

A theoretical investigation of the photo-induced intramolecular charge transfer excitation of cuprous (I) bis-phenanthroline by density functional theory

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Abstract

This work reported an investigation on the excited state and electronic transfer excitation of cuprous (I) bis-phenanthroline complex by density functional theory. The intramolecular charge transfer from central metal to ligand (MLCT) during the excitation was observed. The transfer direction and degree were discussed on the basis of analyzing the Mulliken charge. The structural distortion caused by the charge transfer in the excited state was confirmed. The excited state was found having the characters similar with Cu(II) complex both in electronic and geometrical properties. The large structural distortion found between ground state and excited state could lead to a decrease in the lifetime of excited state as well as a non-radiative decay. The excitation energies and oscillator strengths of cuprous (I) bis-phenanthroline were derived using time-dependent density functional method. The values of excitation energies are good agreement with the results of the experimental measuring.

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1. Introduction

Photochemical conversion of solar energy, which is an inexpensive and renewable energy source, to produce environmentally clean fuels, is an important and active research area because of the serious energy crisis caused by a sharp increase in the need of fuels and decrease in the supply of resources [1–6]. The processes of conversion and storage of solar energy are the transform of the abundant and low-cost raw materials like H₂O, CO₂, and N₂ into fuels like H₂, CH₃OH, CH₄, and

NH₃. However, the raw materials to be converted into a fuel usually cannot be electronically excited directly by visible light. For instance, water produces the electronic absorption at 167 nm in the far ultraviolet region [7,8]. Thus, the conversion must be intermediated by a suitable photosensitive compound that is called as photosensitizer. In the solar energy conversion and storage, the photosensitizer captures solar energy and is converted to an electronically excited state that is a better oxidant or reductant than the ground state. The photo-induced electron transfer (ET) and charge separation could occur at this process. Such photo-induced electron movement will cause nuclear movements in order to adapt the electron density redistribution in molecules, leading to molecular structural changes, or reorganization. Based on the well understanding of the nature for the charge separation and a particular nuclear

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movement that assists the charge separation, we can rationally design and identify photosensitive materials with high efficiency for solar energy conversion as well as other potential applications.

The classic example of photosensitizers is $\text{Ru}(\text{bpy})_3^{2+}$ where bpy is 2,2'-bipyridine. It is the most well studied coordination complex in history with numerous papers being published [9–12]. It has highly desirable properties as photosensitizer including high quantum yield with the forming of excited state, microsecond lifetimes, intense visible absorption and emission, and well-defined redox chemistry. However, the application of Ru(II)-based photosensitizer has been largely limited due to the problem of high costs and environmental pollution. For some other alternatives, such as Re(I) and Os(II)-based complexes, have the same inherent drawbacks. It is therefore worthwhile to design and develop new photosensitive materials that circumvent these difficulties. Recently, the Cu(I) coordination complexes is emerging as an attractive alternative [13–16]. Copper is less toxic, less expensive, and less environmentally hazardous than ruthenium. In fact, Cu(I) complexes with diimines ligands, have outstanding excited state properties that are comparable to $\text{Ru}(\text{bpy})_3^{2+}$. They generally absorb UV–Vis light over the range of 350–650 nm with relatively high extinction coefficients ($\sim 10^3$ – $10^4 \text{ M}^{-1} \text{ cm}^{-1}$). With phenanthroline ligands (as illustrated by the skeleton structure in Fig. 1) that possess alkyl in the 2- and 9-positions, the MLCT excited states are emissive with the lifetimes of 10^{-9} – 10^{-7} s at room temperature in CH_2Cl_2 solution [17–19]. Furthermore, it has been found that the substituents in the 2- and 9-positions could influence the lifetime of the excited state and then the efficiency of solar energy conversion very much. Therefore, a theoretical investigation of the influence of different substituents on the properties of excited state, electronic redistribution, and structural distortion during the excitations is important, which allows deep understanding of the mechanism and efficiency improvement of solar energy conversion for these cuprous complexes. It is

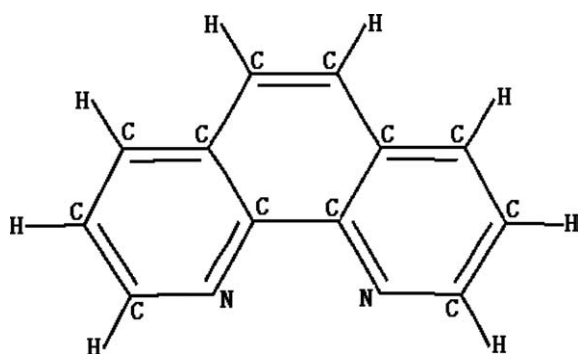


Fig. 1. The skeleton structure of phenanthroline (phen).

noted that the theoretical insights to these important applications are barely reported up to date.

