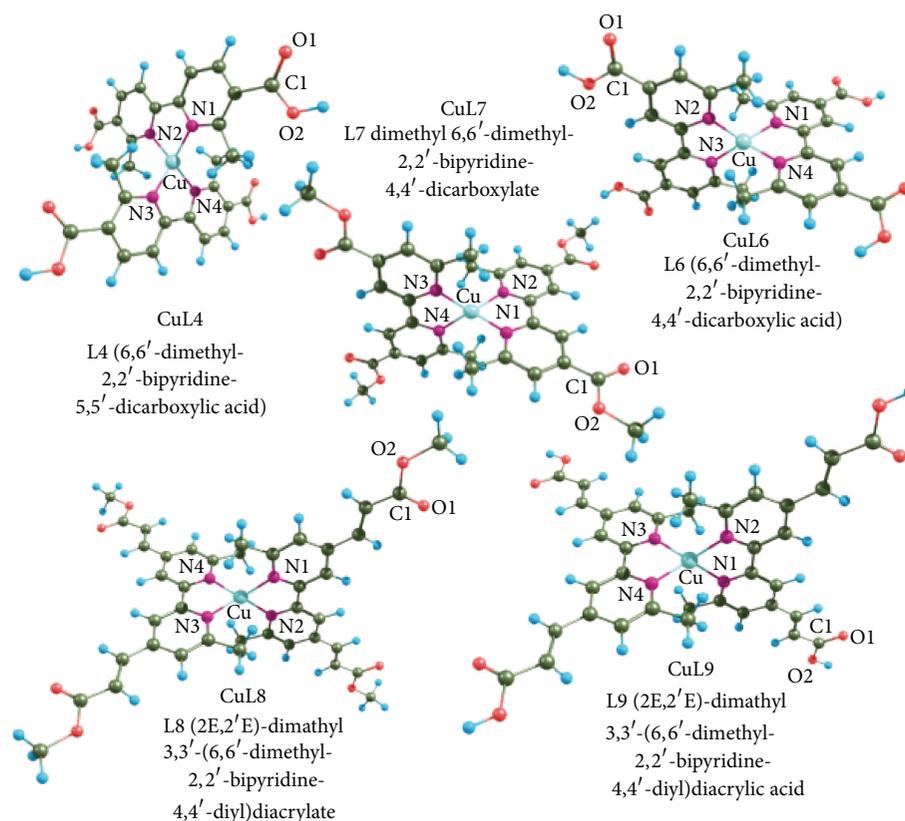


FIGURE 1: Optimized molecular structures of copper complexes in solution at the M06/LANL2DZ + DZVP level of theory.

ligands; in order to calculate from the theoretical point of view their geometric and spectroscopic properties, as well as chemical reactivity.

2. Molecular Modeling

Molecular calculations were carried out with density functional theory (DFT) [19–21] and time-dependent (TD) DFT [22–24] in the Gaussian09 program [25]. The hybrid-meta-GGA functional considered in this study is the M06 [26] due to the ability to study properties of organometallic compounds; our group has done a preliminary study [27]. The LANL2DZ (D95V on first row) for C, H, O, and N atoms [28] and DZVP for Cu atom [29] basis sets were used for the geometrical optimizations, as well as electrical and optical properties of all of the copper-based dye sensitizers considered, both in the gas phase and in solution. Ultraviolet-visible spectra (UV-Vis) have been simulated using the TD-DFT approach and analyzed through the SWizard program [30, 31], through pseudo-Voigt band shape with relative weight of Gaussian functions; solvent effects have been taken into account by an implicit approach, namely, the polarizable continuum model (PCM) [32] using the nonequilibrium version of the IEF-PCM model [33]; the equations were solved for 20 excited states.

Using the DFT framework makes it possible to find the chemical reactivity descriptors values, such as electron affinity (A), ionization potential (I), electronegativity (χ), hardness (η), and electrophilic index (ω); all these values were obtained using system energy calculations. The electronegativity, hardness, and electrophilic index are defined as

$$\begin{aligned}\chi &= -\frac{(I + A)}{2}, \\ \eta &= \frac{(I - A)}{2}, \\ \omega &= \frac{\mu^2}{2\eta},\end{aligned}\quad (1)$$

where μ denotes the chemical potential and is calculated as $-\chi$.

