PROGRESS IN NATURAL SCIENCE Vol. 14, No. 9, September 2004

REVIEW ARTICLE

Photo-functional materials based on copper(Ⅰ) complexes*

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Received January 15, 2004; revised February 24, 2004

Abstract Copper(Ⅰ) complexes are attractive photo-functional materials due to their rich photochemical and photophysical properties. It has been proved that these new materials have potential application in many fields, such as organic light-emitting diodes, optical sensor, nonlinear optics and dye sensitized solar cells. The goal of this review is to outline the progress in this field. Many aspects, including new ligands, stereochemical control and the construction of supramolecules, design of the excited states, the high-energy emission and low-energy emission, the Cu—Cu bonding interactions and applications, are discussed.

Keywords: **copper(Ⅰ) complexes, photo-functional materials.**

Nowadays, photons have begun to replace electrons as the carrier of information, and photo-functional materials have played an important role in the information society. Because of their rich photochemical and photophysical properties, copper(Ⅰ) complexes have been proved to be good materials in many fields, such as organic light-emitting diodes, optical sensor, nonlinear optics, dye sensitized solar cells and so on. Many scientists, such as Ford[1,2], Che[3], Yam[4,5] have achieved prominent results in this field. The goal of this article is to outline the progress and hotspots in this field.

1 Ligands diversity and various coordination modes

Most common ligands for photo-functional copper(Ⅰ) complexes are composed mainly of nitrogen, phosphorus, sulphur, olefin, acetylide and so on. The ligand can be monochelate (such as triphenylphosphine and cylhexaphosphine) or multichelate (such as 4,4′-bipyridine). In designing a new complex, soft or rigid ligand can be selected. In luminescent copper(Ⅰ) complexes, several kinds of electron transition modes can occur, including LMCT (ligand to metal charge transfer), MLCT (metal to ligand charge transfer), LLCT (ligand to ligand charge transfer), ILCT (intraligand charge transfer) and so on, by which copper(Ⅰ) complexes can emit lights of various colors, such as red, green or blue. Since the first stable copper(Ⅰ)-olefin complex stabilized by a tridentate ligand hydrotris(3,5-dimethylpyrazol-1-yl) borate was reported, many copper(Ⅰ)-olefin complexes[6~8] have been synthesized. However, all these complexes are air-sensitive. Recently, an unprecedented stable copper(Ⅰ)-olefin polymer displaying strong red emission ($\lambda_{\max} = 647$ nm) in the solid state have been reported by Zhang et al.[9] (see Fig. 1). In the TGA curve of the complex, no weight loss happens below 229 ℃. This is an excellent emissive material. Yam et al. have done a lot in the study of copper(Ⅰ) acetylide complexes[10~12], and the trinuclear complexes $[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-Ph})_2]^+$ (see Fig. 2) and $[\mathrm{Cu_3}(\mu\text{-dppm})_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{C-Ph})]^{2+}$ were reported by her group. All the two complexes exhibit intense and long-lived luminescence upon photoexcitation (the solid state emission for the first one: $\lambda_{\max} = 493$ nm, $\tau_0 = 14 \pm 1$ μs). These properties imply that they are suitable materials for phosphorescent organic light-emitting diodes. If the lifetime of the emitting material is too long, device efficiency will decrease due to the saturation of the emitting points.

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* Supported by the Major State Basic Research Development Program of China (Grant No. 2003CB314707), the National Natural Science Foundation of China (Grant Nos. 10374001 and 90301004), the Natural Science Foundation of Beijing City (Grant No. 2032015) and RFDP (Grant No. 20020004004)

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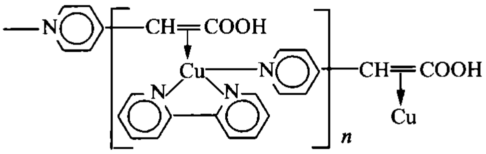


Fig. 1. The stable copper(I)-olefin 1D polymer.