As the beginning of the series researches, in this paper the properties of excited state and electronic transition excitation of the complex cuprous (I) bis-phenanthroline was investigated. The principal purpose of this work is to determine the structural changes and charge transfer processes that occur in the complex of cuprous (I) bis-phenanthroline ($\text{Cu}(\text{phen})_2^+$) upon oxidation to copper (II), $\text{Cu}(\text{phen})_2^{2+}$, and relate these changes to the MLCT excited state of $\text{Cu}(\text{phen})_2^+$. The data will be used as the comparison with the other complexes with the different substituents in 2- and 9-position in the future research. The stable geometry of $\text{Cu}(\text{phen})_2^+$, the excited states of $\text{Cu}(\text{phen})_2^+$, and $\text{Cu}(\text{phen})_2^{2+}$ are obtained by optimizing the total energy to the minimum using the density functional theory (DFT). The charge transfer direction and degree during excitation are discussed on the basis of analyzing the Mulliken population both in ground state and excited state. The electronic excitation energies and oscillator strengths of $\text{Cu}(\text{phen})_2^+$ are derived by time-dependent density functional theory (TDDFT).

2. Computational details

All calculations in this investigation have been performed using density functional theory by using Gaussian 98 (G98) and Amsterdam density functional program package (ADF2000) [20,21]. In the case of G98, a mixture of Hartree–Fock and DFT along with a Becke three-parameter hybrid functional of Lee, Yang and Parr (B3LYP) was used as the exchange and correlation functional [22]. The standard LANL2DZ basis sets were applied to all atoms [23]. In the case of ADF, the Perdew and Wang’s 1991 exchange and correlation functional (PW91XC) was used at the generalized gradient approximation (GGA) [24], and the basis sets of triple- ξ STO were applied to the valence electrons of all atoms. The inner electrons within the atomic shells (i.e. 1s for C, H, and N, 2p for Cu) were handled as a frozen-core approximation. The relativistic terms were calibrated by a combined scalar relativistic zero-order regular approximation (ZORA) [25]. The vertical excitation energies and oscillator strengths of low-lying singlet and singlet excitation states were derived by TDDFT [26], in which the diffuse basis sets were added to hydrogen, carbon, and nitrogen [27]. The geometry and electronic properties of excited states were obtained by differential self-consistent-field density functional theory ($\Delta\text{SCF-DFT}$). The relative bond lengths and angles in the two phenanthroline ligands (phen) were fixed during optimization. The pictures of the molecular orbitals and optimized structures were illustrated using a MOLEKEL 4.1 molecular visualization program [28].

3. Results and discussion

The optimized structure of $\text{Cu}(\text{phen})_2^+$ (phen = 1,10-phenanthroline) in ground state was obtained and depicted in Fig. 2. It shows a four-coordinated tetrahedral structure. Several selected bond lengths and bond angles obtained by G98 and ADF2000 methods were listed in Table 1 together with the experimental values. It is clear that the consistent geometries were derived by two methods. ADF method could well reproduce experimental data. The structure of corresponding Cu(II) complex, $\text{Cu}(\text{phen})_2^{2+}$, was optimized using the same computational conditions of ADF and the optimized result was shown in Fig. 3. It can be found that the geometrical structures of these cuprous complexes largely depend on the charge of central copper. The complexes of copper(I) and copper(II) own different structures. Although the distances between copper and the ligands in two complexes are not changed so much (Table 1), there are large variation for the relative direction of two phen ligands. By losing one electron from Cu^+ to become Cu^{2+} , the structures change from a tetrahedral of $\text{Cu}(\text{phen})_2^+$ to flatten toward a nearly planar structure of complex $\text{Cu}(\text{phen})_2^{2+}$. It matches with the coordination rule of cuprous complexes [29]. The electronic configuration of Cu(I) is d^{10} and it generally prefers to be four-coordinate with a tetrahedral geometry, while

