

Application of Cu (I) Complexes as Sensitizers for Solar Cells: A Conceptual DFT Study

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Abstract

The molecular geometry, electronic structure, energetics and some important chemical parameters of heteroleptic Cu(I) based complexes with thiophene functionalised bipyridyl and dimethyl phenanthroline ligands are studied theoretically for application as sensitizers in solar cells. Within the framework of first-principles density functional theory (DFT) using B3LYP exchange correlation functional and 6-311G+(d,p) basis set. the optimized geometries, the molecular orbitals energetics, absorption spectra and various parameters of chemical reactivity arising from conceptual DFT are determined. These results may be helpful for synthesis of new efficient sensitizers.

Keywords

Dye sensitized solar cells, Sensitising Dyes, Conceptual DFT

Introduction

Design of dye sensitizers with cost-effective, safe, and more sustainable materials for photovoltaic devices is an active research area. Designing and synthesising new sensitizer molecules for DSSCs requires an understanding of the relationship between their structure, properties and performance. In this context the theoretical studies using density functional theory (DFT) play an important role to evaluate photo physical and photochemical properties of dye-sensitizers. Ruthenium (II) complexes have been theoretically investigated as sensitizers and have been reported to have strong absorption in the visible range and relatively long-lived excited states. However, ruthenium being an expensive, toxic and scarce metal cannot be used for commercial scale production of DSSCs. This necessitates the search for novel dyes using environmental-friendly, inexpensive and abundantly available metal for next-generation DSSCs. Sauvage and co-workers showed that Cu(I) complexes have similar photo-physical properties as that of ruthenium complexes. Hence the iterative chemical optimization of its complexes may lead to sensitizers comparable to that of ruthenium complexes. However, literature reveals very limited investigations on DSSCs coupled with copper-based dye sensitizers.

The present work reports theoretical investigation of two heteroleptic bipyridyl Cu(I) based complexes - **complex (1)** with 6,6'-dimethyl-2,2'-bipyridine-4,4'-dicarboxylic acid as anchoring ligand and thiophene functionalised 2,9-dimethyl-1,10-phenanthroline ligands as ancillary ligand and **complex (2)** with 6,6'-dimethyl-2,2'-bipyridine-4,4'-diacrylic acid as anchoring ligand and thiophene functionalised 6,6'-dimethyl-2,2'-bipyridine as ancillary ligands. A detailed analysis of the ground state molecular geometries and electronic structure is presented using first principles DFT. The chemical reactivity parameters such as the electronegativity, chemical potential, chemical hardness and chemical softness of these complexes in their neutral and charged states are determined with the help of Conceptual DFT. These results may be valuable to determine the solubility and stability of the molecule,

Theory

Conceptual DFT helps to calculate the chemical properties of atomic and molecular systems by providing sharp definitions of a number of reactivity descriptors for these systems. It provides a theoretical basis for important qualitative chemical descriptors like electron affinity (A), ionization potential (I), electronegativity (χ), chemical hardness (η), and electrophilicity index (ω). Some of these chemical reactivity parameters may be defined as

$$\text{Electronegativity } \chi = -\mu = -\frac{(I + A)}{2} \text{ where } I = \text{ionisation potential and } A = \text{electron affinity}$$

$$\text{Chemical hardness } \eta = \frac{(I - A)}{2}$$

$$\text{Chemical softness } S = 1/2\eta$$

$$\text{and Global electrophilicity index } \omega = \frac{\mu^2}{2\eta}$$

Computational Details

All calculations are performed by using the Gaussian 09 software package. Geometry optimisations of both complexes are performed at the 6-311G+(d, p) level by using the B3LYP functional in gas phase. Chemical reactivity descriptors like electron affinity (A), ionization potential (I), electronegativity (χ), chemical hardness (η), and electrophilicity index (ω) for the studied dyes are determined by energy calculations of optimised ground state geometry in neutral and ionic state.

Results and Discussion

Molecular Geometries

Figure 1 represents the optimized molecular structures of copper(I) sensitizing dyes in the gas phase. The optimized parameters of the molecular structure (Table 1) show a very small structural variation of bond lengths and bond angles from those reported in literature. Cu-N (bpy) bond lengths are in the range of 2.084 -2.088 Å and the bite-angles N1-Cu-N2 and N3-Cu-N4 are 80.12° and 80.81°. These values are very close to the typical ranges of 2.003 Å to 2.039 Å and 80.93° to 81.21°, which were reported by T. Bessho *et al.* A slight fluctuation in Cu-N₃ and Cu-N₄ (2.097 Å) in complex (2) indicates that increasing δ -conjugation on ancillary ligands weakens the interaction between the Cu(I) centre and N atoms in bipyridyl ligands resulting in elongation of their bond lengths to some extent.