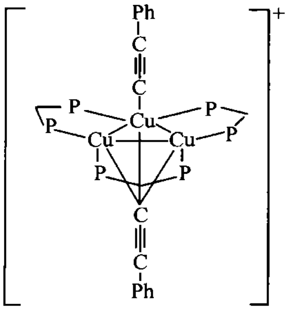


Fig. 2. The molecular structure of [Cu_3(μ-dppm$)_3$(μ_3-η^1-C ≡ C-Ph$)_2$] $^+$.

The first luminescent tetranuclear copper (I) phosphinidene complex [Cu_4(-dppm $)_4$(4-PPh)] ($BF_4$$)_2$ has also been reported by Yam (see Fig. 3)[5] . The red-light emitting properties (solid, 298 K, λ_{max} = 718 nm) and air-stability of this new class of compounds may have great potential in the future development of semiconducting luminescence materials and in LED technology. Moreover, the complex is soluble in common solvents, which makes it possible to fabricate devices by spin-casting method. For π coordination, the first pentaphenylcyclopentadienyl-copper complex (Ph_5Cp) Cu(PPh_3) (see Fig. 4) have been reported by Quynh[13] and it is a rare example of a π-bound Cu-Cp complex. Structure of the complex has been characterized by X-ray diffraction. The copper is bound to the Ph_5Cp ligand in an η_5-fashion. The Cp-Cu-P angle is 179.1°.

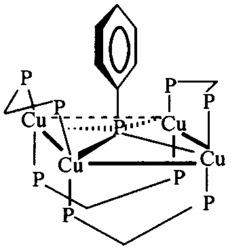


Fig. 3. The phosphinidene complex.

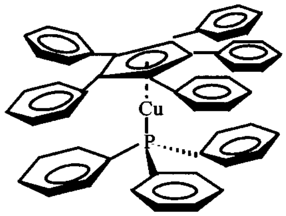


Fig. 4. The molecular structure of (Ph_5Cp)Cu(PPh_3).

Ligands have different coordination modes under different conditions. As a result, the same reactants produce different products. This skill of " killing many birds with one stone" attracts many scientists. For example, ligand -C ≡N R can coordinate with metal in various modes (see Fig. 5). When it coordinate with [M_3(μ-dppm $)_3$] (M = Ni, Pd, Pt), the fashion is μ_3-η^1. However, Josefina[14] discovered that the fashion is μ-η^1 in complex [Cu_3 (μ_3-η^1-C ≡$CC_6H_4CH_3$-4) (μ-η^1-C ≡NC_6H_4-CH_3-4)(μ-dppm $)_3$] $_2$ °3CH_2Cl_2.

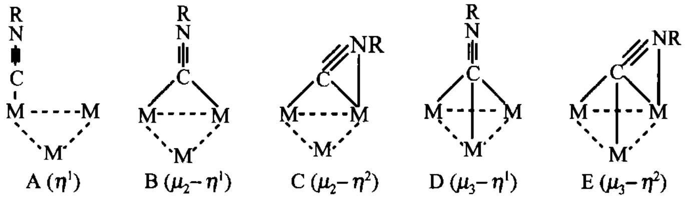


Fig. 5. Coordination modes of ligand -C≡NR.

In addition, as polyfunctional ligands, multi-chelate linear ligands also attract considerable interest for the construction of heterometallic complexes. For example, there are five kinds of modes when ligand dpnapy coordinates with Ir(I), Rh(I), Pt(II) or Pd(II). However, Chan et al.[15] discovered a new mode when they let the ligand coordinate with copper (I). X-ray diffraction data indicate that, in [Cu_3(μ-dpnapy$)_3$ (CH_3CN)] [ClO_4] $_3$ °CH_3CN, three copper atoms are located at the same line and coordinate with the two N atoms and the P atom, respectively. Distance between the two copper atoms is 2.449(2) Å, and the total coordination modes is six (see Fig. 6).