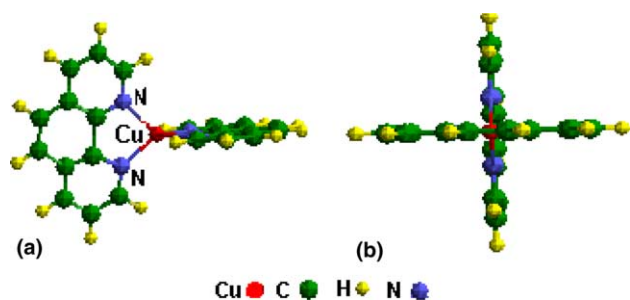


Fig. 2. The optimized structure of $\text{Cu}(\text{phen})_2^+$. Figures (a) and (b) display the structures viewed from the different directions.

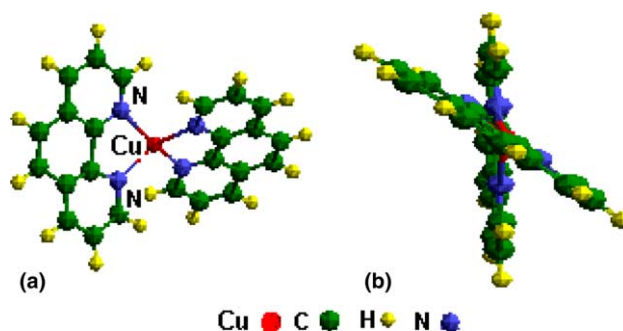


Fig. 3. The optimized structure of $\text{Cu}(\text{phen})_2^{2+}$. Figures (a) and (b) display the structures viewed from the different directions.

$\text{Cu}(\text{II})$ is d^9 and it adopts a Jahn-Teller distorted geometry that is usually 5- or 6-coordinate [30]. The relative direction of two phen ligands is changed in order to adapt the geometries of tetrahedral structure in Cu(I) complex and planar structure in Cu(II) complex. When the complex absorbs the light energy, the electrons are promoted to the higher energy levels to form the excited states. The optimization of the first excited state was performed by promoting the electrons from the HOMO to the LUMO orbitals using ADF method. The structure obtained was listed in Fig. 4. It is found that the

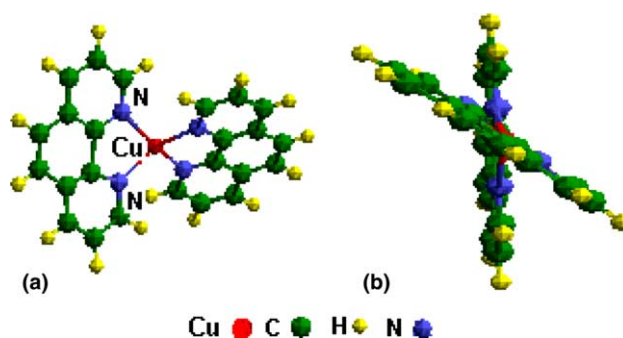


Fig. 4. The optimized structure of the excited state of $\text{Cu}(\text{phen})_2^+$. Figures (a) and (b) display the structures viewed from the different directions.

Table 1

The data of geometrical structure in the complexes $\text{Cu}(\text{phen})_2^+$, the excited state of $\text{Cu}(\text{phen})_2^+$, and $\text{Cu}(\text{phen})_2^{2+}$

Method:	G98	ADF			Expt. ^a
Molecule:	$\text{Cu}(\text{phen})_2^+$	$\text{Cu}(\text{phen})_2^+$	$\text{Cu}(\text{phen})_2^+$ -excited state	$\text{Cu}(\text{phen})_2^{2+}$	
Cu–N1	2.08	2.03	2.00	2.04	2.02
Cu–N2	2.08	2.04	2.02	2.04	2.04
Cu–N3	2.08	2.03	2.00	2.04	2.02
Cu–N4	2.08	2.07	2.04	2.07	2.05
N1–Cu–N2	82.1	85.9	87.2	85.7	81.7
N2–Cu–N3	124.7	126.4	101.1	101.7	128.4
N3–Cu–N4	82.1	85.0	86.8	84.9	82.2
N4–Cu–N1	124.6	120.9	99.6	96.7	122.9
Torsional (phen1–phen2)	90.0	92.1	43.7	35.5	

^a The experimental data coming from [31].

structure of excited state of $\text{Cu}(\text{phen})_2^+$ is very similar to that of $\text{Cu}(\text{phen})_2^{2+}$. This structure of the excited state $\text{Cu}(\text{phen})_2^+$ has less steric energy barrier for the further conversion to form $\text{Cu}(\text{phen})_2^{2+}$. Oppositely, there is a large structural distort in the excited process from $\text{Cu}(\text{I})$ complex to its excited state. According to the energy gap law [31], we have known that the large structural distortion between the ground and excited state equilibrium geometries, may increase the amount of vibrational overlap between ground state and excited states, leading to large non-radiative decay rate constants and thus decrease the lifetime of excited state. This is the one of reasons that the cuprous (I) bis-phenanthroline is non-emissive with a short excited state lifetime.

