

# Synthesis, Characterization, Spectroscopic and Electrochemical Properties of New Mono- and Binuclear Copper(I) Complexes with Substituted 2,2'-Bipyridine

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The mono- and binuclear Cu(I) complexes with substituted 2,2'-bipyridine and iodide ligands,  $[\text{CuL}_2]\text{BF}_4$  (L = 4-methoxycarbonyl-6-(4-methylphenyl)-2,2'-bipyridine (**a**), 6-(4-hydroxymethylphenyl)-2,2'-bipyridine (**b**) and 6-(4-methoxyphenyl)-2,2'-bipyridine (**c**)) and  $[\text{Cu}_2(\mu\text{-I})_2\text{L}_2]$  were prepared, and the crystal structures of the complexes were obtained from single-crystal X-ray diffractometric analysis. The spectroscopic properties of the complexes in dichloromethane are dominated by low energy MLCT bands from 360 to 650 nm. The electrochemical studies of mononuclear complexes reveal that the complexes have stable copper(I) state.

**Keywords** copper(I) complex, substituted bipyridine, crystal structure, spectroscopy, cyclic voltammogram

## Introduction

Copper(I) complexes have received much attention for their being less expensive and environmentally friendly, various coordination geometry, rich photochemical and photophysical properties.<sup>1-7</sup> It is well known that copper complexes with diimine (2,2'-bipyridine, 1,10-phenanthroline and their substituted derivatives designated as diimine) generally exhibit low energy metal-to-ligand charge-transfer (MLCT) states located in the regions of 350—650 nm ( $\epsilon \approx 10^3\text{—}10^4 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). The complexes only with phenanthroline ligand that possesses alkyl or aryl substituents at the 2- and 9-positions display weak photoluminescence.<sup>1-3</sup> Meanwhile bulky substituents in the phenanthroline ring greatly improve the quantum yield by both inhibiting flattening distortion and suppressing ligand-addition reactions in the excited state.<sup>8,9</sup> Most of the structure studies of Cu(I) complexes with phenanthroline-based ligands have been reported before, but structure of copper(I) complexes with substituted 2,2'-bipyridine is relatively little known.<sup>10-12</sup> However the complexes containing bipy-based and planar aromatic phen-based ligands could have significantly different coordination geometries, spectroscopic and electrochemical properties due to the bipy that can either sustain a substantial dihedral twist between the aromatic rings or chelate to metal. Here we report the synthesis, structural characterization, spectroscopic and electrochemical properties of mononuclear  $[\text{CuL}_2]\text{BF}_4$  and dinuclear  $[\text{Cu}_2(\mu\text{-I})_2\text{L}_2]$  complexes.

## Experimental

All reactions were performed under a nitrogen atmosphere. Solvents were distilled using standard techniques and saturated with nitrogen before use. CuI was purchased from Aldrich.  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$  and ligand L were prepared by a modification of the literature method.<sup>13,14</sup>

### Syntheses of $[\text{CuL}_2]\text{BF}_4$ (**1a—1c**)

A mixture of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$  and ligand (L) (L = 4-methoxycarbonyl-6-(4-methylphenyl)-2,2'-bipyridine, 6-(4-hydroxymethylphenyl)-2,2'-bipyridine and 6-(4-methoxyphenyl)-2,2'-bipyridine) with 1 : 2 stoichiometry in dichloromethane was stirred for 1 h under a nitrogen atmosphere at room temperature, respectively. The reaction mixture was concentrated in vacuum and the crude product was precipitated by adding diethyl ether. The solid was filtered and redissolved in a minimum of dichloromethane. The single crystal suitable for X-ray diffractometric analysis was obtained from a dichloromethane solution of the complexes by vapor diffusion with diethyl ether.

**1a:** (Scheme 1) Brown solid, yield 82%. Anal. calcd for  $\text{C}_{38}\text{H}_{32}\text{BCuF}_4\text{N}_4\text{O}_4$ : C 60.13, H 4.25, N 7.38; found C 60.45, H 4.03, N 7.22.