In short, the kinds and coordination modes are key factors for ligands. For example, in the molecular design of luminescent copper(I) complexes, by using pyridine or its derives that have low energy π^* orbit, one can obtain emission with longer wavelength, because metal-to-ligand charge transfer can occur in the

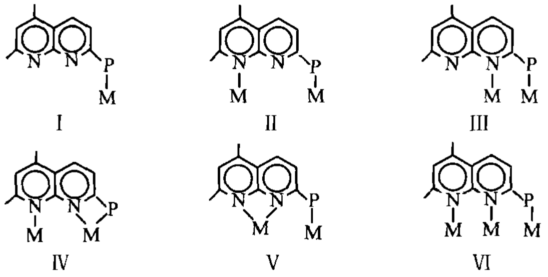


Fig. 6. Coordination modes of ligand dpnapy.

complex. If the ligands have rich electron but no low energy π* orbit, such as tricyclohexylphosphine, short wavelength emission probably can be obtained because ligand-to-metal charge transfer can occur. Moreover, in order to improve the emission efficiency, rigid ligands or rigid coordination modes should be selected.

2 Stereochemical control and the construction of supramolecules

By molecular design, rational selection of ligands and metal allows us to obtain 1-D, 2-D or 3-D coordination polymer that displays beautiful supermolecular structure or with cave, pipe, cage functional units. Hong et al.[16] let ligand tpst coordinate with M^+ (Cu^+, Ag^+, Au^+) and obtain beautiful nanopipes. All the nanopipes are connected by M^+ with each other to form 1-D polymer chain, as shown in Fig. 7.

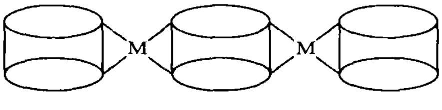


Fig. 7. The 1D polymer chain.

However, a common problem in the design of porous inorganic/organic systems arises because most coordination polymers carry an overall positive charge, which means that anions have to be present to balance the charge, and they will occupy space that may hamper the construction of open channels or void space. Therefore it is important to select suitable raw materials. For instance, copper(I) halides can form many neutral 1-D polymeric networks. Christer et al.[17] have achieved 2-D inorganic/organic lamellar structure using CuX as starting material. Brendan[18] reported a 3-D polymer based on $[Cu_3(tpt)_4](ClO_4)_3$ unit and the color of the crystal is deep red. Such a polymer has a wide absorption band (from 420 nm to 550 nm) which corresponds to electronic transition from metal ion to ligands. Moreover, the structure is formed by big cages with a diameter of 18.241(4) Å. Recently, many of these kinds of functional coordination polymers have been reported. Stuart[19] has reported many 1-D, 2-D and 3-D ones.

3 Design of the excited state for $[Cu(phen)_2]^+$ system

Phenanthroline is a common ligand in coordination chemistry. Its copper(I) complexes usually show a certain color and good luminescence because it has low energy π* orbit and it is easy to realize metal-to-ligand charge transfer. However, some of these complexes, such as $[Cu(phen)_2]^+$, are abnormal. They are not luminescent or luminescent but with very short lifetime (even under low temperature and rigid conditions). Many scientists are interested in the mechanism research. David et al.[20~22] suggest that this is the result of flattening distortion of the excited states (see Fig. 8). When the system is excited, metal-to-ligand charge transfer occurs. The development of copper(II) character in the excited-state encourages a flattening distortion. The consequences of the distortion include a decrease of the energy available in the excited state and a reduction of the excited state lifetime. The distortion is very easy. However, Steric forces limit the extent of the distortion, especially when there are bulky substituents in the 2, 9 positions of the phenanthroline ligand. Experiments indicated that the lifetime and the emission energy increased with the size of the substituent in the 2, 9 positions in methylene chloride. In addition, copper(II) is five-coordinate, so the relaxed excited state is easy to accept a solvent molecule and to form exciplex. Finally, the excited state is quenched and the lifetime decreases. The effective method to avoid the exciplex is to increase the size of the substituent in the 2, 9 positions or use media with deficient electron. Although there is no evidence of exciplex in the spectrum, experiments agree well with theory. When the 2, 9 positions are occupied by phenyl in phenanthroline ligand, $[Cu(2,9\text{-diphphen})_2]^+$ can emit well even in electron-rich media.

