

6-甲氧羰基-4,4'-二甲基-2,2'-联吡啶单核铜(I)双膦发光配合物

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摘要: 合成并表征了 2 个新的基于 6-甲氧羰基-4,4'-二甲基-2,2'-联吡啶的单核铜(I)双膦配合物 $[\text{Cu}(\text{mmbpy})(\text{dppp})]\text{ClO}_4$ (**1**) 和 $[\text{Cu}(\text{mmbpy})(\text{dppb})]\text{ClO}_4$ (**2**)。研究表明,铜(I)配合物 **1** 和 **2** 均表现为扭曲变形的 N_2P_2 四面体几何构型,其 P-Cu-P 键角受辅助双膦配体控制。在常温下,这 2 个铜(I)配合物在固态时均具有发光性质,并且相对于双膦配体亚甲基链的长度,P-Cu-P 键角对其光物理性质的影响更为显著。在 2,2'-联吡啶环上引入 2 个甲基取代基对改善铜(I)配合物的发光性能也被证明是有效的。

关键词: 铜(I)配合物; 甲氧羰基; 甲基; 双膦; 发光

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Luminescent Mononuclear Copper(I) Diphosphine Complexes with 6-Methoxycarbonyl-4,4'-dimethyl-2,2'-bipyridine

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Abstract: Two new mononuclear copper(I) diphosphine complexes based on 6-methoxycarbonyl-4,4'-dimethyl-2,2'-bipyridine (mmbpy), $[\text{Cu}(\text{mmbpy})(\text{dppp})]\text{ClO}_4$ (**1**) and $[\text{Cu}(\text{mmbpy})(\text{dppb})]\text{ClO}_4$ (**2**), have been synthesized and characterized. It is revealed that Cu(I) complexes **1** and **2** all exhibit distorted N_2P_2 tetrahedral geometries with varied P-Cu-P angles regulated by auxiliary diphosphine ligands. The two Cu(I) complexes are all emissive in the solid state at ambient temperature, and their photophysical properties are more markedly influenced by the P-Cu-P angle than the methylene chain length of diphosphine. It is also demonstrated that the introduction of two methyl substituents into the 2,2'-bipyridyl ring is effective for improving luminescence properties of Cu(I) complexes. CCDC: 1543374, **1**; 1543375, **2**.

Keywords: Cu(I) complex; methoxycarbonyl; methyl; diphosphine; luminescence

0 Introduction

Luminescent copper(I) complexes have received considerable research attention, because of their

promising potential applications in materials science and the high relative abundance and environmental friendliness of copper^[1-12]. Recently, a rapidly increasing interest has been paid to tetrahedral Cu(I)

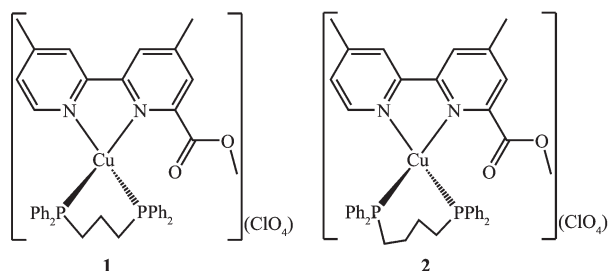
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complexes, especially mononuclear Cu(I) heteroleptic complexes with one diimine plus one diphosphine or two monophosphine, due to the markedly enhanced emission properties^[13-16].

The emissions of tetrahedral Cu(I) complexes usually exhibit appreciable metal-to-ligand charge transfer (MLCT) character, which is sensitive to the peripheral ligand and coordination environment^[13-21]. It is demonstrated that structural modification of the peripheral ligands is an effective way for tuning emission properties of Cu(I) complexes^[19-21]. Herein, we report the synthesis, characterization, and photophysical properties of two new mononuclear copper (I) diphosphine complexes based on 6-methoxycarbonyl-4,4'-dimethyl-2,2'-bipyridine (mmbpy) (Scheme 1), and the effect of the variation of auxiliary diphosphine ligands on the structures and photophysical properties of Cu(I) complexes.