**1b:** Dark purple solid, yield 85%. Anal. calcd for  $\text{C}_{34}\text{H}_{28}\text{BCuF}_4\text{N}_4\text{O}_2$ : C 60.50, H 4.18, N 8.30; found C 60.32, H 4.01, N 8.11.

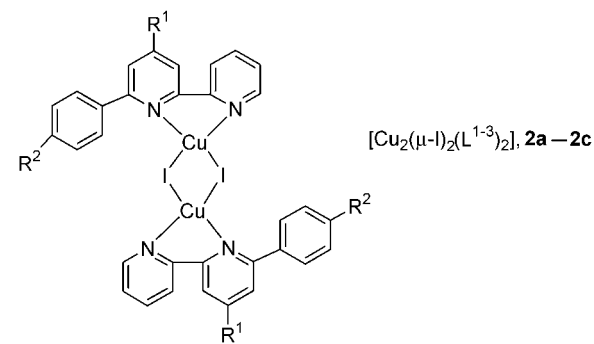
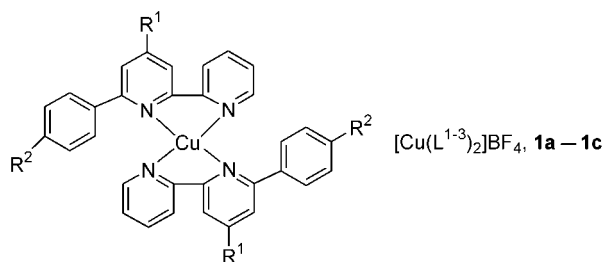
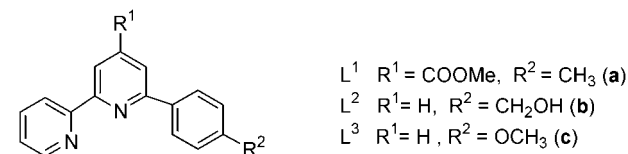
**1c:** Dark purple solid, yield 87%. Anal. calcd for  $\text{C}_{34}\text{H}_{28}\text{BCuF}_4\text{N}_4\text{O}_2$ : C 60.50, H 4.18, N 8.30; found C

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Received February 16, 2004; revised and accepted July 15, 2004.

Project supported by the National Natural Science Foundation of China (Nos. 50273045, 90210033), Chinese Government for support of Chinese Academy of Science Hundred Talents and the foundation for Key Project of Yunnan Provincial Science and Technology Commission (No. 2001E0005Z).

60.32, H 4.04, N 8.52.

## Scheme 1

Syntheses of  $[\text{Cu}_2(\mu\text{-I})_2(\text{L})_2]$  (**2a—2c**)

A mixture of ligand (L) and CuI in the equal molar ratio was dissolved in 30 mL of dichloromethane at room temperature. After being stirred for 20 h, the resulting solution was filtered. Addition of diethyl ether after concentration of the solution afforded the product as a brown solid that was filtered, and washed with diethyl ether. The recrystallization of crude product by slow diffusion of diethyl ether into a dichloromethane solution gave the single crystal for X-ray analysis.

**2a:** (Scheme 1) Brown solid, yield 67%. Anal. calcd for  $\text{C}_{38}\text{H}_{32}\text{Cu}_2\text{I}_2\text{N}_4\text{O}_4$ : C 46.12, H 3.26, N 5.66; found C 45.93, H 3.30, N 5.61.

**2b:** Purple red solid, yield 73%. Anal. calcd for  $\text{C}_{34}\text{H}_{28}\text{Cu}_2\text{I}_2\text{N}_4\text{O}_2$ : C 45.10, H 3.12, N 6.19; found C 45.24, H 3.01, N 6.03.

**2c:** Purple red solid, yield 65%. Anal. calcd for  $\text{C}_{34}\text{H}_{28}\text{Cu}_2\text{I}_2\text{N}_4\text{O}_2$ : C 45.10, H 3.12, N 6.19; found C 44.95, H 3.20, N 6.23.