Recently, many papers have been published on the excited state design and quenching mechanism of $[Cu(phen)_2]^+$, which propose methods on how to tune the lifetime and quantum efficiency. They are helpful for the study of other systems.

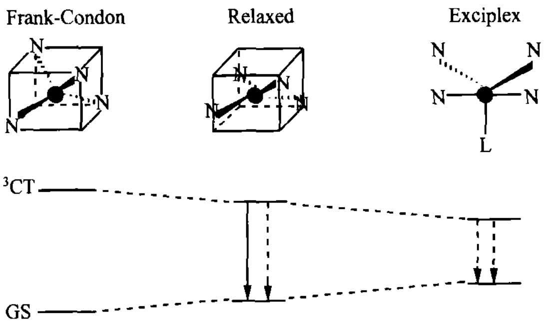


Fig. 8. Influences of a D_2-flattening distortion and formation of a five-coordinate adduct on the relative energies of the ground state and the lowest energy CT state of a copper phenanthroline.

4 The high-energy emission and low-energy emission

Hardt and co-workers[23] discovered that the emission spectra of $[CuI(Py\text{-}X)]$ solids were markedly temperature dependent and coined the term "luminescent thermochromism". Kyle[24] found that, for $[Cu_4I_4Py_4]$ system, the high energy (HE) band and low energy (LE) band vary sharply with temperature: at room temperature, the LE band dominates, but the HE band is quite prominent at low temperature (especially below 80 K). They thought that the phenomenon was due to the excited state. Subsequently, many scientists have taken part in the study on the nature of HE and LE.

Hardt[25] has suggested that LE can be affected by MLCT ($d^9 \rightarrow \pi_L^*$), but Vogler[26] found that solution-phase emission spectrum of the saturated amine cluster Cu_4I_4(morpholine)$_4$ ($\lambda_{max} = 654$ nm in benzene) at room temperature is similar to the broad red emission from $Cu_4I_4py_4$ (698 nm) under comparable conditions, and both only exhibit the LE band, so MLCT excited states are not the essential conditions for LE. Volger[26] has proposed that a metal-centered excited state of d^9s^1 orbital parentage modified by Cu—Cu interactions is responsible for the emission. In addition, the LE band is related to the crystal symmetry. However, Hu et al.[27] denied the suggestion by investigating the $Cu_4I_4L_4$ (symmetrical) and $Cu_4I_4L_2L_2'$ (unsymmetrical) system. They discovered that only complexes with d_{Cu-Cu} less than twice of the van der Waals radius (1.4 Å) of Cu(I) show the LE emission. They concluded that it was d_{Cu-Cu} (rather than crystal symmetry) that was the crucial parameter defining the emission behavior. Moreover, Kyle et al.[24] found ligands have effect on the emission too. Position of LE band shows modest dependence on the nature of the ligand and shows little dependence on the substituents, but HE band was found to be sensitive to the nature of the ligand substituents. Furthermore, LE band was found to be insensitive to the solvent, but stronger donor solvents shift the HE band to the shorter wavelengths. Based on the ligands and solvents effects, Kyle et al.[24] suggested that LE band is derived from a triplet cluster centered excited state of d-s character.

In order to clarify the nature of the excited state that affects the LE and HE band, *ab initio* calculations have been carried out by Vitale et al.[28]. They studied $[Cu_4I_4Py_4]$ and found HOMO of a molecule is largely (80%) composed of iodide 5p-orbitals with only small contributions of the metal d orbits, and so the earlier assignment of the HE emission from MLCT excited state is wrong. A more correct assignment is from I to pyridine (XLCT), and the LUMO is mainly from the contribution of Cu 4s orbit. Subsequently, Vitale[29] performed more rigorous calculations and concluded that LE emission is composed of roughly equal contributions from d-s and XLCT components.

