

# A density functional investigation of charge transfer and structural distortions of cuprous(I) bis-phenanthroline under photo-induced excitation

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## Abstract

The charge transfer and structural distortions that occurred in the complexes cuprous(I) bis-phenanthroline ( $\text{Cu}(\text{NN})_2^+$ ) (NN denotes 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and 2,9-di(trifluoromethyl)-1,10-phenanthroline) upon excitation with an irradiation of light were studied by density functional theory (DFT). The calculations showed that the electrons transferred from central metal Cu to ligands with the transition of the complexes  $\text{Cu}(\text{NN})_2^+$  from ground state to excited state. As a consequence, the central copper in the excited state of  $\text{Cu}(\text{NN})_2^+$  exhibited similar electronic density to that in the corresponding complex  $\text{Cu}(\text{NN})_2^{2+}$ . Accompanying with this transfer process, the coordination polyhedra of  $\text{Cu}(\text{NN})_2^+$  became distorted upon excitation. The structural distortion was significantly reduced by increasing the steric bulk of the 2- and 9-positions substituents in the ligands NN, which is helpful for the increase of the life time of the excited state. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Cuprous(I) bis-phenanthroline; Density functional theory; Excited state; Photo-induced excitation; Structural distortion

## 1. Introduction

The conversion of solar energy to chemical energy is an important and active research area because of the worldwide energy crisis [1–4]. The conversion and storage processes of solar energy can be achieved by transforming the abundant low-cost raw materials like  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{N}_2$  into the useful fuels like  $\text{H}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$  and  $\text{NH}_3$ . However, these raw materials cannot be electronically excited by solar energy for direct fuel conversion. One of the effective conversion methods is to adopt a suitable photosensitive material, photosensitizer. The frequently studied classic example photosensitive material is the Ru(II)-based complex of  $\text{Ru}(\text{bpy})_3^{2+}$  (bpy denotes 2,2'-bipyridine) [5,6]. However, the applica-

tions of Ru(II)-based complexes as photosensitive materials meet challenges mainly from the high expenses of Ru and its related environmental pollution. Re(I) and Os(II)-based complexes have been taken as the alternatives, but still have the similar drawbacks. Recently, the Cu(I) coordination complexes are emerging as an attractive alternative photosensitizer [7–10]. From a practical standpoint, solar energy conversion devices and sensors based on inexpensive copper are more promising than the systems based on the ruthenium or osmium because copper is less toxic, cheap and minor environmental risk. McMilin and co-workers [11,12] have established that Cu(I) complexes with phenanthroline derivatives ligands have outstanding excited state properties comparable to  $\text{Ru}(\text{bpy})_3^{2+}$ . These complexes generally absorb UV–vis light over the range of 350–650 nm with relatively high extinction coefficients ( $\sim 10^3$  to  $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). When phenanthroline ligands have alkyl in the 2- and 9-positions,

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the excited states are emissive with the lifetimes of  $10^{-9}$  to  $10^{-7}$  s at room temperature [13]. Some literature work has proved that the photo-induced electron transfer (ET) and charge separation occur in these complexes during the irradiation of light [14,15]. This photo-induced electronic transfer will cause nuclear movements in the complexes, leading to distinct variations in structure, or reorganization. It has been proposed that the phenanthroline derivatives with moderately bulky substituents have an important impact both on the intensity of the metal–ligand charge transfer (MLCT) absorption bands as well as the photochemical behavior [16,17]. Since the complexes with long luminescent lifetimes are very useful for solar energy conversion and many other potential applications, a theoretical identification of the important factors that govern the conversion efficiency is highly needed, which allows the rational design and synthesis of photosensitive materials with high efficiency by understanding the nature of the charge separation and its closely related nuclear movement.