## X-ray crystallography

Crystals of complexes **1a** or **2b** were obtained by vapor diffusion of diethyl ether into  $\text{CH}_2\text{Cl}_2$  solution. A summary of the crystallographic parameters and data is given in Table 1. Diffraction data were collected at room temperature with graphite monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.071073$  nm) on a Rigaku R-AXIS RAPID IP X-ray diffractometer. An absorption correc-

tion was applied by correction of symmetry-equivalent reflections using the ABSCOR program. The structure was solved by direct methods using the SHELXS 97 program and refined by full-matrix least squares on  $F^2$  using the SHELXL 97 program. The non-hydrogen atoms were refined anisotropically. Crystallographic data for **1a** and **2b** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication with No. CCDC-223957 (**1a**) and CCDC-223958 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21 1EZ, UK (fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1 Selected crystallographic data for complexes **1a** and **2b**

Complexes	<b>1a</b>	<b>2b</b>
Formula	$\text{C}_{38}\text{H}_{32}\text{BCuF}_4\text{N}_4\text{O}_4$	$\text{C}_{34}\text{H}_{28}\text{Cu}_2\text{I}_2\text{N}_4\text{O}_2$
Formula weight	759.03	905.48
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2(1)$	$P2(1)/c$
Color	Brown	Purple red
Crystal size/mm	$0.40 \times 0.25 \times 0.20$	$0.33 \times 0.27 \times 0.25$
<i>a</i> /nm	2.9538(6)	0.98442(2)
<i>b</i> /nm	0.73784(15)	2.13940(6)
<i>c</i> /nm	3.2247(6)	0.79623(3)
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	110.0870(3)
$\gamma/^\circ$	90	90
$V/\text{nm}^3$	7.028(2)	1.57491(8)
<i>Z</i>	8	4
$D_c/(\text{Mg}\cdot\text{m}^{-3})$	1.435	1.909
<i>T</i> /K	293(2)	293(2)
Refl. No.	19634	3608
$\theta/^\circ$	2.34—25.03	2.20—27.48
$\mu/(\text{mm}^{-1})$	0.690	3.349
<i>F</i> (000)	3120	880
$R_1, wR_2 [I > 2\sigma(I)]$	0.0674, 0.1474	0.0377, 0.0766
Goodness for fit on $F^2$	0.929	0.761

## Electronic absorption spectra and electrochemical measurements

Absorption spectra were recorded on a Hitachi U-3010 spectrophotometer and cyclic voltammetry was performed using a Solartron SI 1287 electrochemical interface in neat dichloromethane containing  $0.1 \text{ mol}\cdot\text{L}^{-1}$  *n*-Bu<sub>4</sub>NClO<sub>4</sub>. The Pt disc was used as a working electrode against SCE (saturated calomel electrode) and Pt coil as counter electrode. The concentrations of copper(I) compounds were about  $1.0 \text{ mmol}\cdot\text{L}^{-1}$ .

## Results and discussion

### Synthesis

The complexes described in this study are illustrated in Scheme 1. All the complexes can be easily obtained in good yield by reaction of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{BF}_4$  or  $\text{CuI}$  with corresponding ligand, and are air-stable in most solvents such as  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$  or  $\text{CH}_3\text{OH}$ . The solution of complexes **1b**, **1c**, **2b** and **2c** in  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  is dark red while complexes **1a** and **1b** are dark green. All the complexes were characterized by elemental analysis.