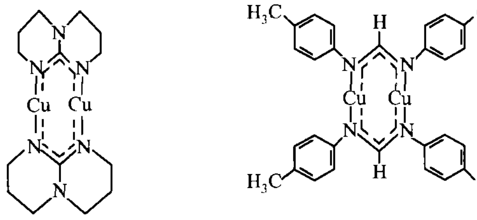
"Luminescent thermochromism" is an important phenomenon in luminescent Cu(I) complexes. If we consider the origin and factors of the HE and LE, it is significant to tune the color of Cu(I) complexes. However, the current conclusion is still controversial, and further study on a higher level is needed.

5 Discussion on Cu—Cu interactions

For d^{10} shell metals, the second and third transition-series metal complexes are easy to form M-M bond even the bond is weak. However, for Cu(I) complexes, whether the Cu—Cu bond exists is not clear even the d_{Cu-Cu} has been as small as 2.412(1) Å[30] and less than twice the van der Waals radius (1.4 Å) of Cu(I).

Many scientists suggest that Cu—Cu bond exists in multinuclear Cu(I) complexes. The bond is the force to form Cu_n core (cluster-centered). This structure has deep effect on the luminescence properties of Cu(I) complexes[31~33]. Zuo et al.[34] have depicted directly the d orbital holes on the copper atoms in Cu_2O, and also demonstrated the existence of Cu—Cu bonding in this compound. Che et al.[3] also reported the Cu—Cu bonding by studying several binuclear Cu (I) complexes. By using different anions, they tune the intramolecular Cu—Cu separations falling in the range 2.639(2)—2.938(2) Å, which are shorter than or close to or longer than twice of the van der Waals radius (1.4 Å) of Cu(I). After studying the absorption and emission spectra, they concluded that Cu—Cu bond existed.

However, some scientists denied the existence of Cu—Cu bonding. Cotton et al.[35] have carried out SCF X α-SW molecular orbital calculations to investigate the possibility of metal-metal bonding in [Cu_2(form)$_2$] (see Fig. 9(a)). Though $d_{Cu—Cu}$ is 2.497(2) Å in the complex, their results indicate that there is no Cu—Cu bond. Later they studied another complex [Cu_2(hpp)][36] (see Fig. 9(b)) in which $d_{Cu—Cu}$ is 2.4527 Å. The density function theory (DFT) calculations revealed that there was no Cu—Cu bond and the short Cu—Cu distance was a result of the strong Cu-N bonds and the small bite angle of the bridging ligand. Yam[37] suggested that short d^{10}-d^{10} separation did not necessarily mean there was a bond established between the metal centers and the effects of the bridging ligands should be taken into account. For Au(I) system, short Au-Au separations were very commonly observed.



(a) [Cu_2(hpp)] (b) [Cu_2(form)$_2$]

Fig. 9. The two complexes that Cotton studied.

6 Applications for photo-functional Cu(Ⅰ) complexes

6.1 Application in organic light emitting diodes

Improving the efficiency is one of the crucial technologies for OLED. During electrical excitation approximately one singlet exciton is created for every three triplet excitons, but because the ground state is typically also spin-antisymmetric, only relaxations of singlet excitons conserve spin and generate fluorescence. Usually the energy in triplet excitons is wasted, which limits the efficiency of OLED to less than 25%. In order to use triplet energy efficiently, phosphorescent materials attract more attention recently[38~42]. Organometallics are considered to be the most potential OLED materials because of their merits of both inorganic and organic materials, and organometallics that contain heavy atoms (such as Ir, Pt, Au, Cu) usually have long-lifetime phosphorescence because of spin-orbital coupling.

