

## 芳香基羧酸根桥联的双核铜(II)配合物研究

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**摘要:** 以具有芳香基团的 3-(9-甲基-芴基)-丙酸(FluCO<sub>2</sub>H)和 *N*-咔唑基丙酸(CarbCO<sub>2</sub>H)为配体, 合成了 5 种具有双核铜结构的配合物 [Cu<sub>2</sub>(FluCO<sub>2</sub>)<sub>4</sub>(CH<sub>3</sub>OH)<sub>2</sub>] (**1**), [Cu<sub>2</sub>(FluCO<sub>2</sub>)<sub>4</sub>(DMF)<sub>2</sub>] (**2**), [Cu<sub>2</sub>(FluCO<sub>2</sub>)<sub>4</sub>(4,4'-bipy)<sub>2</sub>] (**3**), [Cu<sub>2</sub>(CarbCO<sub>2</sub>)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (**4**), [Cu<sub>2</sub>(CarbCO<sub>2</sub>)<sub>3</sub>(2,2'-bipy)<sub>2</sub>]ClO<sub>4</sub> (**5**)。晶体结构测试表明: 配合物 **1**, **2** 和 **4** 都具有羧酸桥联的车轮状结构单元, 其结构单元轴向位置分别由甲醇, 二甲基甲酰胺和乙腈分子占据。配合物 **3** 中, 车轮状双核铜结构单元通过 4,4'-联吡啶连接构成一维链。配合物 **5** 的双核铜结构单元则是通过三个羧酸桥联形成。

**关键词:** 车轮状; 双核铜; 晶体结构

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## Syntheses and Characterization of Bulky Aryl-carboxylate-bridged Dicopper(II) Complexes

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**Abstract:** Five complexes, [Cu<sub>2</sub>(FluCO<sub>2</sub>)<sub>4</sub>(CH<sub>3</sub>OH)<sub>2</sub>] (**1**), [Cu<sub>2</sub>(FluCO<sub>2</sub>)<sub>4</sub>(DMF)<sub>2</sub>] (**2**), [Cu<sub>2</sub>(FluCO<sub>2</sub>)<sub>4</sub>(4,4'-bipy)<sub>2</sub>] (**3**), [Cu<sub>2</sub>(CarbCO<sub>2</sub>)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (**4**) and [Cu<sub>2</sub>(CarbCO<sub>2</sub>)<sub>3</sub>(2,2'-bipy)<sub>2</sub>]ClO<sub>4</sub> (**5**), (FluCO<sub>2</sub>H=3-(9-methyl-9-H-fluorene-9-yl)-propionic acid, CarbCO<sub>2</sub>H=*N*-carbazolylpropionic acid, 4,4'-bipy=4,4'-bipyridine, 2,2'-bipy=2,2'-bipyridine) were synthesized and characterized. Compound **1**, **2** and **4** consist of carboxylato bridged dicopper(II) paddle-wheel cores, and the axial positions are filled with CH<sub>3</sub>OH, DMF and CH<sub>3</sub>CN, respectively. Compound **3** has a one-dimensional structure, where the paddle-wheel units are bridged by 4,4'-bipy. Compound **5** has a dinuclear structure with copper atoms are bridged by three carboxylates. CCDC: 981495, **1**; 981496, **2**; 981497, **3**; 981498, **4**; 981499, **5**.

