

基于功能化 6-甲氧羰基-2,2'-联吡啶配体的 铜(I)铁(II)异金属双核配合物

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摘要: 以 $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ 、6-甲氧羰基-2,2'-联吡啶(mbpy)、6-甲氧羰基-4,4'-二甲基-2,2'-联吡啶(mmbpy)和 1,1'-双(二苯基膦)二茂铁(dppf)为起始原料, 合成得到了 2 个新的铜(I)铁(II)异金属双核配合物: $[\text{Cu}(\text{mbpy})(\text{dppf})]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$ (**1**)和 $[\text{Cu}(\text{mmbpy})(\text{dppf})]\text{ClO}_4$ (**2**)。X 射线单晶衍射分析表明, 配合物 **1** 和 **2** 均为铜(I)铁(II)异金属双核配合物, 并且均表现为四配位变形四面体构型。配合物 **1** 和 **2** 在 330~520 nm 波长范围有一个弱的低能量宽吸收峰, 其主要来源于金属到配体的电荷转移跃迁(MLCT)。由于 1,1'-双(二苯基膦)二茂铁的引入, 配合物 **1** 和 **2** 常温下在溶液和固态时均未检测到任何发光。

关键词: 铜(I)配合物; 1,1'-双(二苯基膦)二茂铁; 甲氧羰基; 甲基化; 晶体结构

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Cu(I)Fe(II) Heterobimetallic Complexes Based on Functionalized 6-Methoxycarbonyl-2,2'-bipyridine Ligands

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Abstract: Two new Cu(I)Fe(II) heterobimetallic complexes, $[\text{Cu}(\text{mbpy})(\text{dppf})]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$ (**1**) and $[\text{Cu}(\text{mmbpy})(\text{dppf})]\text{ClO}_4$ (**2**), were synthesized by using $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$, 6-methoxycarbonyl-2,2'-bipyridine (mbpy), 6-methoxycarbonyl-4,4'-dimethyl-2,2'-bipyridine (mmbpy), and 1,1'-bis(diphenylphosphino)ferrocene (dppf) as the starting materials. As revealed by single-crystal X-ray diffraction analysis, complexes **1** and **2** are all Cu(I)Fe(II) heterobimetallic species and exhibit tetra-coordinated and distorted tetrahedral configuration. Complexes **1** and **2** all show a weak low-energy broad absorption in the wavelength range of 330~520 nm, which is mainly assigned to metal-to-ligand charge-transfer (MLCT) transition. No emission is detected in solution and solid states at room temperature for **1** and **2**, due to the introduction of 1,1'-bis(diphenylphosphino)ferrocene. CCDC: 1835415, **1**; 1835416, **2**.

Keywords: copper(I) complex; 1,1'-bis(diphenylphosphino)ferrocene; methoxycarbonyl; methylation; crystal structure

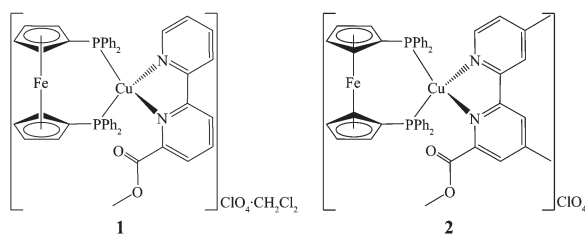
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0 Introduction

Much effort has been devoted to the development of the metal-based luminophors with the emission wavelengths in the entire visible region, particularly the late transition-metal emissive complexes^[1-3], and the most representative examples are d^6 - and d^8 -metal complexes of the third-row transition metal series such as Os, Ir, and Pt^[4-6]. However, because of the high cost and limited availability of these noble metals, more interest has been paid to explore inexpensive alternatives. Recently, copper(I) complexes have received considerable attention, due to their promising potential in materials science and the high relative abundance and low toxicity of copper metal as compared to noble metal, such as Ir, Os, and Pt^[7-16]. In this context, Cu(I) heteroleptic complexes have been most widely investigated, particularly Cu(I)-diimine-phosphine complexes. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) has been extensively used in catalysis and materials science as a very useful chelating or bridging ligand, and the introduction of dppf can bring the metal-based system desirable stability, steric bulk, and oxidizability^[17]. Thus, we expect to synthesize new Cu(I)Fe(II) heterobimetallic complexes using dppf and functionalized 6-methoxycarbonyl-2,2'-bipyridine ligands. Herein, we will describe the synthesis and characterization of two new Cu(I) heterodinuclear complexes with 1,1'-bis(diphenylphosphino)ferrocene (dppf) and functionalized 6-methoxycarbonyl-2,2'-bipyridine ligands (Scheme 1).