Scheme 1 Molecular structures of complexes **1** and **2**

1 Experimental

1.1 Materials and measurements

All reactions were carried out under a N₂ atmosphere, using anhydrous solvents or solvents treated with an appropriate drying reagent. Commercially available reagents were used without further purification unless otherwise stated. 6-Methoxycarbonyl-4,4'-dimethyl-2,2'-bipyridine (mmbpy) was synthesized according to the literature method^[22]. Infrared (IR) spectra were recorded on a Bruker Optics ALPHA FT-IR spectrometer using KBr pellets. Elemental analyses (C, H and N) were performed on a Perkin-Elmer model 240C elemental analyzer, where all the crystal samples are used after grinding and drying under vacuum. Ultraviolet-visible absorption spectra in CH₂Cl₂ solution were recorded on a Shimadzu UV-

2550 spectrometer. The photoluminescence properties in the solid state were determined on an Edinburgh analytical instrument (F900 fluorescence spectrometer) with a thermoelectrically cooled Hamamatsu R3809 photomultiplier tube. An integrating sphere (lab sphere) was applied to measure the emission quantum yield in the solid state.

Caution! Perchlorate salts are potentially explosive and should be handled carefully in small amount.

1.2 Preparations of complexes **1** and **2**

1.2.1 [Cu(mmbpy)(dppp)]ClO₄ (**1**)

A mixture of [Cu(CH₃CN)₄]ClO₄ (19.6 mg, 0.060 mmol) and 1,3-bis(diphenylphosphino)propane (dppp) (24.9 mg, 0.060 mmol) in CH₂Cl₂ (3 mL) was stirred for 1 h at room temperature; mmbpy (14.6 mg, 0.060 mmol) was then added and the mixture was stirred for another 3 h to get a light yellow solution. The solvent was evaporated to dryness under reduced pressure. The resulting residue was then extracted with CH₂Cl₂, and slow diffusion of petroleum ether into the above mixture gave yellow crystals of **1** (41.8 mg, 0.051 mmol, 85%). Anal. Calcd. for C₄₁H₄₀ClCuN₂O₆P₂(%): C, 60.22; H, 4.93; N, 3.43. Found(%): C, 60.18; H, 4.95; N, 3.45. IR (KBr, cm⁻¹): 3 448(m), 3 055(w), 2 939(w), 1 731(s, -CO₂CH₃), 1 611(s), 1 480(w), 1 435(s), 1 341(m), 1 263(m), 1 222(m), 1 159(w), 1 093(vs), 833(w), 750(m), 699(s), 624(m), 511(s).

1.2.2 [Cu(mmbpy)(dppb)]ClO₄ (**2**)

Complex **2** was synthesized according to the procedure for **1** by using [Cu(CH₃CN)₄]ClO₄ (21.2 mg, 0.065 mmol), 1,4-bis(diphenylphosphino)butane (dppb) (27.8 mg, 0.065 mmol), and mmbpy (15.8 mg, 0.065 mmol). Orange red crystals were afforded by slow diffusion of petroleum ether into a CH₂Cl₂ solution of **2** (40.7 mg, 0.049 mmol, 75%). Anal. Calcd. for C₄₂H₄₂ClCuN₂O₆P₂ (%): C, 60.65; H, 5.09; N, 3.37. Found(%): C, 60.69; H, 5.06; N, 3.35. IR (KBr, cm⁻¹): 3 854(w), 3 441(s), 3 055(w), 2 923(w), 2 857(w), 1 733(s, -CO₂CH₃), 1 611(s), 1 481(w), 1 436(s), 1 344(w), 1 265(m), 1 221(m), 1 096(vs), 896(w), 839(w), 746(m), 698(s), 625(m), 515(m).

1.3 X-ray crystallography

Diffraction data for complexes **1** and **2** were

collected on a Bruker D8 QUEST diffractometer at room temperature using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). The program CrystalClear was used for integration of the diffraction profiles. Structures were solved by direct methods and refined by full-matrix least-squares technique on F^2 using the SHELXL-97 software package^[23]. The heavy atoms were located from E -map and other non-hydrogen atoms were found in successive difference

Fourier syntheses. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were generated geometrically with isotropic thermal parameters. The crystallographic data and structure refinement details of **1** and **2** are summarized in Table 1, and the selected bond lengths and angles are given in Table 2.

CCDC: 1543374, **1**; 1543375, **2**.