### Crystal structure of complexes **1a** and **2b**

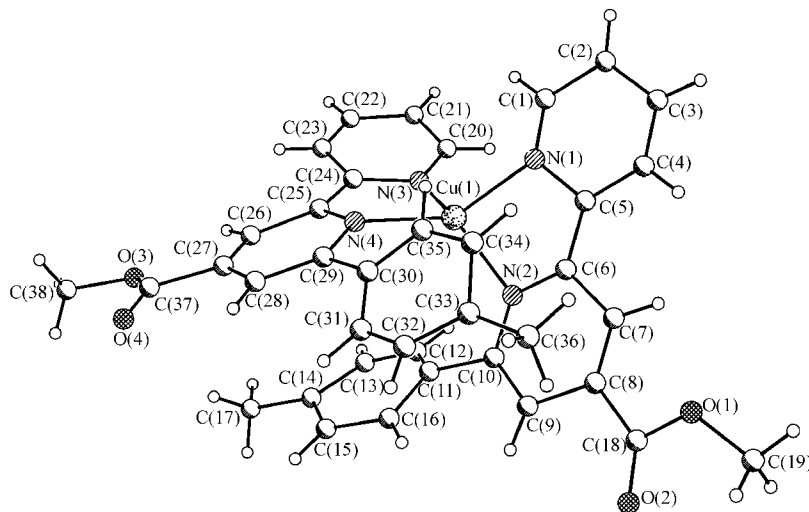
A perspective view with atom numbering scheme of the cation **1a** containing two crystallographic independent molecules and **2b** molecule are given in Figures 1 and 2, and their selected bond lengths and angles are compiled in Table 2. For the complex **1a** the copper center adopts a twisted tetrahedral coordination geometry, with the dihedral angles of  $63.6(6)^\circ$  and  $56.8(6)^\circ$  (dihedral angle is  $0^\circ$  for planar complexes and  $90^\circ$  for tetrahedral complexes) between two  $\text{CuNN}$  planes, which are less than the typical  $70^\circ$ – $80^\circ$  of  $\text{Cu}(\text{NN})_2$  ( $\text{NN}$ =substituted bipyridines and phenanthrolines).<sup>11,12</sup> The pendant aromatic rings are twist with the adjacent pyridine fragments (the torsion angles *ca.*  $41.2^\circ$ ,  $29.3^\circ$ ,  $49.8^\circ$ ,  $28.1^\circ$  respectively). The bipyridine units are not co-planar with dihedral angles varying from  $7.9^\circ$  to  $21.2^\circ$ . The  $\text{Cu—N}$  bond distances vary from 0.1942(12) to 0.2189(10) nm which are within the normal  $\text{Cu—N}$  distance of most  $[\text{Cu}(\text{NN})_2]^+$  complexes, where  $\text{NN}$  signifies substituted 2,2'-diimine). Compound **2b** has distorted tetrahedral configuration, and the major distortion arises from the wider  $\text{I}\#(1)\text{—Cu—N}(1)$  angle  $128.5(1)^\circ$  and the narrower  $\text{N}(1)\text{—Cu—N}(2)$   $79.5(2)^\circ$  due to the chelating and steric effect of bulky ligands with  $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$  group, resulting in the dihedral angle of  $84.82(15)^\circ$  between  $\text{CuN}_2$  and  $\text{CuI}_2$  planes. However, twist of  $\text{CuN}_2\text{I}_2$  core compared to that ( $\text{N}(3)\text{—Cu}(1)\text{—N}(2)$   $141.0(5)^\circ$ ) of  $\text{CuN}_4$  for **1a** indicates that the distortion

from pseudo-tetrahedral symmetry is more pronounced for **1a** than for **2b**. The bridging  $\text{Cu—I—Cu}$  linkage of complex **2b** shows a significant symmetry with  $\text{Cu—I}$  distances of 0.25955(8) and 0.26502(7) nm, and variation of  $\text{Cu—N}$  distance from 0.2060(4) to 0.2147(4) nm is similar to that observed in **1a**. Through the  $\text{Cu—I—Cu}$  bridging bond angle of  $72.93(2)^\circ$  is not much more acute than that of  $\text{Cu—I—Cu}$  of  $70.97(1)^\circ$  in  $(\text{CuIPCy}_3)_2$ ,<sup>15</sup> leading to a short  $\text{Cu}\cdots\text{Cu}$  contact of 0.3118 nm. The  $\text{I}^-$  ion