The composition of orbitals for $\text{Cu}(\text{phen})_2^+$ were analyzed and the data of several selected orbitals were listed in Table 2. The orbitals of HOMO and near HOMO (HOMOs) are mainly made up of the d orbitals of central copper. The sets of LUMOs are mainly made up of the ligands. It can be seen clearly from the pictures of the HOMO and LUMO orbitals, which are illustrated in Fig. 5, that the HOMO are degenerate orbitals, and are mainly made up of dxz and dyz of metal. The LUMO is made up of π orbital in one of the ligands. For the purpose of comparison, the compositions of HOMO and LUMO orbitals obtained for the complex $\text{Cu}(\text{phen})_2^{2+}$ and the excited state of $\text{Cu}(\text{phen})_2^+$ were listed in Table 3. Obviously, the compositions are different for $\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ complexes. The HOMO orbital contains a large fraction of ligands in $\text{Cu}(\text{phen})_2^+$ and the fraction of metal is only 25.3%, unlike in the complex $\text{Cu}(\text{phen})_2^{2+}$ whose HOMO is nearly made up of pure metal (72.4%). Another noticeable fact is that the compositions of HOMO and LUMO orbitals in the excited state of $\text{Cu}(\text{phen})_2^+$ are different from its parent

Table 3

Compositions of HOMO and LUMO orbitals in the complexes $\text{Cu}(\text{phen})_2^+$, the excited state of $\text{Cu}(\text{phen})_2^+$, and $\text{Cu}(\text{phen})_2^{2+}$ by ADF method

	$\text{Cu}(\text{phen})_2^+$	$\text{Cu}(\text{phen})_2^+$ -excited state	$\text{Cu}(\text{phen})_2^{2+}$
HOMO			
Cu	72.4	31.97	25.27
phen1	13.19	46.52	53.86
phen2	1.08	8.48	7.64
LUMO			
Cu	3.28	2.51	2.33
phen1	85.57	27.44	44.20
phen2	0	56.72	45.41

complex $\text{Cu}(\text{phen})_2^+$. The HOMO of $\text{Cu}(\text{phen})_2^+$ excited state is a mixture of metal and ligands and LUMO is made up of two ligands. In fact the compositions of the excited state both in HOMO and LUMO are much closer to those of $\text{Cu}(\text{II})$ complex than to its parent $\text{Cu}(\text{I})$ complex. It proves that the characters of the excited state are more approaching to the properties of $\text{Cu}(\text{phen})_2^{2+}$.

Fig. 6 illustrated the energy levels of $\text{Cu}(\text{phen})_2^{2+}$ in ground state, in which the compositions of each orbital are also given. The five highest energy occupied orbitals are made up of five d orbitals with a slight mixing of ligands. The energy levels of these five d orbitals are split due to the effect of ligand field. The sets of lowest energy unoccupied orbitals are made up of the ligands, but each orbital has different assembly of ligands. Thus clearly the low-lying excitations are originated from the transfer of electron from d orbital of copper to the π^* orbitals of phen ligands.

The Mulliken charges of ground and excited states have been calculated, respectively. The results were listed in Table 4. It is observed that the complex has

Table 2

Compositions and energies of several selected orbitals in $\text{Cu}(\text{phen})_2^+$ by ADF method

Orbital	73	74 (HOMO)	75 (HOMO)	76 (LUMO)	77	78	79
Energy (eV)	-7.76	-7.37	-7.37	-5.50	-5.43	-5.42	-5.23
Cu	89.98	73.54	72.40	3.28	0	0	3.22
Phen1	1.23	5.12	13.19	85.57	46.16	46.11	0
Phen2	0	10.45	1.08	0	40.82	41.40	89.05