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

1 Experimental

1.1 Materials and measurements

All reactions were performed under a N_2 atmosphere, using anhydrous solvents or solvents

treated with an appropriate drying reagent. Commercially available reagents were used without further purification unless otherwise stated. $[Cu(CH_3CN)_4]ClO_4$, 6-methoxycarbonyl-2,2'-bipyridine (mbpy), and 6-methoxycarbonyl-4,4'-dimethyl-2,2'-bipyridine (mmbpy) were synthesized according to the literature methods^[18-19]. Infrared (IR) spectra were recorded on a Bruker Optics ALPHA FT-IR spectrometer using KBr pellets. C, H and N elemental analyses were conducted on a PerkinElmer model 240C elemental analyzer, where all the crystal samples are used after grinding and drying under vacuum. UV-Vis absorption spectra in CH_2Cl_2 solution were measured on a Shimadzu UV-2550 spectrometer. Crystal structures were determined on a Bruker D8 QUEST diffractometer.

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 $[Cu(mbpy)(dppf)]ClO_4 \cdot CH_2Cl_2$ (**1**)

A solution of $[Cu(CH_3CN)_4]ClO_4$ (19.6 mg, 0.06 mmol) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) (33.3 mg, 0.06 mmol) in CH_2Cl_2 (3 mL) was stirred for 1 h at room temperature; mbpy (14.5 mg, 0.06 mmol) was then added and this mixture was stirred for another 3 h. The solvent was evaporated to dryness at reduced pressure. The resultant residue was again dissolved in CH_2Cl_2 , and slow diffusion of petroleum ether into the above solution gave yellow crystals of **1** (51.8 mg, 0.051 mmol, 85%). Anal. Calcd. for $C_{46}H_{38}ClCuFeN_2O_6P_2$ (%): C, 59.31; H, 4.11; N, 3.01. Found (%): C, 59.01; H, 4.23; N, 3.21. IR (KBr, cm^{-1}): 3 454 (m), 3 056(w), 2 952(w), 1 732(s, $-CO_2CH_3$), 1 633(w), 1 592 (m), 1 480(m), 1 436(s), 1 322(m), 1 284(m), 1 250(m), 1 198(w), 1 157(m), 1 093(vs, ClO_4^-), 1 030 (m), 827(w), 752(s), 699(s), 627(m), 493(s).

1.2.2 $[Cu(mmbpy)(dppf)]ClO_4$ (**2**)

Complex **2** was prepared according to the procedure for **1**, using $[Cu(CH_3CN)_4]ClO_4$ (19.6 mg, 0.06 mmol), dppf (33.3 mg, 0.06 mmol), and mmbpy (14.8 mg, 0.061 mmol). Yellow crystals were afforded by slow diffusion of petroleum ether into a CH_2Cl_2 solution of **2** (40.1 mg, 0.048 mmol, 80%). Anal. Calcd. for $C_{48}H_{42}ClCuFeN_2O_6P_2$ (%): C, 60.08; H, 4.41; N, 2.92.

Found(%): C, 60.24; H, 4.37; N, 2.86. IR (KBr, cm^{-1}): 3 845(w), 3 453(s), 3 055(w), 2 954(w), 1 735(s, $-\text{CO}_2\text{CH}_3$), 1 479(m), 1 436(s), 1 389(w), 1 344(m), 1 267(m), 1 222(s), 1 161(m), 1 094(vs, ClO_4^-), 1 031(m), 893(w), 828(w), 746(s), 698(s), 625(m), 493(s).

1.3 X-ray crystallography

Single-crystal X-ray diffraction data for **1** and **2** were performed on a Bruker D8 QUEST diffractometer at room temperature using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). Structures were solved by direct methods and refined by full-matrix least-squares technique on F^2 using the SHELXL-97

software package^[20]. The heavy atoms were located from E-map and other non-hydrogen atoms were located in subsequent difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . The hydrogen atoms of the ligands and solvent molecules were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The crystallographic data and structure refinement details of **1** and **2** are provided in Table 1, and the selected bond lengths and angles are listed in Table 2.

CCDC: 1835415, **1**; 1835416, **2**.

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

Complex	1	2
Empirical formula	$\text{C}_{47}\text{H}_{40}\text{Cl}_3\text{CuFeN}_2\text{O}_6\text{P}_2$	$\text{C}_{48}\text{H}_{42}\text{ClCuFeN}_2\text{O}_6\text{P}_2$
Formula weight	1 016.49	959.62
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	1.089 89(16)	1.727 29(10)
b / nm	1.109 22(17)	1.420 12(7)
c / nm	1.925 9(3)	1.759 41(9)
$\alpha / (^\circ)$	77.217(4)	
$\beta / (^\circ)$	81.909(4)	92.611 0(10)
$\gamma / (^\circ)$	89.575(4)	
V / nm^3	2.247 3(6)	4.311 3(4)
Z	2	4
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.502	1.478
Absorption coefficient / mm^{-1}	1.097	1.019
θ range / $(^\circ)$	2.91~27.40	2.93~27.48
$F(000)$	1 040	1 976
Reflection collected, unique	38 247, 10 163	74 514, 9 839
Data, restraint, parameter	10 163, 4, 577	9 839, 0, 562
R_{int}	0.052 1	0.034 5
Goodness-of-fit (GOF) on F^2	1.039	1.035
$R_1, wR_2 [I > 2\sigma(I)]$	0.079 2, 0.206 1	0.043 2, 0.106 5
R_1, wR_2 (all data)	0.117 6, 0.239 4	0.065 0, 0.120 6
Largest difference peak and hole / $(\text{e} \cdot \text{nm}^{-3})$	2 884 and -976	751 and -645