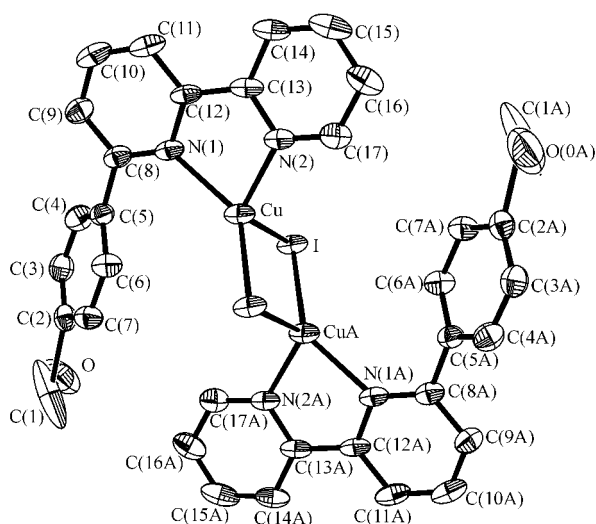
**Table 2** Selected bond lengths (nm) and angles ( $^\circ$ )

Complex <b>1a</b>			
$\text{Cu}(1)\text{—N}(3)$	0.2004(13)	$\text{Cu}(1)\text{—N}(4)$	0.2080(12)
$\text{Cu}(1)\text{—N}(2)$	0.2062(10)	$\text{Cu}(1)\text{—N}(1)$	0.2093(11)
$\text{Cu}(2)\text{—N}(6)$	0.1942(12)	$\text{Cu}(2)\text{—N}(5)$	0.2037(12)
$\text{Cu}(2)\text{—N}(7)$	0.1971(10)	$\text{Cu}(2)\text{—N}(8)$	0.2189(10)
$\text{N}(3)\text{—Cu}(1)\text{—N}(2)$	141.0(5)	$\text{N}(2)\text{—Cu}(1)\text{—N}(4)$	115.5(4)
$\text{N}(3)\text{—Cu}(1)\text{—N}(4)$	83.3(5)	$\text{N}(3)\text{—Cu}(1)\text{—N}(1)$	109.3(5)
$\text{N}(2)\text{—Cu}(1)\text{—N}(1)$	83.2(4)	$\text{N}(4)\text{—Cu}(1)\text{—N}(1)$	133.3(5)
$\text{N}(6)\text{—Cu}(2)\text{—N}(7)$	152.6(5)	$\text{N}(6)\text{—Cu}(2)\text{—N}(8)$	111.4(4)
$\text{N}(6)\text{—Cu}(2)\text{—N}(5)$	79.8(5)	$\text{N}(7)\text{—Cu}(2)\text{—N}(8)$	79.1(4)
$\text{N}(7)\text{—Cu}(2)\text{—N}(5)$	111.8(5)	$\text{N}(5)\text{—Cu}(2)\text{—N}(8)$	134.2(4)
Complex <b>2b</b>			
$\text{I—Cu}$	0.25955(8)	$\text{Cu—N}(1)$	0.2147(4)
$\text{I—Cu}\#1^a$	0.26502(7)	$\text{Cu—Cu}\#1$	0.3118(5)
$\text{Cu—N}(2)$	0.2060(4)		
$\text{Cu—I—Cu}\#1$	72.93(2)	$\text{N}(2)\text{—Cu—I}$	111.88(12)
$\text{N}(2)\text{—Cu—N}(1)$	79.53(17)	$\text{N}(1)\text{—Cu—I}$	118.06(11)
$\text{N}(2)\text{—Cu—I}\#1$	106.39(12)	$\text{I—Cu—I}\#1$	107.07(2)
$\text{N}(1)\text{—Cu—I}\#1$	128.45(11)		

<sup>a</sup>Symmetry code:  $1-x, 1-y, -z$ .