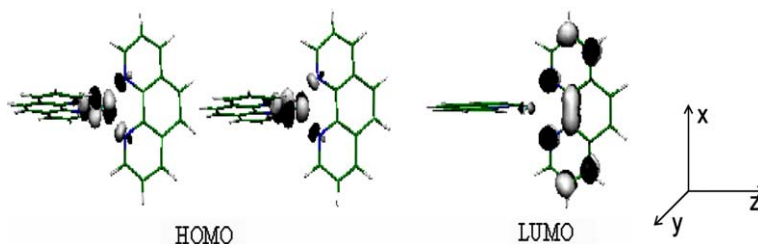


Fig. 5. The profiles of HOMO and LUMO orbitals of the complex $\text{Cu}(\text{phen})_2^+$.

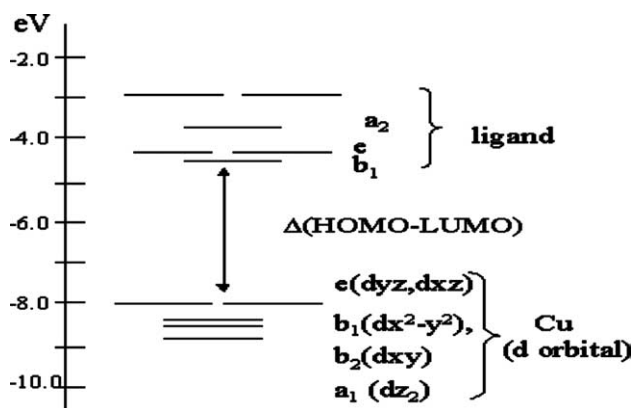


Fig. 6. The orbital level diagram of the complex $\text{Cu}(\text{phen})_2^+$.

Table 4

Mulliken charges of complexes $\text{Cu}(\text{phen})_2^+$, the excited state of $\text{Cu}(\text{phen})_2^+$, and $\text{Cu}(\text{phen})_2^{2+}$ by ADF method

	$\text{Cu}(\text{phen})_2^+$	$\text{Cu}(\text{phen})_2^+$ -excited state	$\text{Cu}(\text{phen})_2^{2+}$
Cu	0.360	0.553	0.574
phen1	0.324	0.177	0.721
phen2	0.316	0.270	0.705

redistributed the electrons from central metal copper to phen ligands (MLCT transfer) during excitation. In this process the metal loses about 0.19e, meanwhile one of phen ligands gains about 0.14e, and the other one gains about 0.05e. It points out that the electron transfers to the two ligands is asymmetric in nature. Most of electrons are transferred to only one ligand. It is attributed to the large variation of geometry during excitation. The d orbital is mixed to match p-orbital of four nitrogen atoms in HOMO orbital for the complex $\text{Cu}(\text{phen})_2^+$ (see Fig. 5). However, when it is changed to its corresponding excited state, the central metal loses the electrons, and the lower of charge in central metal makes the complex change its structure from four-coordinate to six-coordinate. Thus the two ligands have to adjust their initial direction to adapt the planar structure for

the $\text{Cu}(\text{II})$ complex. The match between initial orbitals is removed by this reorganization of structure, and thus it becomes difficult for the electron to flow into two ligands. Additionally, it is agreement with the results revealed by time resolved Raman spectroscopy that the excited electron is localized on only one ligand [32,33]. It is also found that the charge of central metal in excited state is nearly same as that of $\text{Cu}(\text{phen})_2^{2+}$ complex. The charge values of metal is 0.55 in the excited state of $\text{Cu}(\text{phen})_2^+$, while it is 0.57 for the complex $\text{Cu}(\text{phen})_2^{2+}$. Again it indicates a similarity between copper(I) excited state and copper(II) ground state.

Due to the presence of the low-energy π^* orbitals of the phen ligand, the complex $\text{Cu}(\text{phen})_2^+$ exhibits strong metal–ligand charge transfer (MLCT) properties and produces electronic absorption bands in the visible region [13]. The excitation energies of singlet to singlet and oscillator strengths of the complex $\text{Cu}(\text{phen})_2^+$ were calculated by TDDFT method with a geometrical structure of ground state produced by ADF method. The results were listed in Table 5. By analyzing the corresponding excitations, it is known that the first electronic adsorption band is coming from the foremost 10 excitations that appear in the lowest energy regions. The first excitation is electron transfer from HOMO to LUMO, and it is the excitation of d orbitals of Cu to π^* orbitals of the ligand one. Similar analysis has been done for these 10 excitations, and the detailed information was listed in Table 5. It indicates clearly that the first band is mainly the electrons transfer from metal to ligand, an MLCT transfer excitation. The electronic absorption spectrum measured in the solution of dichloromethane has been published in [19], in which the first band began at 2.43 eV and ended at 2.82 eV, with the maximum at 2.71 eV. For our calculative result, the first band begins at 1.87 eV and ends at 2.35 eV, with the maximum at 2.19 eV (Table 5). All values have a small shift about 0.5 eV. The solvent effect maybe responsible for this error between experiment and calculation because the experimental spectrum was obtained in