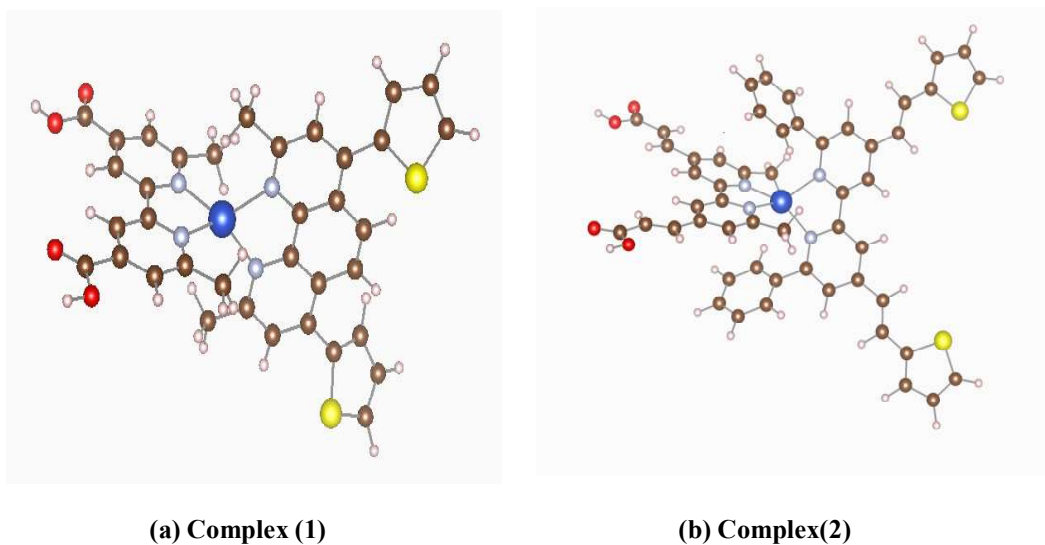


Figure 1 : Optimized geometries of Cu(I) complexes (a)complex 1 with L=(6,6'-dimethyl-2,2'-bipyridine-4,4'-dicarboxylic acid and L'= thiophene functionalised 2,9-dimethyl-1,10-phenanthroline ligands] and **complex (2)** with L= 6,6'-dimethyl-2,2'-bipyridine-4,4'-diacrylic acid and L'=thiophene functionalised 6,6'-dimesityl-2,2'-bipyridyl ligands] in gas phase.

Table 1: Selected bond lengths (angstroms), bond angles, and dihedral angles (degrees) for copper (I) dyes.

Parameter	Complex 1	Complex 2
Cu-N1	2.08622	2.08835
Cu-N2	2.08461	2.08878
Cu-N3	2.07832	2.09747
Cu-N4	2.07584	2.09740
C-S1	1.75160	1.75433
C-S2	1.75306	1.75434
N1-Cu-N2	80.121	80.198
N2-Cu-N3	126.006	119.417
N3-Cu-N4	80.811	80.931
N1-Cu-N4	125.818	119.627
C-S1-C	91.761	91.542
C-S2-C	91.724	91.541
N1-N2-N3-N4	81.680	70.850

Molecular Orbitals and Electronic Structure

The frontier molecular orbitals of both dyes are represented in Figure 2 in which the HOMO electron density is localised on copper atom, while that of LUMO orbital is localised in the bpy ligand and tends to move toward the carboxyl groups. The band gap is 2.925 eV and 2.654 eV for complex 1 and complex 2 respectively, which is an appropriate value for its consideration as a potential sensitizer for photovoltaic devices. Table 2 lists the calculated oscillator strengths, HOMO and LUMO Energies, HOMO-LUMO Gaps, Lowest Vertical Excitation Energies (EA) for the most characteristic transitions for both Cu(I) Dyes.