This work is to address the effect of substituents on the electron transfer and structural distortions that occur in the complexes of cuprous(I) bis-phenanthroline upon the irradiation of light energy. The stable geometries of  $\text{Cu}(\text{NN})_2^+$ ,  $\text{Cu}(\text{NN})_2^{2+}$  and the excited states of  $\text{Cu}(\text{NN})_2^+$  with different bis-phenanthroline ligands (NN) were calculated by optimizing the total energy via density functional theory (DFT). We discussed the charge transfer direction and degree during the excitation by comparing the Mulliken population both in ground state and excited state. The relationships among the steric effect of ligands and the charge transfer and geometrical distortions are studied by comparing the electronic and structural properties of the cuprous complexes with the different bis-phenanthroline ligands.

## 2. Computational details

All calculations in this investigation have been performed by using Gaussian98 (G98) and Amsterdam density functional program package (ADF2000) [18,19]. In the case of G98, a mixture of Hartree–Fock and DFT along with a Becke three-parameter hybrid function of Lee, Yang and Parr (B3LYP) was used as the exchange and correlation potential function [20]. The standard LANL2DZ basis sets

were applied to all atoms [21]. In the case of ADF2000, the Perdew and Wang's 1991 exchange and correlation functional (PW91XC) was taken at the generalized gradient approximation (GGA) [22], and the basis sets of triple- $\xi$  STO with polarization function were applied to the valence electrons of all atoms. The inner electrons within the atomic shells (i.e. 1s for C 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) [23]. The geometrical and electronic properties of excited states were obtained using orbital occupations method by controlling the assignment of spin- $\alpha$  and spin- $\beta$  electrons to molecular orbitals. The net spin–polarization of the system was specified to be two [24]. The relative bond lengths and angles in the two phenanthroline derivatives ligands were fixed during optimization. The pictures of the molecular orbitals and optimized structures were illustrated using a MOLEKEL4.1 molecular visualization program [25].

## 3. Results and discussion

The structures of  $\text{Cu}(\text{NN})_2^+$  in ground state were optimized by minimizing the total energy using ADF2000 and Gaussian98 programs, where NN ligands were chosen to be 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp) and 2,9-di(trifluoromethyl)-1,10-phenanthroline (bft), respectively (Fig. 1). Several selected bond lengths and bond angles are listed in Table 1 together with the experimental values [17,26,27]. The consistent geometries have been yielded by two methods. The optimized stereoviews of  $\text{Cu}(\text{NN})_2^+$  with the different NN are depicted in Fig. 2. The structures of the corresponding Cu(II) complexes,  $\text{Cu}(\text{NN})_2^{2+}$  were also optimized using the same computational conditions and the results are shown in Fig. 3. It is clear that all these three complexes,  $\text{Cu}(\text{NN})_2^+$ , show quite similar structures even though the ligands are different. The frame structure involving a central Cu(I) atom coordinated with four N atoms is of almost perfect Td symmetry. The angles between two NN ligands are  $92.1^\circ$ ,  $91.6^\circ$  and  $93.2^\circ$  for phen, dmp and bft, respectively. It matches the coordination rule of the cuprous complexes [28]. Although there is no difference in the coordination number of central copper between  $\text{Cu}(\text{NN})_2^+$  and  $\text{Cu}(\text{NN})_2^{2+}$ , Cu(I) has the electronic

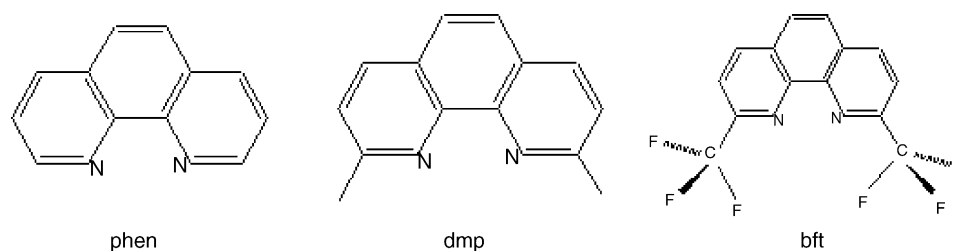


Fig. 1. The skeleton structures of the ligands, 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp) and 2,9-di(trifluoromethyl)-1,10-phenanthroline (bft).