**Figure 1** Perspective drawing of one of the two independent units of **1a** cation.

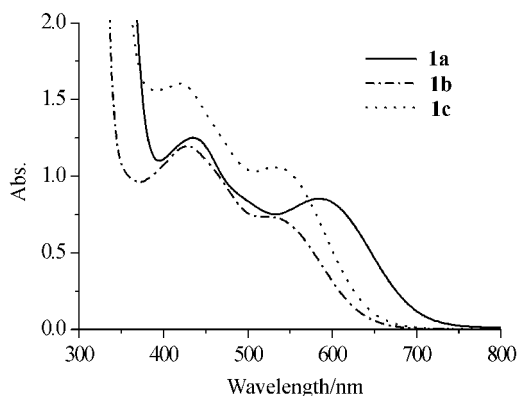


**Figure 2** Perspective drawing of the complex **2b**.

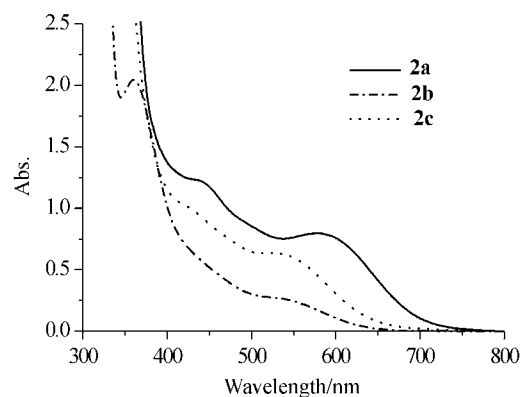
adopts a  $\mu_2$ -coordination mode that is similar to  $\text{Cu}_2\text{I}_2\text{L}_4$  ( $\text{L} = \text{pyridine}$  or  $\text{pyridine derivatives}$ ),<sup>16</sup>  $\text{Cu}_2\text{I}_2(\text{phen})_2$  and  $\text{Cu}_2\text{I}_2(\text{dmphen})_2$ ,<sup>17</sup> in which the closest  $\text{Cu}\cdots\text{Cu}$  distances are 0.2535(9)—0.3576(2), 0.2609(2) and 0.3024(2) nm, respectively. Though there are two hydroxyl groups in complex **2b**, inter- or intramolecular hydrogen bonds have not been observed.

### Absorption spectra

The UV-Vis absorption spectra for compounds **1a**—**1c** and **2a**—**2c** in dichloromethane are shown in Figures 3 and 4. All spectral and electrochemical data are listed in Table 3. The intense absorptions at  $\lambda_{\text{max}} < 340$  nm are assigned to intraligand ( $\text{IL } \pi \rightarrow \pi^*$ ) transitions of the ligands, based on similarities with the absorptions of the free ligands. The low-energy absorption bands at 435 nm and 585 nm for **1a**, 428 nm and 537 nm (sh) for **1b** and 421 nm and 537 nm for **1c** are characteristic for MLCT transition (Figure 3). Compared with mononuclear complexes **1a**—**1c**, it can be found that for **2b** the broad peak at about 440 nm disappeared, and a new absorption peak at 360 nm appeared (Figure 4). A com-



**Figure 3** UV-Vis absorption spectra of complexes **1a**—**1c** ( $3.2 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  (**1a**),  $4.6 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  (**1b**),  $5.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  (**1c**)) in dichloromethane at room temperature.



**Figure 4** UV-Vis absorption spectra of complexes **2a**—**2c** ( $6.1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  (**2a**),  $6.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  (**2b**),  $6.8 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$  (**2c**)) in dichloromethane at room temperature.

parison of spectral data for MLCT bands indicates that effect of electron-donating substituents on MLCT bands of the ligands is in the order  $-\text{CH}_2\text{OH} < -\text{OCH}_3 < -\text{CH}_3$ . These observations are in good agreement with those reported before.<sup>11</sup>

**Table 3** UV-Vis spectral and electrochemical data

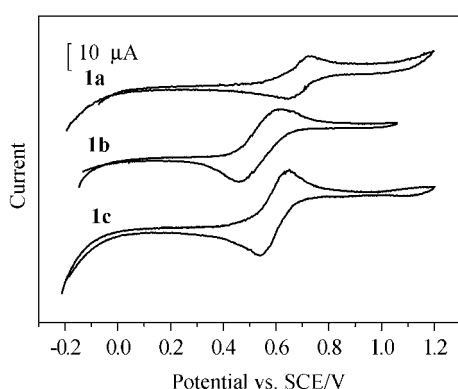
Complex	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon$ , $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ) <sup>a</sup>	$E_{1/2}/\text{V}$ ( $\Delta E_{\text{pp}}$ , mV) <sup>b</sup>
<b>1a</b>	271 (51,300); 333 (28,200)	+0.69 (80)
	435 (3,900); 585 (2,700)	
<b>1b</b>	265 (31,500); 308 (25,800)	+0.55 (140)
	428 (3,100); 537 (sh, 1,900)	
<b>1c</b>	271 (56,500); 316 (sh, 25,500)	+0.60 (100)
	421 (3,200); 533 (2,100)	
<b>2a</b>	269 (43,700); 334 (22,800)	
	438 (1,900); 580 (sh, 1,300)	
<b>2b</b>	265 (21,100); 307 (18,200)	
	360 (3,800); 538 (sh, 480)	
<b>2c</b>	272 (34,600); 320 (19,200)	
	550 (sh, 880)	