**Key words:** paddle-wheel; dinuclear copper; crystal structure

The syntheses and characterization of metal carboxylates have attracted great attention due to their intriguing structures<sup>[1]</sup>, and biological<sup>[2]</sup>, catalytic<sup>[3]</sup>,

magnetic<sup>[4]</sup>, electrochemical<sup>[5]</sup> properties. The types of organic ligands are essential for the construction of special metal-organic complexes. For example, trimesic

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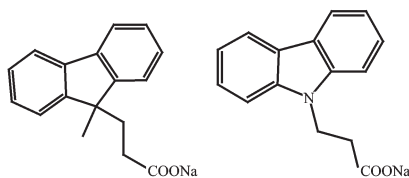
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acid, terephthalic acid and isophthalic acid have been well used in the preparations of various porous coordination polymers<sup>[6]</sup>. While, the monocarboxylate ( $\text{RCO}_2^-$ ) ligands are always used to build discrete clusters, which would be tuned by changing the steric hinderance of R groups<sup>[7]</sup>. Besides, the involving auxillary chelating ligand 2,2'-bipy or bridging ligand 4,4'-bipy could generate some interesting coordination architectures<sup>[8]</sup>. Recently, we used *N*-carbazolyacetate to construct four manganese carboxylates with dinuclear and 1D structures. It is found that the steric hinderance of benzene rings have larger conjugated  $\pi$ -systems are important for the formation of complexes<sup>[9]</sup>. To study the copper arylcarboxylates, we choose 3-(9-methyl-9-*H*-fluorene-9-yl)-propionate and *N*-carbazolypropionate as ligands. Five copper complexes  $[\text{Cu}_2(\text{FluCO}_2)_4(\text{CH}_3\text{OH})_2]$  (**1**),  $[\text{Cu}_2(\text{FluCO}_2)_4(\text{DMF})_2]$  (**2**),  $[\text{Cu}_2(\text{FluCO}_2)_4(4,4'\text{-bipy})_2]$  (**3**),  $[\text{Cu}_2(\text{CarbCO}_2)_4(\text{CH}_3\text{CN})_2]$  (**4**) and  $[\text{Cu}_2(\text{CarbCO}_2)_3(2,2'\text{-bipy})_2]\text{ClO}_4$  (**5**) were obtained and characterized.

## 1 Experimental

### 1.1 Materials and methods

$\text{FluCO}_2\text{Na}$  and  $\text{CarbCO}_2\text{Na}$  (Scheme 1) was prepared according to the literature method<sup>[10]</sup>. All other starting materials were used as obtained from Aldrich. The elemental analyses were performed on a PE 240 elemental analyzer. The IR spectra were recorded on a NICOLET 380 spectrometer with pressed KBr pellets.



Scheme 1 Carboxylate ligands

### 1.2 Syntheses

$[\text{Cu}_2(\text{FluCO}_2)_4(\text{CH}_3\text{OH})_2] \cdot 2\text{CH}_3\text{OH}$  (**1** · 2 $\text{CH}_3\text{OH}$ ): To a  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  (1:1, V/V) mixed solution (5 mL) of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.187 0 g, 0.5 mmol) was added a  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  (1:1, V/V) solution (5 mL) of  $\text{FluCO}_2\text{Na}$  (0.139 2 g, 0.5 mmol). The resulting mixture was stirred for 1 h gave blue precipitate, which was recrystallized with  $\text{CH}_3\text{OH}$ . Yield: 56% based on  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

$\text{C}_{72}\text{H}_{76}\text{Cu}_2\text{O}_{12}$  (1 260.41): Calcd.(%): C 68.61, H 6.08; Found(%): C 68.55, H 6.20. IR (KBr): 3 429.03 (vs), 2 962.41 (w), 2 922.83 (w), 1 607.86 (vs), 1 414.63 (vs), 1 045.63 (w), 735.53 (s), 619.59 (w), 593.91 (m)  $\text{cm}^{-1}$ . The two very strong bands centered at 1 607.86 and 1 414.63  $\text{cm}^{-1}$  with  $\Delta\nu=193.23 \text{ cm}^{-1}$ , attributed to the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  of bidentate bridging  $\text{FluCO}_2^-$ <sup>[11]</sup>.