Table 1  
Selected bond lengths and angles of the complexes  $\text{Cu}(\text{NN})_2^+$ ,  $\text{Cu}(\text{NN})_2^{2+}$  and the excited state (ET) of  $\text{Cu}(\text{NN})_2^+$ , (NN = phen, dmp, bft)

Methods	$\text{Cu}(\text{phen})_2^+$		ET of $\text{Cu}(\text{phen})_2^+$		$\text{Cu}(\text{phen})_2^{2+}$	
	ADF2000	G98	ADF2000	G98	ADF2000	G98
Cu–N1	2.03(2.02)	2.08	2.00	2.03	2.04	2.08
Cu–N2	2.04(2.04)	2.08	2.04	2.05	2.04	2.10
Cu–N3	2.03(2.02)	2.08	2.02	2.04	2.04	2.10
Cu–N4	2.07(2.05)	2.08	2.00	2.03	2.07	2.13
Angle (NN–NN)	92.1	90.0	43.7	41.8	35.5	33.0
Methods	$\text{Cu}(\text{dmp})_2^+$		ET of $\text{Cu}(\text{dmp})_2^+$		$\text{Cu}(\text{dmp})_2^{2+}$	
	ADF2000	G98	ADF2000	G98	ADF2000	G98
Cu–N1	2.04(2.09)	2.02	2.03	2.08	2.04(2.04)	2.08
Cu–N2	2.05(2.09)	2.05	2.06	2.10	2.04(2.04)	2.08
Cu–N3	2.05(2.08)	2.06	2.07	2.10	2.02(2.06)	2.06
Cu–N4	2.06(2.09)	2.08	2.14	2.15	2.05(2.05)	2.07
Angle (NN–NN)	91.6(91.5)	82.0	67.0	68.1	71.2(71.4)	69.3
Methods	$\text{Cu}(\text{bft})_2^+$		ET of $\text{Cu}(\text{bft})_2^+$		$\text{Cu}(\text{bft})_2^{2+}$	
	ADF2000		ADF2000		ADF2000	
Cu–N1	2.06		2.01		2.06	
Cu–N2	2.06		2.02		2.06	
Cu–N3	2.03		2.07		2.05	
Cu–N4	2.03		2.05		2.05	
Angle (NN–NN)	93.2		93.8		93.9	

Note: The experimental data listed in bracket are cited from refs. [26,27,17].

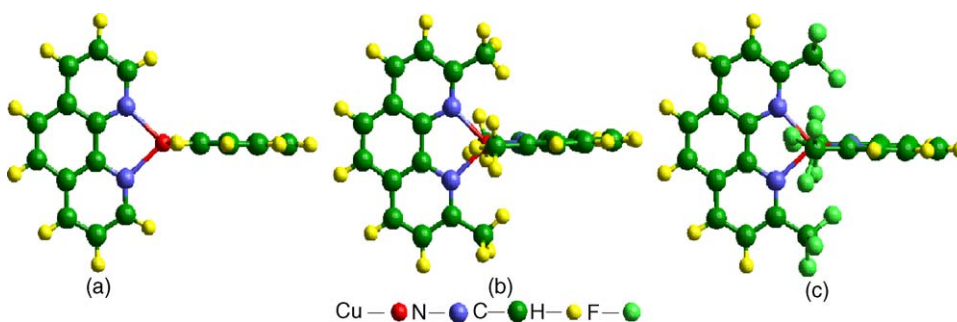


Fig. 2. The optimized structure of  $\text{Cu}(\text{NN})_2^+$  (a) NN = phen, (b) NN = bmp and (c) NN = bft.