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

Complex 1					
Cu1-N1	0.217 3(5)	Cu1-N2	0.212 3(4)	Cu1-P1	0.228 37(14)
Cu1-P2	0.230 54(13)	Cu1...O1	0.291 4(5)		
N1-Cu1-N2	77.95(17)	N1-Cu1-P1	120.62(13)	N1-Cu1-P2	96.65(12)
N2-Cu1-P1	120.53(12)	N2-Cu1-P2	119.44(12)	P1-Cu1-P2	113.78(5)

Continued Table 2

Complex 2					
Cu1-N1	0.213 5(2)	Cu1-N2	0.208 7(2)	Cu1-P1	0.225 86(7)
Cu1-P2	0.228 98(7)	Cu1...O1	0.280 7(2)		
N1-Cu1-N2	78.57(8)	N1-Cu1-P1	120.29(6)	N1-Cu1-P2	98.95(6)
N2-Cu1-P1	119.78(6)	N2-Cu1-P2	117.95(6)	P1-Cu1-P2	114.38(3)

2 Results and discussion

2.1 Synthesis and characterization

To investigate the influence of 1,1'-bis(diphenylphosphino)ferrocene (dppf) and the introduction of two methyl groups into the 2,2'-bipyridyl ring on the structures and photophysical properties of Cu(I) complexes, two heterodinuclear Cu(I) complexes **1** and **2** (Scheme 1) were synthesized by treating $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ with dppf and diimine (mbpy and mmbpy) ligands in a 1:1:1 molar ratio. In the IR spectra, a strong absorption peak is observed at 1 732 and 1 735 cm^{-1} for **1** and **2**, respectively, which originates from the carbonyl stretching vibration ($\nu_{\text{C=O}}$) of the methoxycarbonyl group. Moreover, another strong absorption peak is also observed at 1 093 and 1 096 cm^{-1} for **1** and **2**, respectively, attributable to the Cl-O stretching vibration of the perchlorate anion.

The molecular structures of **1** and **2** were established by single-crystal X-ray crystallography. The molecular structures of the cations of **1** and **2** are shown in Fig.1. Complexes **1** and **2** crystallize in the $P\bar{1}$

space group of triclinic crystal system and the $P2_1/c$ space group of the monoclinic crystal system, respectively. In addition, complex **1** includes one disordered CH_2Cl_2 solvent molecule, while complex **2** contains one disordered ClO_4^- anion. As depicted in Fig.1, the Cu(I) cations are all tetra-coordinated and in a distorted N_2P_2 tetrahedral array formed by two N donors of the 2,2'-bipyridyl fragment and two P atoms of dppf, where the N-Cu-N bond angles are $77.95(17)^\circ$ and $78.57(8)^\circ$ and the P-Cu-P bond angles are $113.78(5)^\circ$ and $114.38(3)^\circ$ for **1** and **2**, respectively, markedly deviating from the idealized bond angle of $109^\circ 28'$. The Cu-N and Cu-P distances are within the normal range^[21-31]. The Cu1-N1 bond distances of **1** (0.217 3(5) nm) and **2** (0.213 5(2) nm) are slightly longer than the Cu1-N2 bond lengths of **1** (0.212 3(4) nm) and **2** (0.208 7(2) nm), owing to the addition of the methoxycarbonyl group. Moreover, the Cu-N bond lengths of **1** (0.217 3(5) and 0.212 3(4) nm) are somewhat longer than those of **2** (0.213 5(2) and 0.208 7(2) nm), consistent with the variation of the Cu1...O1 distance of **1** (0.291 4(5) nm) and **2** (0.280 7(2) nm),