3. Results and Discussion

Optimized molecular structures of copper complexes in the presence of solvent are shown in Figure 1. A selection of geometric parameters of these five molecules is listed in Table 1 (for more details, see supplementary material available online at <http://dx.doi.org/10.1155/2013/613064>). The molecular structures in gas phase and in solution are

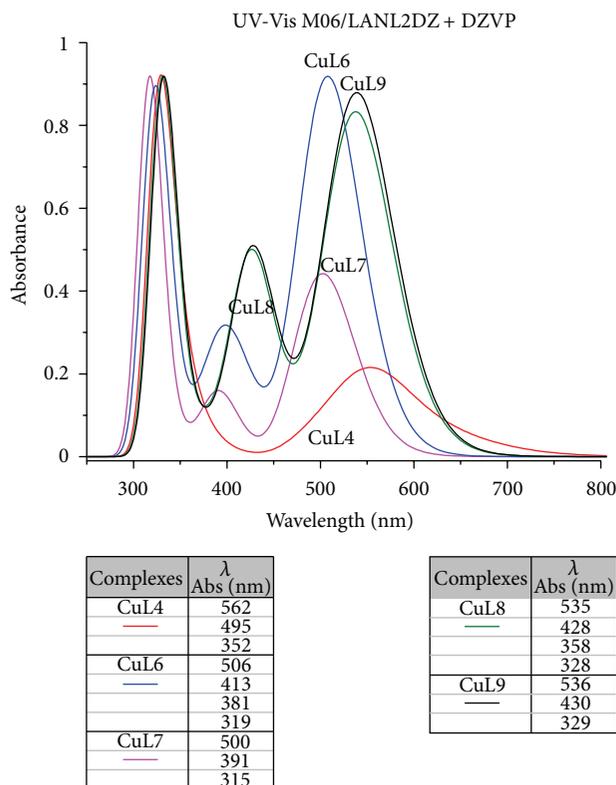


FIGURE 2: Ultraviolet-visible (UV-Vis) spectra of copper complexes analyzed in this study.

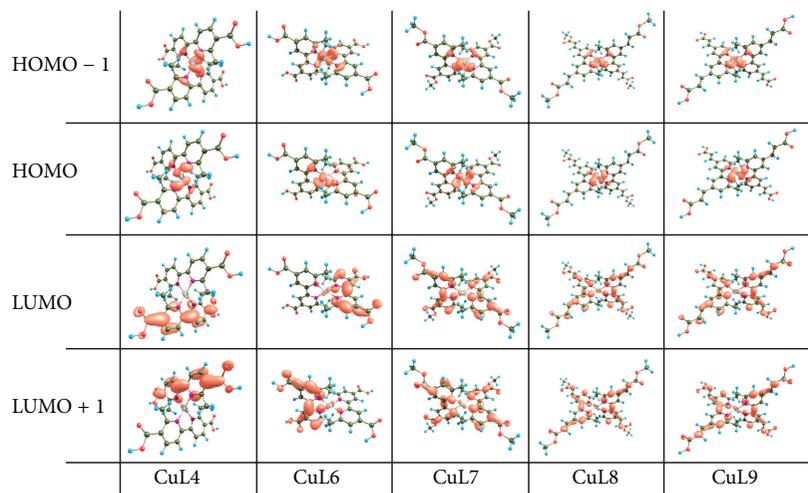


FIGURE 3: Molecular orbitals for Cu complexes calculated at the M06/LANL2DZ + DZVP level of theory.

qualitatively similar; however, the greatest change is observed in bond angles and dihedral angles. The 5,5' position of the carboxylic acid on the bipyridine ligands for CuL4 copper complex favors the increase of distance between the copper atom and the nitrogen atoms with respect to 4,4' positions of the other complexes, because of the position of the acceptor. Substitution of the carboxylic acid with methyl ester groups do not change radically the distance of the metal center to the ligand.

Absorption spectra for the proposed copper complexes are shown in Figure 2. These spectra were performed in the presence of solvent, under the same optimization conditions. The calculated value of the absorption wavelength (λ) is an important parameter, which indicates that these molecular systems should be considered for use as a functional material (as dye in this case) in a DSSC, the value of this parameter meets the requirement of the absorption property whose wavelength of maximum absorption (λ_{\max}) should not be

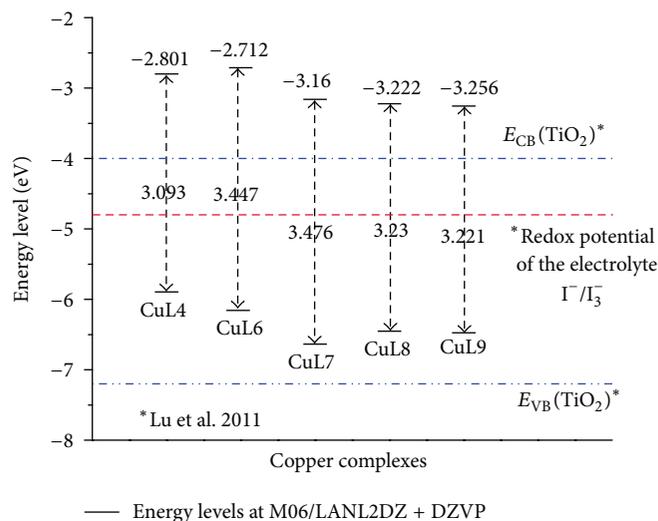


FIGURE 4: Molecular orbitals energy levels diagram.