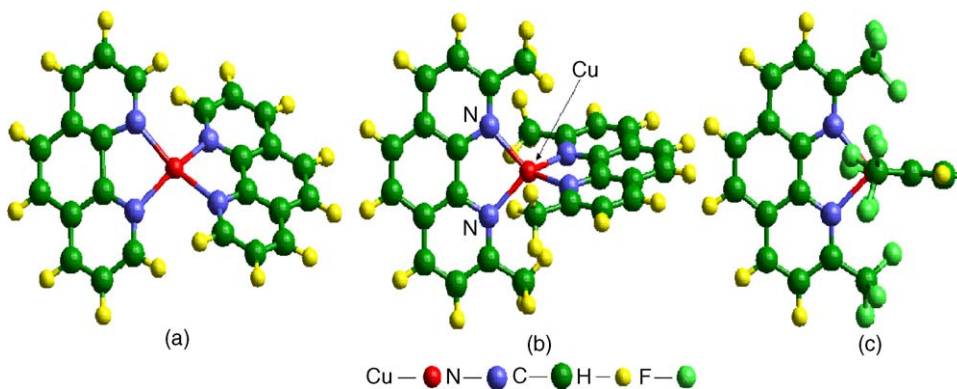


Fig. 3. The optimized structure of  $\text{Cu}(\text{NN})_2^{2+}$  (a) NN = phen, (b) NN = bmp and (c) NN = bft.

configuration of  $d^{10}$ , and prefers to be four-coordinated with a tetrahedral geometry, while the electronic configuration of Cu(II) is  $d^9$  and intends to adopt a Jahn–Teller distorted geometry that is usually 5- or 6-coordinate [28]. Therefore the geometries of  $\text{Cu}(\text{NN})_2^{2+}$  should be close to a planar structures, leaving the empty positions for the solvent or other ligands to be the fifth or sixth coordination species, as is indicated by our calculation on the complex  $\text{Cu}(\text{phen})_2^{2+}$  (Fig. 3a). The torsional angle between the two phen ligands is  $35.5^\circ$  for  $\text{Cu}(\text{phen})_2^{2+}$ , which is far from the angle of  $92.1^\circ$  for  $\text{Cu}(\text{phen})_2^{2+}$ , showing a change from a tetrahedral of Cu(I) complex to a close planar structures of Cu(II) complex. However, by looking over our results, it is obvious that the geometrical structures of the Cu(II) complexes,  $\text{Cu}(\text{NN})_2^{2+}$  are significantly different depending on the ligands, which might be associated with the steric hindrance of the NN ligands. In fact, the distances between central copper and N atoms in all these Cu(I) and Cu(II) complexes did not change so much (see Table 1). However the torsional angle between two ligands of  $\text{Cu}(\text{NN})_2^{2+}$  complexes is  $35.5^\circ$  for phen,  $71.2^\circ$  for dmp and  $93.9^\circ$  for bft. Thus with the increase of steric hindrance of ligands from phen, dmp, to bft, the torsional angles between two ligands in the Cu(II) complexes are increased. The steric clashes between opposing substituents in the 2- and 9-positions of the two phenanthroline ligands inhibit the flattening distortion when Cu(I) complex was oxidized to Cu(II) complex.

The optimization of  $\text{Cu}(\text{NN})_2^{2+}$  in the first triplet excited state was performed with a model by promoting one electron from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) with the opposite spin using ADF2000 program. The optimized structures in Fig. 4 indicate a significant rotation of the NN ligands in the lowest energy excited states of  $\text{Cu}(\text{NN})_2^{2+}$  that display a distorted tetrahedral geometry very similar to the corresponding  $\text{Cu}(\text{NN})_2^{2+}$ . In the excited state, the torsional angles between two NN ligands are  $43.7^\circ$  for NN = phen,  $67.0^\circ$  for NN = dmp and  $93.8^\circ$  for NN = bft (Table 1). The more steric hindrance of the two NN ligands gives rise to the torsional angles close to  $90^\circ$ . It could be thus expected that when the Cu(I) complex is changed from ground state to excited state, in the case of small steric bulk of the NN ligands, the excited state will have a large structural distortion. However if steric bulk of the NN