Table 1 Crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	$\text{C}_{41}\text{H}_{40}\text{ClCuN}_2\text{O}_6\text{P}_2$	$\text{C}_{42}\text{H}_{42}\text{ClCuN}_2\text{O}_6\text{P}_2$
Formula weight	817.68	831.71
Crystal system	Monoclinic	Monoclinic
Space group	Pc	$P2_1/c$
a / nm	1.437 56(8)	3.007 14(14)
b / nm	1.029 62(6)	1.374 90(6)
c / nm	2.679 61(15)	1.982 77(9)
$\beta / (^\circ)$	102.260(1)	98.287(1)
V / nm^3	3.875 7(4)	8.112 2(6)
Z	4	8
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.401	1.362
Absorption coefficient / mm^{-1}	0.765	0.732
θ range / $(^\circ)$	2.90~27.19	2.75~27.20
$F(000)$	1 696	3 456
Reflection collected, unique	90 911, 17 135	139 569, 17 990
Data, restraint, parameter	17 135, 16, 956	17 990, 0, 973
R_{int}	0.039 5	0.108 9
Goodness-of-fit (GOF) on F^2	1.072	1.043
$R_1, wR_2 [I > 2\sigma(I)]$	0.062 9, 0.135 7	0.071 4, 0.119 3
R_1, wR_2 (all data)	0.094 8, 0.151 7	0.160 0, 0.146 0
Largest difference peak and hole / $(\text{e} \cdot \text{nm}^{-3})$	574 and -331	536 and -353

Table 2 Selected bond lengths (nm) and angles $(^\circ)$ for **1** and **2**

Complex 1					
Cu1-N1	0.207 7(4)	Cu1-N2	0.207 5(4)	Cu1-P1	0.224 08(15)
Cu1-P2	0.223 78(15)	Cu1...O1	0.292 1(6)	Cu2-N3	0.208 5(4)
Cu2-N4	0.208 2(4)	Cu2-P3	0.223 67(15)	Cu2-P4	0.223 89(14)
Cu2...O3	0.294 8(5)				
N1-Cu1-N2	80.01(18)	N1-Cu1-P1	110.76(14)	N1-Cu1-P2	125.85(12)
N2-Cu1-P1	121.97(12)	N2-Cu1-P2	116.14(13)	P1-Cu1-P2	102.70(6)
N3-Cu2-N4	79.61(17)	N3-Cu2-P3	127.81(12)	N3-Cu2-P4	107.69(14)
N4-Cu2-P3	118.05(13)	N4-Cu2-P4	122.61(12)	P3-Cu2-P4	101.84(6)

Continued Table 2

Complex 2					
Cu1-N1	0.205 8(3)	Cu1-N2	0.213 1(3)	Cu1-P1	0.222 79(11)
Cu1-P2	0.225 74(11)	Cu1...O1	0.299 8(3)	Cu2-N3	0.205 8(3)
Cu2-N4	0.212 1(3)	Cu2-P3	0.222 97(11)	Cu2-P4	0.224 86(11)
Cu2...O3	0.298 1(3)				
N1-Cu1-N2	78.69(11)	N1-Cu1-P1	117.19(9)	N1-Cu1-P2	115.43(9)
N2-Cu1-P1	125.02(8)	N2-Cu1-P2	104.29(8)	P1-Cu1-P2	112.25(4)
N3-Cu2-N4	79.72(12)	N3-Cu2-P3	124.00(9)	N3-Cu2-P4	111.60(9)
N4-Cu2-P3	107.53(9)	N4-Cu2-P4	117.04(9)	P3-Cu2-P4	112.92(4)

2 Results and discussion

2.1 Synthesis and characterization

In order to understand the effect of the methylene chain distance of auxiliary diphosphine ligand on the structures and spectral properties, mononuclear Cu (I) heteroleptic complexes **1** and **2** (Scheme 1) were prepared by the reaction of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ with mmbpy and diphosphine (dppp and dppb) in a 1:1:1 molar ratio. Complexes **1** and **2** show a strong absorption peak at 1 731 and 1 733 cm^{-1} , respectively, originating from the carbonyl stretching vibration ($\nu_{\text{C=O}}$) of the methoxycarbonyl group. Another strong absorption peak is observed at 1 093 and 1 096 cm^{-1} for **1** and **2**, respectively, attributed to the Cl-O stretching vibration of the perchlorate anion.