$[\text{Cu}_2(\text{FluCO}_2)_4(\text{DMF})_2]$  (**2**): The preparation of **2** is similar to that of **1** except that the precipitate was recrystallized with DMF. Block-shaped crystals of **2** formed after one week. Yield: 40% based on  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ .  $\text{C}_{74}\text{H}_{74}\text{Cu}_2\text{N}_2\text{O}_{10}$  (1 278.43): Calcd.(%): C 69.52, H 5.83, N 2.19; Found (%): C 69.20, H 5.75, N 1.75. IR (KBr): 3 438.59 (m), 2 963.57 (w), 2 922.48 (w), 1 665.62 (w), 1 610.37 (vs), 1 414.09 (vs), 1 097.33 (w), 735.24 (s), 674.31 (m), 592.84 (w)  $\text{cm}^{-1}$ . The two very strong bands centered at 1 610.37 and 1 414.09  $\text{cm}^{-1}$  with  $\Delta\nu=196.28 \text{ cm}^{-1}$ , attributed to the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  of bidentate bridging  $\text{FluCO}_2^-$ .

$[\text{Cu}_2(\text{FluCO}_2)_4(4,4'\text{-bipy})_2] \cdot \text{DMF}$  (**3** · DMF): The preparation of **3** is similar to that of **1** except that the bridging ligand 4,4'-bipy (0.159 8 g, 1 mmol) was added. Block-shaped crystals of **3** formed after slow concentration of the reaction solution at room temperature over one week. Yield: 45% based on  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ .  $\text{C}_{42}\text{H}_{41}\text{Cu}_2\text{N}_2\text{O}_5$  (717.31): Calcd.(%): C 70.32, H 5.76, N 3.91; Found (%): C 70.40, H 5.55, N 3.85. IR (KBr): 3 433.03 (m), 2 959.44 (w), 2 922.80 (w), 1 611.08 (vs), 1411.37 (vs), 1 399.86 (vs), 1 218.72 (w), 1 073.62 (w), 765.46 (s), 593.47 (w)  $\text{cm}^{-1}$ . The two very strong bands centered at 1 611.07 and 1 411.37  $\text{cm}^{-1}$  with  $\Delta\nu=199.71 \text{ cm}^{-1}$ , attributed to the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  of bidentate bridging  $\text{FluCO}_2^-$ .

$[\text{Cu}_2(\text{CarbCO}_2)_4(\text{CH}_3\text{CN})_2]$  (**4**): A solution of  $\text{CarbCO}_2\text{Na}$  (0.052 2 g, 0.2 mmol) in  $\text{CH}_3\text{OH}$  (10 mL) was carefully layered on an aqueous solution (10 mL) of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.024 2 g, 0.1 mmol) with  $\text{CH}_3\text{CN}$  (5 mL) placed between the two layers. Deep green block-shaped crystals of **4** formed after five days. Yield: 31% based on  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ .  $\text{C}_{64}\text{H}_{54}\text{Cu}_2\text{N}_6\text{O}_8$  (1162.21): Calcd.(%): C 66.14, H 4.68, N 7.23; Found (%): C 66.05, H 4.65, N 7.35. IR (KBr): 3 427.98 (m),

3 049.67 (w), 2 969.30 (w), 1 621.32 (vs), 1 427.34 (vs), 1 327.76 (s), 1 231.21 (w), 1 057.09 (w), 749.63 (s), 600.08 (w)  $\text{cm}^{-1}$ . The two very strong bands centered at 1 621.32 and 1 427.34  $\text{cm}^{-1}$ , attributed to the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  of  $\text{CarbCO}_2^-$  with  $\Delta\nu=193.98 \text{ cm}^{-1}$ , which indicate the  $\text{CarbCO}_2^-$  adopts the bidentate bridging mode.