Table 2

Mulliken charges of the complexes  $\text{Cu}(\text{NN})_2^+$ ,  $\text{Cu}(\text{NN})_2^{2+}$  and the excited state of  $\text{Cu}(\text{NN})_2^+$  (NN = phen, dmp, bft)

	Cu	NN <sub>1</sub>	NN <sub>2</sub>
NN = phen			
$\text{Cu}(\text{NN})_2^+$	0.360	0.324	0.316
Excited state of $\text{Cu}(\text{NN})_2^+$	0.553	0.178	0.270
$\text{Cu}(\text{NN})_2^{2+}$	0.574	0.721	0.705
NN = dmp			
$\text{Cu}(\text{NN})_2^+$	0.251	0.375	0.375
Excited state of $\text{Cu}(\text{NN})_2^+$	0.422	0.297	0.281
$\text{Cu}(\text{NN})_2^{2+}$	0.435	0.803	0.761
NN = bft			
$\text{Cu}(\text{NN})_2^+$	0.546	0.227	0.228
Excited state of $\text{Cu}(\text{NN})_2^+$	0.648	0.175	0.177
$\text{Cu}(\text{NN})_2^{2+}$	0.640	0.680	0.680

ligands is large, the structural distortion associated with the excited state become small. Thus a picture of the structural distortion can be drawn that firstly, the bulky ligands in the 2- and 9-positions of the phenanthroline will hinder the relax of stereostructure both for the process of the excitation from the ground state to excited state and for the oxidation from Cu(I) to Cu(II) complex. Secondly, the ground state structure of  $\text{Cu}(\text{NN})_2^{2+}$  provides a reasonable view of the MLCT excited state of  $\text{Cu}(\text{NN})_2^+$ .

The Mulliken charges of  $\text{Cu}(\text{NN})_2^+$  and  $\text{Cu}(\text{NN})_2^{2+}$  in their stable ground states, as well as  $\text{Cu}(\text{NN})_2^+$  in its lowest excited state were calculated using ADF2000 program. The first excited state was performed with a model by promoting one electron from the HOMO to LUMO with the opposite spin using orbital occupations method of ADF2000 program. The results are listed in Table 2. It is observed that the distribution of electronic density is different in the ground and excited states for each  $\text{Cu}(\text{NN})_2^+$  complex. In order to understand the direction of electronic transfer clearly, the difference of the charge between ground state and excited state for the corresponding metal and ligands are calculated and shown in Table 3. It shows that during the excitation from ground state to excited state of  $\text{Cu}(\text{NN})_2^+$ , the charge transfer from metal to ligands occurs. However the transfer degree, in particular, the transfer manner is varied depending on the different ligands. In the complex of phen ligand,

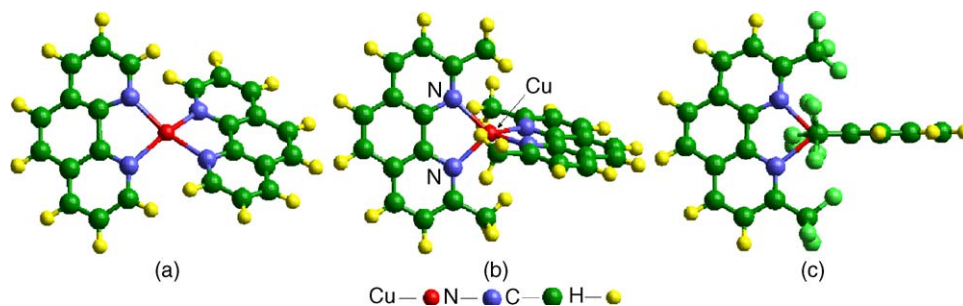


Fig. 4. The optimized structures of the excited states of the complexes  $\text{Cu}(\text{NN})_2^+$  (a) NN = phen, (b) NN = bmp and (c) NN = bft.