The exact structures of complexes **1** and **2** were established by single-crystal X-ray crystallography. Complexes **1** and **2** crystallize in the monoclinic system, space group Pc and $P2_1/c$, respectively. As

shown in Fig.1, the Cu(I) ions of **1** and **2** are four-coordinate by two N atoms of the 2,2'-bipyridyl ring and two P atoms from a chelating diphosphine ligand (dppp and dppb), which generate a distorted N_2P_2 tetrahedral arrangement with the N-Cu-N angle ($78.69^\circ \sim 80.01^\circ$) obviously deviating from the idealized value ($109^\circ 28'$). The average values of P-Cu-P angles are $102.27(6)^\circ$ and $112.59(4)^\circ$ for **1** and **2**, respectively, which are in reasonable agreement with the methylene chain distances, suggesting that the methylene chain distance of auxiliary diphosphine ligand has an impact on the P-Cu-P bond angle. Moreover, it is noted that the 2,2'-bipyridyl rings of two mmbpy ligands of two adjacent cations are basically parallel and show a favorable pairwise π - π stacking in **1**. The inter-bipyridyl separations are in the range of 0.325~0.395 nm, indicating the presence of a weak π - π interaction between intermolecular two adjacent mmbpy ligands^[24]. However, similar π - π stacking interaction is not observed in the crystal lattice of **2**.

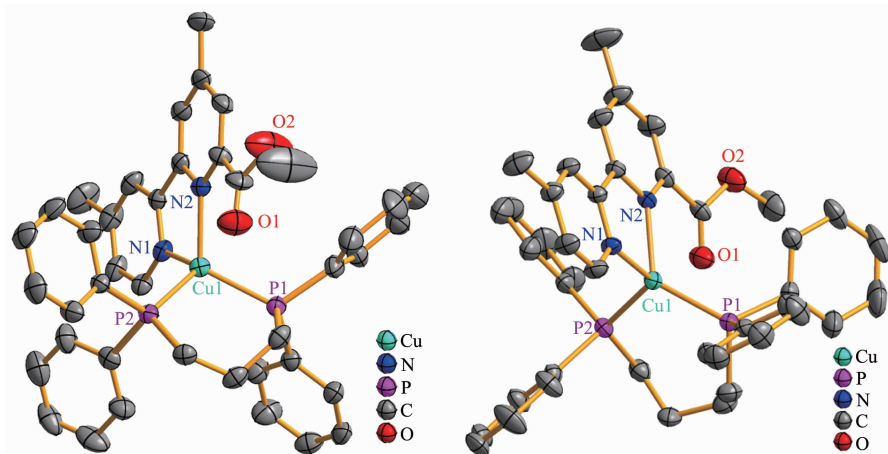


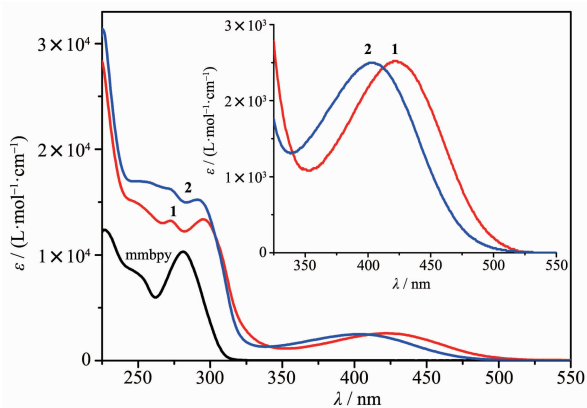
Fig.1 Molecular structures of the cations of **1** (left) and **2** (right) with 30% probability ellipsoids

2.2 Photophysical properties

The absorption spectra of the free ligand mmbpy and its Cu(I) derivatives **1** and **2** were investigated in CH_2Cl_2 solution at room temperature. As depicted in Fig.2, the mmbpy ligand gives multiple absorption peaks in the UV region (<325 nm), attributed to the ligand-centered ${}^1\pi\pi^*$ transitions. Two mononuclear Cu(I) complexes **1** and **2** display several strong absorption peaks in the 225 ~350 nm region; those are assigned to the spin-allowed ${}^1\pi\pi^*$ transitions of both mmbpy and diphosphine ligands, which are slightly red-shifted, due to the more-extended π -conjugation, relative to the free mmbpy ligand. In addition, a relatively weak low-energy broad absorption band is also clearly observed at 423 and 403 nm for **1** and **2**, respectively. The slightly stronger electron-donating dppb in place of dppp can raise the HOMO level localized at the Cu(I) center mixed with some contributions of diphosphine and less influence the LUMO level located on the mmbpy ligand, which results in a smaller HOMO-LUMO energy gap and a lower energy of absorption. Besides, it has been reported that a larger P-Cu-P angle can reduce the $d\sigma^*$ interactions and increase the energy required for MLCT excitation^[25-26]. It is noted that the low-energy absorption ($\lambda_{\text{max}}=403$ nm) of **2** is blue-shifted (not red-shifted) by 20 nm, compared to that ($\lambda_{\text{max}}=423$ nm) of **1**. Therefore, it is suggested that the weak low-energy absorptions of **1** and **2** are more markedly influenced

by the P-Cu-P bond angle and not the electron-donating properties of diphosphine, and these low-energy absorptions can be tentatively attributed to the charge transfer transitions with appreciable metal-to-ligand charge transfer (${}^1\text{MLCT}$, $\text{Cu} \rightarrow \text{diimine}$) character^[25-27].