$[\text{Cu}_2(\text{CarbCO}_2)_3(2,2'\text{-bipy})_2]\text{ClO}_4$  (**5**): To a  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  (1:1,  $V/V$ ) mixed solution (5 mL) of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.187 0 g, 0.5 mmol) was added a  $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  (1:1,  $V/V$ ) solution (5 mL) of  $\text{CarbCO}_2\text{Na}$  (0.261 g, 1 mmol) and 2,2'-bipy (0.078 g, 0.5 mmol). The resulting mixture was stirred for 1 h and filtered. Green needle-like crystals of **5** formed after slow evaporation of the solution over one week. Yield: 36% based on  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ .  $\text{C}_{65}\text{H}_{52}\text{ClCu}_2\text{N}_7\text{O}_{10}$  (1 253.67): Calcd. (%): C 62.27, H 4.18, N 7.82; Found(%): C 62.40, H 4.36, N 8.85. IR (KBr): 3 441.36 (m), 3 051.75 (w), 2 928.99 (w), 1 605.22 (vs), 1 451.99 (vs), 1 380.01 (s), 1 330.69 (s), 1 247.19 (w), 1 093.54 (vs), 757.65 (s), 622.54 (w)  $\text{cm}^{-1}$ .

### 1.3 X-ray crystallography

Single crystals with dimensions 0.15 mm×0.18 mm×0.20 mm for **1**, 0.20 mm×0.25 mm×0.30 mm for **2**, 0.15 mm×0.18 mm×0.20 mm for **3**, 0.15 mm×0.22 mm×0.25 mm for **4** and 0.14 mm×0.17 mm×0.20 mm for **5** were selected for indexing and intensity data collection with a Rigaku SCX mini CCD diffractometer by using graphite-monochromated Mo  $K\alpha$  radiation

( $\lambda=0.071\ 073 \text{ nm}$ ) at room temperature. A hemisphere of data was collected in the  $\theta$  range  $3.01^\circ\sim27.49^\circ$  for **1**,  $3.13^\circ\sim25.00^\circ$  for **2**,  $3.13^\circ\sim25.00^\circ$  for **3**,  $3.01^\circ\sim25.00^\circ$  for **4** and  $3.09^\circ\sim25.00^\circ$  for **5**, by using a narrow-frame method with scan widths of  $0.03^\circ$  in  $\omega$  and an exposure time of 10 s per frame. The numbers of observed and unique reflections are 16 857 and 7 432 ( $R_{\text{int}}=0.0646$ ) for **1**, 14 216 and 5 779 ( $R_{\text{int}}=0.055\ 5$ ) for **2**, 29 819 and 6 513 ( $R_{\text{int}}=0.078\ 4$ ) for **3**, 2 3461 and 9 758 ( $R_{\text{int}}=0.057\ 2$ ) for **4**, 24 302 and 10 081 ( $R_{\text{int}}=0.034\ 5$ ) for **5**. Cell parameters were refined by using the program CrystalClear<sup>[12]</sup> on all observed reflections. The collected data were reduced by using the program CrystalClear, and an absorption correction (multiscan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least squares using SHELXTL<sup>[13]</sup>. All the non-hydrogen atoms were located from the Fourier maps and were refined anisotropically. All H atoms were refined isotropically with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystallographic and refinement details of **1**~**5** are listed in Table 1. Selected bond lengths and angles are given in Tables 2 for **1**~**5**, respectively.

CCDC: 981495, **1**; 981496, **2**; 981497, **3**; 981498, **4**; 981499, **5**.