Table 2. The HOMO and LUMO Energies, HOMO-LUMO Gaps, Lowest Vertical Excitation Energies (EA), and Oscillator Strengths (f) for Cu(I) Dyes

Copper (I) dye	HOMO (eV)	LUMO (eV)	Bangap HOMO-LUMO (eV)	EA (eV)	F
Complex (1)	8.196	5.271	2.925	2.4117	0.2344
Complex (2)	7.677	5.023	2.654	2.2275	0.1940

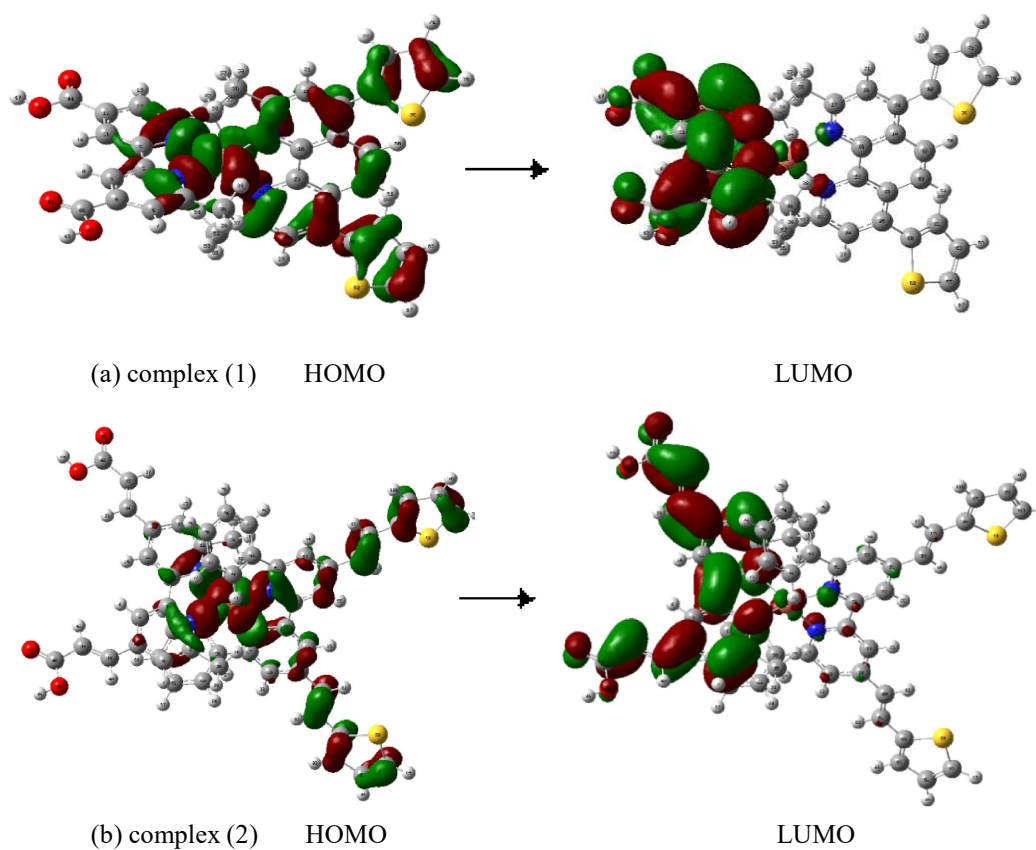


Figure 2. The frontier molecular orbitals of (a) complex (1) and (b) complex (2) calculated at the B3LYP/6-311G level in gas phase.

Ionisation potential, electron affinity and global reactivity descriptors

Table 3 gives values of the ionisation potential and the electron affinity, both vertical and adiabatic, as calculated for each both complexes. For both the complexes the adiabatic ionisation potential has lower value than that of the vertical ionisation potential. However, the adiabatic EA is greater than the corresponding vertical electron affinity. These results are in agreement with the basic principle that relaxation stabilises the molecules.

Table 3: Chemical reactivity parameters using Conceptual DFT descriptors.

η	Copper (I) Dye ω	Chemical reactivity descriptors (eV)				$\chi - \mu$	S	
		Ionisation Potential (eV)		Electron affinity (eV)				
		Vertical	Adiabatic	Vertical	Adiabatic			
Complex (1) 8.621		9.205	8.977	4.084	4.220	6.645	0.195	2.561
Complex (2) 9.139		8.529	8.355	4.139	4.212	6.334	0.228	2.195

The reactivity of the molecule can be quantitatively analysed from reactivity descriptors (Table 3) which can be calculated from the vertical ionisation potential and electron affinity. Hardness ($5\theta\beta$) provides a measure of the stability of a molecule, and softness provides a measure of its reactivity. The $5\theta\beta$ value for both the complexes (Table3) indicate that these dyes are quite stable.

Conclusion

This work presents a preliminary studies to explore the application of heteroleptic Cu(I) complexes with thiophene functionalised ancillary ligand as light harvesters in dye-sensitized solar cells. A detailed first-principles density functional theory calculation of the structures and energetics are presented. Ionisation potentials and electron affinities (both the vertical and adiabatic), as well as other chemical properties of two Cu(I) complexes are calculated. The results of this work suggest that these complexes are quite stable and have a band gap value suitable for their use as sensitizers.

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