The emission properties of **1** and **2** were investigated at room temperature in degassed CH_2Cl_2 solution and using powder samples. Unfortunately, any detectable emission is unobserved for **1** and **2** in CH_2Cl_2 solution at ambient temperature, similar to their Cu(I) derivatives without the methyl substituents on the 2,2'-bipyridyl ring, perhaps due to fast structural relaxation occurring in degassed solution^[28-29]. It is noteworthy that complexes **1** and **2** display a broad and unstructured solid-state emission profile (Fig.3), maximized at 575 and 561 nm with the quantum yields of 0.176 and 0.094 and the emission lifetimes of 158.4 and 132.7 μs , respectively. The solid-state emission of **2** (561 nm) is blue-shifted by 14 nm relative to that of **1** (575 nm), which is similar to the wavelength trend of weak low-energy absorptions of **1** (423 nm) and **2** (403 nm) in CH_2Cl_2 solution, indicating that the emissions of **1** and **2** are also affected by both the P-Cu-P angle and the electron-donating properties of diphosphine. Actually, the emission of **1** is also influenced by weak π - π stacking interactions between intermolecular two adjacent mmbpy ligands of **1** revealed via X-ray crystallography, which lower the energy level of its LUMO localized on the mmbpy ligand and less influence its HOMO localized at the Cu(I) and P



Inset: absorption spectra of complexes **1** and **2** in CH_2Cl_2 solution from 325 to 550 nm

Fig.2 Absorption spectra of mmbpy and complexes **1** and **2** in CH_2Cl_2 solution

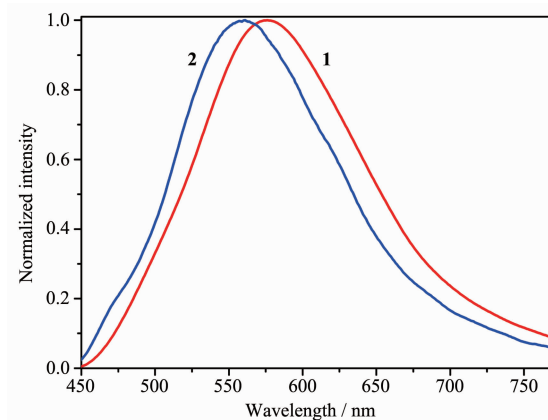


Fig.3 Emission spectra of **1** and **2** in the solid state

atoms. Moreover, it is noted that complexes **1** and **2** with two methyl substituents on the 2,2'-bipyridyl ring are all emissive with moderate quantum yields (0.176 and 0.094) in the solid state at ambient temperature, whereas their Cu(I) derivatives with no methyl substituents on the 2,2'-bipyridyl ring are non-emissive or only show very weak solid-state emissions^[28-29], suggesting that the introduction of two methyl substituents into the 2,2'-bipyridyl ring is effective for enhancing luminescence properties of Cu(I) complexes.

3 Conclusions

We have synthesized and characterized two new mononuclear Cu(I) diphosphine complexes with 6-methoxycarbonyl-4,4'-dimethyl-2,2'-bipyridine. It is revealed that two Cu(I) complexes all show distorted N₂P₂ tetrahedral geometries with varied P-Cu-P angles regulated by auxiliary diphosphine ligands. The two Cu(I) complexes are all emissive in the solid state at ambient temperature, and their photophysical properties are more remarkably influenced by the P-Cu-P angle than the methylene chain length of diphosphine. It is also shown that the introduction of two methyl substituents into the 2,2'-bipyridyl ring is effective for improving luminescence properties of Cu(I) complexes. We believe that the results presented herein might provide new insight into the design and synthesis of highly efficient Cu(I) phosphine complexes with functionalized 6-alkoxycarbonyl-2,2'-bipyridine ligands.

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