Cu(I) complexes are luminescent materials based on electrons transfer. When a transition metal complex is excited, an electron is promoted to an unoccupied orbit. With the assumption that the electronic state can be described approximately by localized molecular orbital configurations, electron transitions can be classified into different origins as depicted in Fig. 10.

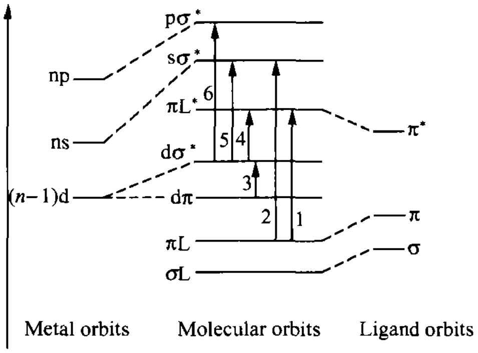


Fig. 10. Schematic energy level diagram of molecular orbits and electronic transitions in an octahedral coordination complex. 1, Intraligand charge transfer; 2, ligand-to-metal charge transfer; 3, ligand field (absent in d^{10} complexes); 4, metal-to-ligand charge transfer; 5, interconfigurational metal-centred, d-s; 6, interconfigurational metal-centred, d-p.

In Fig. 10, the ligand-to-metal charge transfer (LMCT) corresponds to electron transition from the ligands to the metal ion. It is usually observed in complexes that the metal is electron deficient and the ligand is electron rich; the metal-to-ligand charge transfer (MLCT) corresponds to electron transition from metal ion to ligands. Normally, charge transfer bands are observed in the UV and short-wavelength visible region. It happens in complexes that the metal ion is electron rich such as Cu(I) and the ligand has a low energy π^* orbit such as bipyridine; the ligand-to-ligand charge transfer (LLCT) corresponds to electron transition from ligands to ligands. It is usually observed in complexes that one ligand has isolated electrons and the other has a low energy π^* orbit; as for the intraligand transition (IL), emission originates from the ligand-centered excited state. The emission is usually highly structured. It resembles the emission that can be observed from the free ligand under the same conditions; in the metal-centered charge transfer, electrons are excited from the non-bonding $d\pi$ orbit to the $d_{\sigma *}$ orbits which are antibonding and associated with metal-ligand bonding. The excited-state would destabilize the metal-ligand bonds, and lead to facile ligand substitution. The MC excited state undergoes very efficient nonradiative deactivation and is photochemically unstable and short-lived.

Because Cu (I) complexes have many kinds of charge-transfer excited states, selecting different ligands can tune the emission color. This has been successfully applied in phosphorescent OLED[43, 44]. Ma et al.[43] have reported the phosphorescent material $Cu_4(C \equiv Cph)_4L_2$ (L= 1, 8-bis (diphenylphosphino)-3, 6-dioxaoctane) that has a lifetime of 26 μs and quantum yield of 48%. They fabricated a device with stucture ITO/Cu_4: PVK/TAZ (4.5 nm)/Al. The turn on voltage of the device is 12 V. The brightness at current density of 20 mA/cm^2 is ca. 50 cd/m^2 and the estimated EL yield is 0.1% (see Fig. 11). They envisage that EL yields can be further improved by using a low work function metal to enhance electron injection. In addition, Mitsuharu[44] used tetranuclear material $[CuN(Si(CH_3)_3)_2]_4$ to fabricate an EL device and achieved maximum brightness of 400 cd/m^2 at 22 V.