<sup>a</sup> Solvent: dichloromethane. <sup>b</sup> Measured in a nitrogen-saturated dichloromethane solution containing  $0.1 \text{ mol}\cdot\text{L}^{-1} n\text{-Bu}_4\text{NClO}_4$  at room temperature at 20 mV/s. Couples are reported in volts vs. SCE. The difference between the anodic and cathodic current peak potentials (in millivolts) is given in parentheses.

### Electrochemical properties

The cyclic voltammograms of complexes **1a**—**1c** were recorded in dichloromethane versus the SCE reference (Table 3 and Figure 5). The redox properties measured, equivalent anodic and cathodic current,  $i_{\text{pa}}/i_{\text{pc}} \approx 1$  and a peak-to-peak separation  $\Delta E_{\text{pp}} \approx 100$  mV, reveal a quasi-reversible one-electron oxidation-reduction wave associated with the  $\text{Cu(II)/Cu(I)}$  couple. The measured half-wave potential  $E_{1/2}$  values for **1a**, **1b** and **1c** were 0.69, 0.55 and 0.60 V respectively, which show significant stabilization of the monovalent oxidation

state. It has been reported that copper(I) complexes with bulky substituents at 2,9-position of 1,10-phenanthroline increase the Cu(II)/Cu(I) redox potential, resulting in stabilization of the copper(I) species.<sup>18,19</sup> Similar results were also found in other copper(I) complexes with 2,2'-bipyridine derivatives,<sup>10,11</sup> and the bulky phenyl group at 6-position of bipyridine can greatly stabilize the copper(I) state. The values of **1b** and **1c** are less than that of copper(I) complex of diphenyl substituted bipyridine such as [Cu(dmdpby)<sub>2</sub>]<sup>+</sup> (dmdpby = 4,4'-dimethyl-6,6'-diphenyl-2,2'-bipyridine,  $E_{1/2} \text{ Cu(II)/Cu(I)} = +0.68 \text{ V vs. SCE}$ ), implying that the increasing steric hindrance of substituents on bipyridine can stabilize the copper(I) state.<sup>20,21</sup>



**Figure 5** Cyclic voltammogram for complexes **1a**–**3c** in dichloromethane solution containing  $0.1 \text{ mol} \cdot \text{L}^{-1} n\text{-Bu}_4\text{NClO}_4$ . Supporting electrolyte, Pt electrode, SCE reference electrode, scan rate  $20 \text{ mV/s}$ .

## Conclusion

Mononuclear copper(I) complexes with substituent 2, 2'-bipyridine [Cu(L)<sub>2</sub>]BF<sub>4</sub> (L = 4-methoxycarbonyl-6-(4-methylphenyl)-2,2'-bipyridine, 6-(4-hydroxymethylphenyl)-2,2'-bipyridine, 6-(4-methoxyphenyl)-2,2'-bipyridine) and binuclear complexes [Cu<sub>2</sub>(μ-I)<sub>2</sub>(L)<sub>2</sub>] linked by iodine-bridge have been synthesized. Crystal structure of **1a** reveals strongly distorted tetrahedral configuration, whereas **2b** shows a centrosymmetric iodine-bridging binuclear structure with copper-copper distance  $0.3118 \text{ nm}$ .

It can be tentatively suggested that the low-energy absorption bands from  $360 \text{ to } 650 \text{ nm}$  for these investi-

gated complexes be attributed to MLCT transition. The electrochemical studies of **1a**–**1c** reveal that the bulky phenyl group at 6-position of 2,2'-bipyridine and electron-withdrawing group can stabilize copper(I) state.

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