Table 3  
Charge difference of Cu and ligands NN between ground and excited states for the complexes  $\text{Cu}(\text{NN})_2^+$  (NN = phen, dmp, bft)

	$\text{Cu}(\text{phen})_2^+$	$\text{Cu}(\text{dmp})_2^+$	$\text{Cu}(\text{bft})_2^+$
Cu	0.20	0.17	0.10
NN1	0.15	0.09	0.05
NN2	0.05	0.08	0.05

$\text{Cu}(\text{phen})_2^+$ , electronic transfer from metal to ligands takes place in an asymmetric way. Metal Cu loses  $0.20 e^-$ , in which  $0.15 e^-$  is transferred to phen1, while only  $0.05 e^-$  to phen2. Most of the electrons are transferred to only one phen ligand. With regards to the  $\text{Cu}(\text{dmp})_2^+$ , it is noticed that each dmp accepts about half amount of electrons that come from the metal. That is, the electrons move away from the central metal Cu and are assigned to the two dmp ligands equally. Similar electronic transfer in a symmetric way is found in  $\text{Cu}(\text{bft})_2^+$ . Obviously, the transfer manners of electrons are influenced by the nature of the ligands in the series of cuprous phenanthrolines. It could be attributed to the structural distortion during the excitation. The d-orbitals of central copper were mixed to match the p-orbital of four nitrogen atoms of the ligands (see Figs. 5 and 6) in the tetrahedral ground states of these three complexes. However when the complex

is transferred to its corresponding excited state, the structure becomes distorted for the complex  $\text{Cu}(\text{phen})_2^+$ . The ligands have to change their initial direction to adapt the planar structure of the corresponding Cu(II)-like complex. The match between initial orbitals is removed by this reorganization of structure. Thus it becomes difficult for the electron to flow to two ligands. However, for the complexes  $\text{Cu}(\text{dmp})_2^+$  and  $\text{Cu}(\text{bft})_2^+$ , the structural distortions are small during the excitation, the coordinating directions of the ligands need not change so much during the excitation. Therefore the match is not affected by the excitation. Instead, electrons can flow to two ligands easily. Thus it can be concluded the transfer manner of the electrons are related to the degree of the structural distortion. Actually, the transfer amount of the charge also related to the structural distortion, that is, MLCT become smaller from NN = phen to NN = bft. Furthermore, by analyzing the data of the net charge for these complexes, a similarity of the net charge of central metal between the ground state of Cu(II) and the excited state of copper(I) is found. The charge of the central metal Cu is 0.57 in  $\text{Cu}(\text{phen})_2^{2+}$  and 0.55 in the excited state of  $\text{Cu}(\text{phen})_2^+$ , while it is decreased to 0.36 in  $\text{Cu}(\text{phen})_2^+$ . Similar charge features have been found for the complexes with dmp and bft ligands. The excited state of  $\text{Cu}(\text{NN})_2^+$  can be viewed as a Cu(II)-like species