Table 1 Crystal data and structure refinements for **1** to **5**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Formula	$\text{C}_{72}\text{H}_{76}\text{Cu}_2\text{O}_{12}$	$\text{C}_{74}\text{H}_{74}\text{Cu}_2\text{N}_2\text{O}_{10}$	$\text{C}_{42}\text{H}_{41}\text{CuN}_2\text{O}_5$	$\text{C}_{64}\text{H}_{54}\text{Cu}_2\text{N}_6\text{O}_8$	$\text{C}_{65}\text{H}_{52}\text{Cu}_2\text{N}_7\text{O}_6\text{ClO}_4$
Formula weight	1 260.41	1 278.43	717.32	1 162.23	1 253.67
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$Cc$
$a / \text{nm}$	0.927 28(19)	1.041 9(2)	3.033 4(9)	0.843 43(17)	2.520 9(5)
$b / \text{nm}$	1.269 8(3)	1.299 5(3)	1.406 4(3)	1.875 8(4)	1.454 9(3)
$c / \text{nm}$	1.453 9(3)	1.328 3(3)	2.203 1(11)	1.919 0(4)	2.007 8(4)
$\alpha / (^\circ)$	76.45(3)	83.76(3)	90.00(3)	69.99(3)	90.00
$\beta / (^\circ)$	86.59(3)	78.40(3)	127.98(3)	79.39(3)	128.41(3)
$\gamma / (^\circ)$	79.74(3)	69.14(3)	90.00(3)	80.45(3)	90.00
$V$	1 637.4(7)	1 644.9(7)	7 408(5)	2 786.6(10)	5 770(2)
$Z$	1	1	8	2	4

Continued Table 1

$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.278	1.291	1.286	1.385	1.443
$\mu / \text{mm}^{-1}$	0.712	0.707	0.636	0.826	0.851
$F(000)$	662	670	3 007	1 204	2 584
$R_{\text{int}}$	0.064 6	0.055 5	0.078 4	0.057 2	0.034 5
GoF on $F^2$	1.08	1.002	1.090	1.000	1.050
$R_1^a, wR_2^a (I > 2\sigma(I))$	0.076 1, 0.140 5	0.052 1, 0.105 6	0.072 7, 0.184 0	0.063 7, 0.116 3	0.053 0, 0.135 5
$R_1^a, wR_2^a (\text{all data})$	0.133 7, 0.140 0	0.071 1, 0.115 5	0.097 5, 0.206 0	0.112 4, 0.129 8	0.052 0, 0.137 6
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	310, -400	316, -384	861, -598	322, -400	760, -1 100

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2 Selected bond lengths (nm) and angles ( $^\circ$ ) for complex 1 to 5

1					
Cu1-O4A	0.194 9(3)	Cu1-O5	0.214 0(3)	Cu1-O2A	0.199 4(2)
Cu1-O3	0.195 6(3)	Cu1-O1	0.198 0(3)		
O1-Cu1-O3	89.58(11)	O1-Cu1-O5	94.22(11)	O1-Cu1-O2A	168.63(12)
O1-Cu1-O4A	89.26(11)	O3-Cu1-O5	96.03(13)	O3-Cu1-O2A	88.45(11)
O4A-Cu1-O3	168.92(12)	O5-Cu1-O2A	97.12(12)	O4A-Cu1-O5	95.04(13)
O4A-Cu1-O2A	90.52(11)				
2					
Cu1-O2	0.196 4(2)	Cu1-O5	0.216 8(2)	Cu1-O4	0.197 6(2)
Cu1-O3A	0.196 9(2)	Cu1-O1A	0.197 2(2)		
O2-Cu1-O3A	90.17(10)	O2-Cu1-O1A	168.48(10)	O3A-Cu1-O1A	87.83(10)
O2-Cu1-O4	88.98(10)	O3A-Cu1-O4	168.40(9)	O1A-Cu1-O4	90.70(11)
O2-Cu1-O5	100.07(10)	O3A-Cu1-O5	98.00(9)	O4-Cu1-O5	95.53(10)
O1A-Cu1-O5	91.44(10)				
3					
Cu1-O2	0.193 1(3)	Cu1-O4	0.199 4(3)	Cu1-N1	0.219 1(5)
Cu2-O3	0.194 6(3)	Cu2-N2B	0.217 3(4)	Cu2-O1	0.200 3(3)
O2A-Cu1-O2	172.06(18)	O2-Cu1-O4	89.35(17)	O2-Cu1-O4A	89.51(17)
O4A-Cu1-O4	163.52(18)	O4-Cu1-N1	98.24(10)	O2-Cu1-N1	93.97(10)
O3A-Cu2-O3	172.02(16)	O3-Cu2-O1A	89.88(13)	O3-Cu2-O1	89.88(13)
O1-Cu2-O1A	163.57(17)	O1-Cu2-N2B	98.22(9)	O3-Cu2-N2B	93.99(9)
4					
Cu1-O1	0.195 7(3)	Cu1-O2A	0.196 3(3)	Cu1-O3	0.196 6(3)
Cu1-O4A	0.196 8(3)	Cu1-N5	0.223 5(4)	Cu2-N6	0.220 5(4)
Cu2-O5	0.195 7(3)	Cu2-O8B	0.196 7(3)	Cu2-O7	0.196 9(3)
Cu2-O6B	0.197 0(3)				
O1-Cu1-O2A	168.32(12)	O1-Cu1-O3	90.43(13)	O1-Cu1-O4A	87.79(13)
O2A-Cu1-O3	90.06(13)	O2A-Cu1-O4A	89.43(12)	O3-Cu1-O4A	168.59(12)
N5-Cu1-O1	91.79(14)	N5-Cu1-O2A	99.87(13)	N5-Cu1-O3	91.85(13)
N5-Cu1-O4A	99.47(13)	O5-Cu2-O6B	168.49(12)	O5-Cu2-O7	89.88(12)
O5-Cu2-O8B	89.45(12)	O7-Cu2-O6B	90.34(12)	O8B-Cu2-O6B	88.12(12)