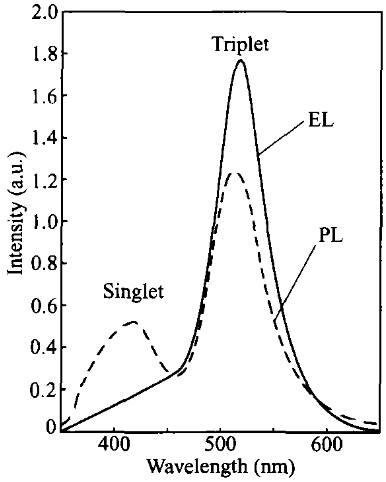


Fig. 11. Photoluminescence spectrum of Cu_4: PVK film (dashed line, λ_{ex} = 290 nm) and electroluminescence spectrum of an ITO/Cu_4: PVK/TAZ/Al device (solid line).

6.2 Application in optical sensor

Many polynuclear d^{10} metal systems often possess very long-lived phosphorescence that is often changed or effectively quenched by minim gas. This organometallic compound can be used as the optical sensor material for this gas. Cariati et al.[45] reported that exposure of the polymeric solid $[CuI(4\text{-pic})]_\infty$ to either liquid or vapor toluene could lead to disappearance of this material's characteristic room temperature blue emission (λ_{max} = 437 nm) and the appearance of the yellow emission (λ_{max} = 580 nm) indicative of the $[CuI(4\text{-pic})]_4$ tetramer; the process is reversed when the latter is exposed to liquid or vapor n-pentane.

$$[CuI(4\text{-picoline})]_4 \underset{\text{toluene (g or l)}}{\overset{n\text{-patane (g or l)}}{\rightleftharpoons}} [CuI(4\text{-picoline})]_\infty$$

$[CuI(4\text{-picoline})]_x$ (x = 4 or ∞) system can be used as optical sensor material for toluene or n-pentane.

6.3 Used as nonlinear optical materials

Recently, the investigation of new materials with emissive and nonlinear optical (NLO) properties has been focused on inorganic-organic compounds, which can properly mingle the advantages of both the inorganic species (higher chemical, thermal, and mechanical stabilities) and the organic ones (appreciable response speed and intensity in a wide spectral range, straightforward synthetic approach). Renouard[46] reported two tetrahedral bis (bipyridyl) copper (I) complexes and their second-order nonlinear optical properties determined by harmonic light scattering (HLS) at 1.34 μm; these new octupolar complexes exhibit large molecular hyperpolarisabilities β (λ_{max}= 424 nm and $\beta^0_{HLS} = 78 \times 10^{-30}$ esu, λ_{max}=420 nm and $\beta^0_{HLS} = 70 \times 10^{-30}$ esu, respectively). They are greater than the currently reported pure organic material [tetrakis (dibutyaminoazo benzenephosphonium) chromophore][47] (λ_{max}= 511 nm and $\beta^0_{HLS} = 56.7 \times 10^{-30}$ esu). Recently, Cariati[48] also reported the emissive and second-order nonlinear optical properties of two inorganic-organic polymeric adducts of CuI with 4-acetylpyridine, which indicates Cu (I) complexes are potential nonlinear optical materials in the future.

6.4 Application in dye-sensitized solar energy cells

The serious energy crisis calls for the green and abundant energy source: solar energy. The effective device for the energy transformation is solar energy cells. However, it is weak for common semiconductor to absorb the red emission from the sun, but many dyes which have small energy gap can absorb the red emission very well. Thus, if we combine these dyes with the semiconductor by chemical bond or physical adsorption, it can absorb the solar emission very well. Generally, the commonly used dyes are Ru complexes. While for copper (I) complexes, ligands which have low energy π^* orbit such as bipyridine or phenathrolin will generate MLCT excited state and the absorption band is located at visible region. Moreover, if we modify the ligand and let it combine with semiconductor, the absorption band of the system will match the solar spectrum better.

7 Conclusion

Photo-functional copper (I) complexes are a hotspot in recent years, and many studies have been focused on it. However, some questions still exist up to date. For example, Cu—Cu interactions have obvious effect on the luminescence, but whether the Cu—Cu bond exists is controversial, and the study on its applications is insufficient. In short, copper source is abundant in the world, and it is meaningful to enforce the study on the copper (I) complexes application.

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