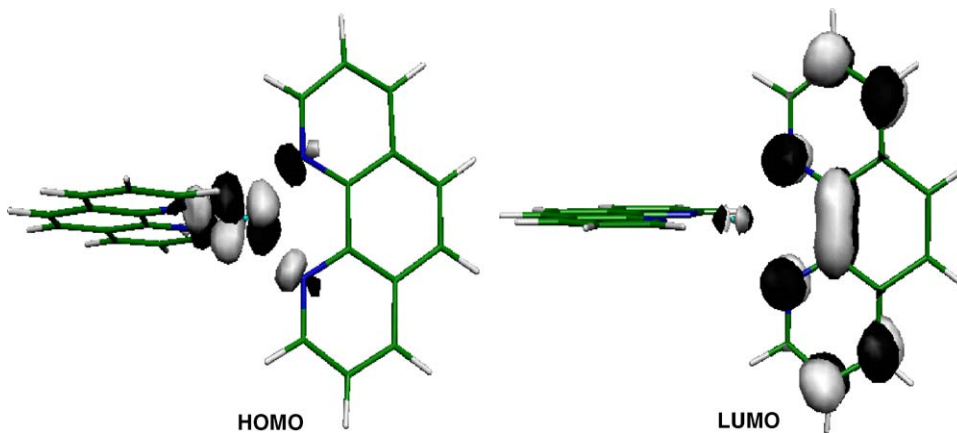


Fig. 5. The profiles of the HOMO and LUMO orbitals of the complex  $\text{Cu}(\text{phen})_2^+$ .

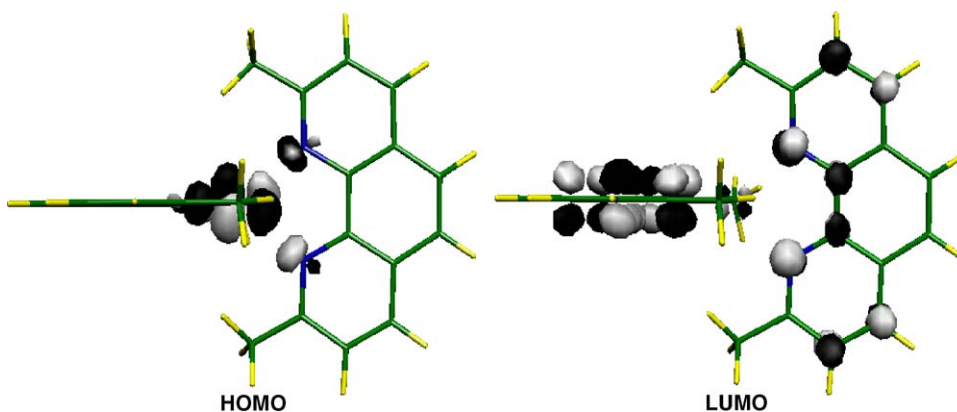


Fig. 6. The profiles of the HOMO and LUMO orbitals of the complex  $\text{Cu}(\text{dmp})_2^+$ .

Table 4  
Compositions of HOMO and LUMO of the complexes  $\text{Cu}(\text{NN})_2^+$  (NN = phen, dmp, bft)

	$\text{Cu}(\text{phen})_2^+$	$\text{Cu}(\text{dmp})_2^+$	$\text{Cu}(\text{bft})_2^+$
<b>HOMO</b>			
Cu	72.4	79.2	78.8
NN1	13.2	5.4	5.5
NN2	1.1	5.8	5.4
<b>LUMO</b>			
Cu	3.3	3.9	0
NN1	85.6	45.2	46.1
NN2	0	46.3	42.2

$[\text{Cu}^{2+}(\text{NN})_2^-]^*$ . This viewing is correct as we have proved that the electrons transfer from central metal Cu to NN ligands in the transition from ground state to excited state of  $\text{Cu}(\text{NN})_2^+$ , which in turn makes the central metal Cu of the excited state of  $\text{Cu}(\text{NN})_2^+$  have the similar electronic density to that of  $\text{Cu}(\text{NN})_2^{2+}$ .

To gain insight into the excited state processes involved, the orbital compositions of  $\text{Cu}(\text{NN})_2^+$  in ground state were analyzed based on the Mulliken population. The data of highest occupied molecular orbital and lowest unoccupied molecular orbital are listed in Table 4. In these complexes, the HOMO is made up of five d-orbitals with a slight mixing of ligands, while the LUMO is predominantly contributed by the ligands. Figs. 5 and 6 illustrate the pictures of the HOMO and LUMO for the complexes with phen and bmp ligands, respectively. It is clear that the HOMOs are the same. However, the compositions of the LUMOs are different for these two complexes. The LUMO of the complex  $\text{Cu}(\text{phen})_2^+$  is asymmetric, whereas the LUMO of  $\text{Cu}(\text{dmp})_2^+$  has a symmetric  $\pi$ -orbital that is contributed equally by two dmp ligands. Here, we do not address the complex  $\text{Cu}(\text{bft})_2^+$ , because its HOMO and LUMO are similar to those of the complex  $\text{Cu}(\text{dmp})_2^+$ . It is known that the first low-lying excitation is associated with the electronic transition from the HOMO to LUMO. Thus for all complexes, the first low-lying excitation is the consequence of electron transfer from d-orbital of copper to the  $\pi^*$ -orbitals of the ligands.