greater than 920 nm as established in the literature [34]. All studied sensitizers reach their λ_{\max} above 500 nm, the largest value corresponds to the CuL4 sensitizer with 562 nm.

Table 2 shows the results of TD-DFT calculations performed using the M06 functional and the LANL2DZ+DZVP basis sets; including the corresponding wavelengths (in nm), the energies (in eV), the oscillator strength (f), and the orbitals involved in the transitions. This information shows that the peak of the wavelength of maximum absorption is due to charge transfer between the metal atom and the ligand molecule, which may be explained more clearly in Figure 3. The excitation contains a mixture of HOMO \rightarrow LUMO, HOMO - 1 \rightarrow LUMO, and HOMO - 1 \rightarrow LUMO + 1, this leads to consider them as degenerate orbitals.

The charge transfer efficiency from the sensitizer to the nanocrystalline oxide is extremely important in the solar cell design. Since the crucial electronic excitations occur from the highest occupied molecular orbitals (HOMO) to the lowest unoccupied molecular orbitals (LUMO), it is, therefore, important to form efficient charge-separated states with the HOMO localized on the donor subunit and the LUMO on the acceptor subunit. Figure 3 shows as the HOMO orbital density is located over around the copper atom in complexes; meanwhile, the density of the LUMO orbital is in the ligand, tending to move toward the carboxyl acid and methyl ester groups. This is beneficial in accordance with the above mentioned.

Figure 4 shows the HOMO-LUMO molecular orbitals' energetic position. These results are of great importance, since they can be used during synthesis to determine the solubility and chemical reactivity of the molecule, as reported in different studies [35, 36]. Additional factors to consider is the sensitizer LUMO level that is greater than the conduction band level of nanocrystalline oxides that are commonly used in such devices, also the HOMO level can be observed below the redox potential of the electrolyte [37]; both considerations

are important to the design of the sensitizer. The CuL4 complex has the smaller energy gap (3.093 eV); however, the values for the other complexes studied are close to this. Molecular orbitals energy levels were calculated in the presence of solvent.

Chemical reactivity parameters such as ionization potential (I), electron affinity (A), electronegativity (χ), chemical hardness (η), and electrophilicity index (ω) for the studied molecular systems (Table 3) were obtained by energy calculations (neutral and ionic state), taking into account the ground state geometry optimization.

According to Table 3, complexes with carboxylic acid as anchor groups exhibit greater electron affinity, electronegativity, and electrophilicity index than those containing methyl ester groups. The trend in ionization potential for the copper complexes is CuL8 < CuL9 < CuL7 < CuL4 < CuL6. The results indicate that CuL6 and CuL7 copper complexes are harder than the rest of the systems studied; this can be interpreted as systems with greater resistance to change with the number of electrons.

4. Conclusions

In this work, the molecular structure and properties of five molecular systems proposed as sensitizers in dye-sensitized solar cells have been calculated. The applied methodology for this study is based on the density functional theory, using the M06 hybrid meta-GGA functional and the LANL2DZ and DZVP basis sets.

The molecular systems characterization includes the calculation of geometric parameters, ultraviolet-visible spectra, electronic excited states, molecular orbitals, and chemical reactivity parameters. The longer wavelength of maximum absorption and the smallest energy gap is for the CuL4 complex. For all cases, the HOMO orbital density is located over around the copper atom; meanwhile, the density of

TABLE 1: Selected bond lengths (angstroms), bond angles, and dihedral angles (degrees) for copper complexes.