Table 5

Excitation energies (Ev: eV) and oscillator strengths (Os.) of the foremost 10 singlet to singlet excitations for the complex $\text{Cu}(\text{phen})_2^+$ by TDDFT method

No.	Excitation (orbital ₁ –orbital ₂ ^a ** ^b)	Origin of excitation	Ev	Os.
1	75–76	Cu → phen1	1.87	0.0003
2	75–77 ^a 0.51 ^b 75–78 0.47	Cu → phen1,phen2	1.90	0.0005
3	74–77 0.35 75–78 0.27 75–77 0.23 74–78 0.10	Cu → phen1,phen2	1.95	0.0045
4	74–77 0.37 75–77 0.23 75–78 0.23 74–78 0.11	Cu → phen1,phen2	1.97	0.0076
5	74–78 0.74 74–77 0.24	Cu → phen1,phen2	2.02	0.0099
6	74–76 0.60 74–79 0.18 75–79 0.13	Cu → phen1	2.19	0.0925
7	74–79 0.78 74–76 0.17	Cu → phen2	2.21	0.0304
8	73–76 0.90	Cu → phen1	2.31	0.0024
9	73–77 0.85 73–78 0.08	Cu → phen1,phen2	2.33	0.0001
10	73–78 0.90	Cu → phen1,phen2	2.35	0.0001

^a Denote the corresponding orbitals related to the excitations in the complex.

^b Denote the fraction of the each separate excitation.

dichloromethane solution while the calculation simulated the vacuum behavior.

As outlined above, the conversion of solar energy assisted by the series of cuprous (I) bis-phenanthroline can be proposed. The $\text{Cu}(\text{phen})_2^+$ absorbs solar energy which is 2.19 eV in our calculation and 2.71 eV in experiment. Then the complex is transformed to higher energy state by a Frank–Condon excitation. In this excitation process, because the HOMO orbital is nearly made up of pure d orbitals of central metal and the LUMO is mainly ligands, the electron is redistributed from central copper to phen ligands, that is, the MLCT excitation is involved. A relaxation of structure distortion occurs after Frank–Condon excitation, and finally a transient stable $\text{Cu}(\text{II})$ -like excited state, having considerable properties of $\text{Cu}(\text{phen})_2^{2+}$, is formed. However it should be noted that according to the energy gap law [31], the large structural distortion between the ground and excited state equilibrium geometries, may increase the amount of vibrational overlap between ground state and excited states leading to large non-radiative decay rate constants and thus decrease lifetime of excited state. Therefore, the improvement of steric and electronic properties for the ligands, to reduce the structural distortion, is necessary to become an efficient photosensitizer in the conversion of solar energy.

4. Conclusions

In this work the properties of excited state and electron transfer excitation of cuprous (I) bis-phenanthroline have been investigated. It was confirmed by our calculation that the shape of stable geometries of the cuprous (I) phenanthroline complexes depended on the charge values of central copper largely. It varied from an tetrahedral structure of $\text{Cu}(\text{I})$ complex flattening to a close square-planer geometry of $\text{Cu}(\text{II})$ complex. It is found that after the Cu complex was excited optically, electrons of the systems were redistributed in a way of MLCT excitation via an electron transfer from metal to the ligands. As a result, a $\text{Cu}(\text{II})$ -like excited state was formed. The relaxed distortion occurred in the excited state, which is because of the preferences of the $\text{Cu}(\text{II})$ ion to a square-planar coordination environment. The large structural distortion between ground state and excited state of $\text{Cu}(\text{phen})_2^+$ reduced the lifetime of excited state and led to a non-radiative decay. Thus the modification in structure to limit the structural distortion between

ground state and excited state are necessary to increase the efficiency of solar energy conversion.

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