All these calculative results showed that with the transition from the ground state to excited state in the complexes  $\text{Cu}(\text{NN})_2^{2+}$ , the electrons transfer from the central metal to the NN ligands. Such a charge transfer makes the central metal of the excited state of  $\text{Cu}(\text{NN})_2^+$  have the electronic densities being similar to that of  $\text{Cu}(\text{NN})_2^{2+}$ . Thus for the excited state of  $\text{Cu}(\text{NN})_2^+$ , the polyhedra became distorted and formed a quite similar structure to Cu(II) complex. This distorted structure has a small steric energy barrier for the further conversion to  $\text{Cu}(\text{NN})_2^{2+}$ . Therefore structural variation shows a potential oxidation ability from Cu(I) to Cu(II) by an intermediated excited state. The absorbed light energy provides a driving force for the conversion of  $\text{Cu}(\text{NN})_2^+$  to  $\text{Cu}(\text{NN})_2^{2+}$ . Furthermore, it is found that the steric bulk of the interligand prevent the excited state from relaxing toward

a flattening square-planer geometry. Thus the bulky groups such as  $\text{CF}_3$  are responsible for the reduction in the structural distortion that occurs in the MLCT excitation by clashing with the sec- $\text{CF}_3$  groups on the other ligand. As illustrated in ref. [16], the equilibrium displacement ( $\Delta Q_e$ ) between the initial and final electronic states can influence the vibrational overlap. As  $\Delta Q_e$  increases, so does vibrational overlap and non-radiative decay, and hence short-lived excited states. The decreased lifetimes limit their use as sensitizers in energy conversion. Thus by reducing structural distortion in the excited state, the equilibrium displacement  $\Delta Q_e$  is decreased and a long lifetime of excited state can be expected. Indeed, it is known that the bft complex exhibited a remarkable emission lifetime [16]. Thus this structural reorganization has an important influence on the excited state behavior, which allows deep understanding of the Cu(II)/Cu(I) redox process in the solar energy conversion.

#### 4. Conclusions

This work reported on a density functional investigation on charge transfer and structural distortions of a series of cuprous bis-phenanthroline. The shape of stable geometries of the cuprous phenanthroline complexes is found to largely depend on the electronic density of central copper and steric hindrance of ligands. With the transition from ground state to the excited state, the ideal tetrahedral structure of Cu(I) complex became distorted in forming a close square-planer geometry of Cu(II) complex with phen ligands. Such a structural distortion can be sterically inhibited by 2- and 9-positions substituents in phenanthroline. Ligand bft has a more bulkier substituent, therefore  $\text{Cu}(\text{bft})_2^{2+}$  had similar tetrahedral structure to  $\text{Cu}(\text{bft})_2^+$ . After the Cu(I) complex captured the light energy, the electrons were redistributed by electronic transfer from the central metal to the ligands in forming a Cu(II)-like excited state. The variations in electronic densities of the central metals can explain the occurrence of structural distortion in the excited state. Such a structural distortion also determined the lifetime of excited state, which provides a hint of structural design for advanced photosensitive materials. The decrease in structural distortion ( $\Delta Q_e$ ) reduced the amount of vibrational overlap between ground state and excited state, leading to smaller non-radiative decay rate constants and hence the extended lifetime of excited state. Reduction of this distortion can be accomplished by increasing the steric bulk of the 2- and 9-substituents in ligands.

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