Parameter	Gas phase					In presence of solvent				
	CuL4	CuL6	CuL7	CuL8	CuL9	CuL4 ^a	CuL6 ^a	CuL7 ^b	CuL8 ^b	CuL9 ^b
Cu-N1	2.0459	2.0310	2.0318	2.0321	2.0320	2.0445	2.0250	2.0289	2.0299	2.0300
Cu-N2	2.0493	2.0282	2.0318	2.0321	2.0320	2.0364	2.0274	2.0290	2.0300	2.0301
Cu-N3	2.0475	2.0332	2.0318	2.0321	2.0320	2.0427	2.0243	2.0289	2.0300	2.0301
Cu-N4	2.0481	2.0284	2.0318	2.0321	2.0320	2.0386	2.0261	2.0289	2.0299	2.0300
Cl-O1	1.2342	1.2314	1.2355	1.2383	1.2359	1.2468	1.2444	1.2408	1.2446	1.2453
Cl-O2	1.3691	1.3675	1.3586	1.3647	1.3706	1.3509	1.3502	1.3555	1.3649	1.3636
N1-Cu-N2	81.67	81.87	81.92	81.56	81.58	81.87	81.85	81.97	81.72	81.77
N1-Cu-N3	129.67	124.35	124.78	124.99	124.98	127.57	125.02	125.37	125.56	125.53
N3-Cu-N4	81.47	81.80	81.91	81.56	81.58	81.87	81.93	81.97	81.72	81.77
N2-Cu-N4	129.16	124.99	124.78	124.99	124.98	132.13	125.26	125.37	125.56	125.53
N1-N2-N3-N4	-73.96	-81.11	-80.87	-80.97	-80.97	-73.13	-81.47	-79.85	-79.85	-79.84

^aMeOH solution, ^bChloroform solution.

TABLE 2: Copper complexes electronic excited states, showing wavelengths (nm), energies (eV), oscillator strength (f), and the orbitals involved in the transitions. Only excited states with $f > 0.02$ are shown.

Copper complex	λ (nm)	E (eV)	f	Assignment; H = HOMO, L = LUMO, and $L + 1 = \text{LUMO} + 1$
CuL4	562	2.21	0.048	H-1 \rightarrow L (61%) H \rightarrow L (26%) H-1 \rightarrow L + 1 (10%)
	495	2.51	0.026	H-1 \rightarrow L + 1 (75%) H \rightarrow L + 1 (17%)
	352	3.52	0.057	H-1 \rightarrow L + 3 (51%) H \rightarrow L + 3 (29%) H-1 \rightarrow L + 4 (11%) H \rightarrow L + 4 (7%)
CuL6	505	2.45	0.243	H \rightarrow L (66%) H-1 \rightarrow L + 1 (29%)
	413	3.00	0.030	H \rightarrow L + 2 (54%) H-2 \rightarrow L (21%) H-1 \rightarrow L + 2 (16%) H \rightarrow L + 3 (6%)
	381	3.25	0.028	H-1 \rightarrow L + 3 (78%) H-2 \rightarrow L + 1 (7%) H-3 \rightarrow L (7%)
	319	3.89	0.092	H-4 \rightarrow L (52%) H-3 \rightarrow L (21%) H-6 \rightarrow L (18%)
CuL7	500	2.48	0.267	H-1 \rightarrow L + 1 (+52%) H \rightarrow L (+47%)
	391	3.17	0.045	H \rightarrow L + 3 (65%) H-1 \rightarrow L + 2 (32%)
	315	3.94	0.285	H-4 \rightarrow L + 1 (46%) H-6 \rightarrow L (43%)
CuL8	535	2.32	0.391	H-1 \rightarrow L + 1 (52%) H \rightarrow L (45%)
	428	2.90	0.112	H \rightarrow L + 3 (60%) H-1 \rightarrow L + 2 (37%)
	358	3.46	0.025	H-1 \rightarrow L + 4 (56%) H \rightarrow L + 5 (40%)
	328	3.78	0.303	H-5 \rightarrow L (47%) H-6 \rightarrow L + 1 (40%) H-7 \rightarrow L (5%)
CuL9	536	2.31	0.376	H-1 \rightarrow L + 1 (52%) H \rightarrow L (45%)
	430	2.88	0.102	H \rightarrow L + 3 (61%) H-1 \rightarrow L + 2 (37%)
	329	3.77	0.280	H-5 \rightarrow L (48%) H-6 \rightarrow L + 1 (39%)

TABLE 3: Chemical reactivity parameters using DFT descriptors.

Copper complex	Chemical reactivity descriptors (eV)				
	I	A	χ	η	ω
CuL4	9.79	4.47	7.13	2.66	9.55
CuL6	10.15	4.53	7.34	2.81	9.58
CuL7	9.74	4.13	6.94	2.80	8.58
CuL8	9.35	4.26	6.80	2.54	9.10
CuL9	9.57	4.44	7.01	2.56	9.58

the LUMO orbital is in the ligand. Moreover, the molecular orbitals levels are appropriate considering the position of the conduction band of nanocrystalline oxides and the redox

potential of the electrolyte. Analyzing these data makes it possible to find potential applications for these copper complexes in photovoltaic devices.

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