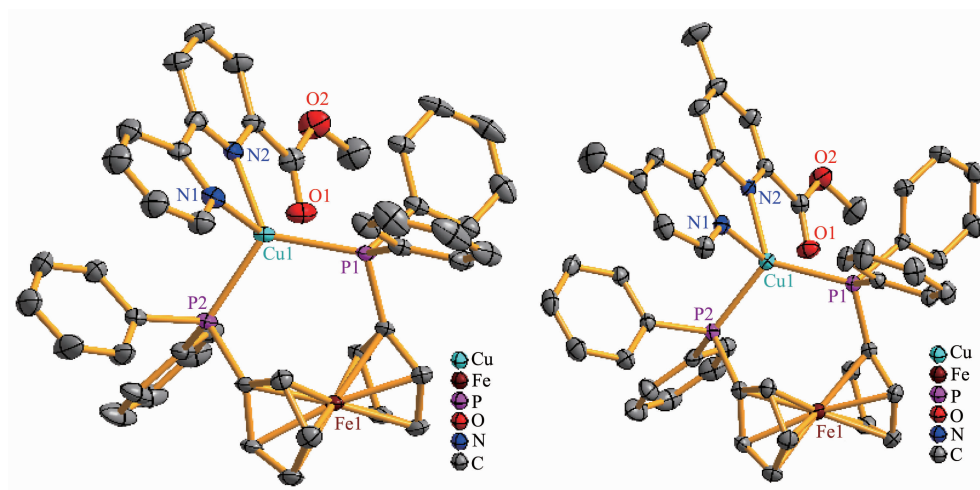


Fig.1 Molecular structures of the cations of **1** (left) and **2** (right) with 30% probability ellipsoids

as a result of the introduction of two methyl groups into the 2,2'-bipyridyl ring. The Cu-N lengths of **1** and **2** are all longer than the Cu-N lengths of previously reported Cu(I) species with functionalized 6-alkoxycarbonyl-2,2'-bipyridine ligands^[21-23], perhaps due to the significant influence of dppf introduced into the [Cu(N[^]N)]⁺ unit. However, the Cu-P lengths of **1** and **2** are almost similar, implying that the introduction of the two methyl groups has a negligible influence on the [Cu(dppf)]⁺ fragment.

2.2 Photophysical properties

The UV-Vis absorption spectra of **1** and **2** were measured in CH₂Cl₂ solution at room temperature. As depicted in Fig.2, two Cu(I)Fe(II) complexes exhibit a broad absorption band at 235~330 nm, which is assigned to the ¹π-π* transitions of functionalized 6-methoxycarbonyl-2,2'-bipyridine and dppf ligands. Moreover, a relatively weak broad absorption band ($\epsilon < 10^4$ L·mol⁻¹·cm⁻¹) is also clearly observed in the range of 330~520 nm for **1** and **2**, which can be tentatively ascribed to the charge transfer transitions with appreciable metal-to-ligand charge transfer (MLCT, Cu(I)/Fe(II)→diimine) character^[21-31]. It is noted that the low-energy absorption of **2** ($\lambda_{\text{max}}=396$ nm) is blue-shifted by 14 nm relative to that of **1** ($\lambda_{\text{max}}=410$ nm), which is attributable to the introduction of two electron-donating methyl groups into the 2,2'-bipyridyl ring, increasing the LUMO level and slightly affecting the HOMO level, and thus leading to a larger HOMO-LUMO energy gap and a higher energy absorption of **2**. Unfortunately, any detectable emission is unobserved in solution and solid states for **1** and **2** at room

temperature, suggesting that the potentially luminescent MLCT state is possibly quenched by a photo-induced fast intramolecular energy transfer to the ferrocene unit^[32].

3 Conclusions

We have synthesized and characterized two new Cu(I)Fe(II) heterobimetallic complexes with functionalized 6-methoxycarbonyl-2,2'-bipyridine and 1,1'-bis(diphenylphosphino)ferrocene ligands. It is revealed that a distorted tetrahedral N₂P₂ geometry around Cu(I) is formed by two N donors of functionalized 6-methoxycarbonyl-2,2'-bipyridine and two P atoms of 1,1'-bis(diphenylphosphino)ferrocene. The two Cu(I)Fe(II) complexes are all fairly air-stable in solution and solid state at room temperature. No detectable emission is observed in solution and solid states at room temperature, possibly because the potentially emissive MLCT state is quenched by a photo-induced intramolecular energy transfer to the ferrocene unit.

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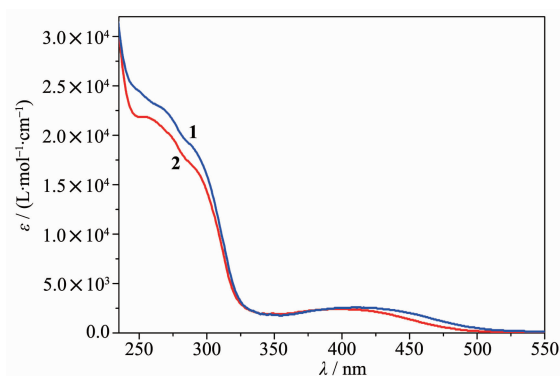


Fig.2 Absorption spectra of **1** and **2** in CH₂Cl₂ solution

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