Continued Table 2

N6-Cu2-O5	94.46(14)	O7-Cu2-O8B	168.87(12)	N6-Cu2-O7	96.68(14)
N6-Cu2-O8B	94.45(14)	N6-Cu2-O6B	96.94(14)		
5					
Cu1-O4	0.194 1(4)	Cu1-O5	0.194 7(3)	Cu1-N6	0.200 0(5)
Cu1-N7	0.200 7(5)	Cu1-O1	0.227 4(11)		
Cu2-N4	0.199 1(5)	Cu2-N5	0.201 1(5)	Cu2-O3	0.194 5(5)
Cu2-O5	0.232 5(7)	Cu2-O1	0.206 2(6)		
O4-Cu1-O1	95.3(3)	O5-Cu1-O1	78.0(3)	O1-Cu1-O6	126.7(2)
N6-Cu1-O1	99.4(2)	N7-Cu1-O1	105.7(3)	O5-Cu1-O6	48.9(3)
O4-Cu1-O5	92.63(19)	O4-Cu1-O6	84.3(2)	O5-Cu1-N6	95.2(2)
O4-Cu1-N7	90.46(19)	O4-Cu1-N6	164.5(3)	N6-Cu1-N7	80.91(19)
O5-Cu1-N7	175.0(3)	O5-Cu-N7	174.9(2)	O6-Cu1-N6	90.8(2)
Cu2-O1-Cu1	95.9(3)	O6-Cu1-N7	127.6(3)	O1-Cu2-O2	51.8(3)
O1-Cu2-O3	94.2(2)	O1-Cu2-O5	74.6(3)	O1-Cu2-N4	94.6(2)
O1-Cu2-N5	172.9(3)	O2-Cu2-O3	92.2(2)	O2-Cu2-O5	126.31(19)
O2-Cu2-N4	90.8(2)	O2-Cu2-N5	122.5(2)	O3-Cu2-O5	88.5(2)
O3-Cu2-N4	170.6(2)	O3-Cu2-N5	90.11(19)	O5-Cu2-N4	96.9(2)

Symmetry code: A:  $-x+1, -y+2, -z$  for **1**; A:  $-x+1, -y, -z$  for **2**; A:  $-x, y, -z+1/2$ ; B:  $x, y-1, z$  for **3**; A:  $-x, -y, -z+1$ ; B:  $-x+1, -y+1, -z+1$  for **4**.

## 2 Results and discussion

### 2.1 Syntheses

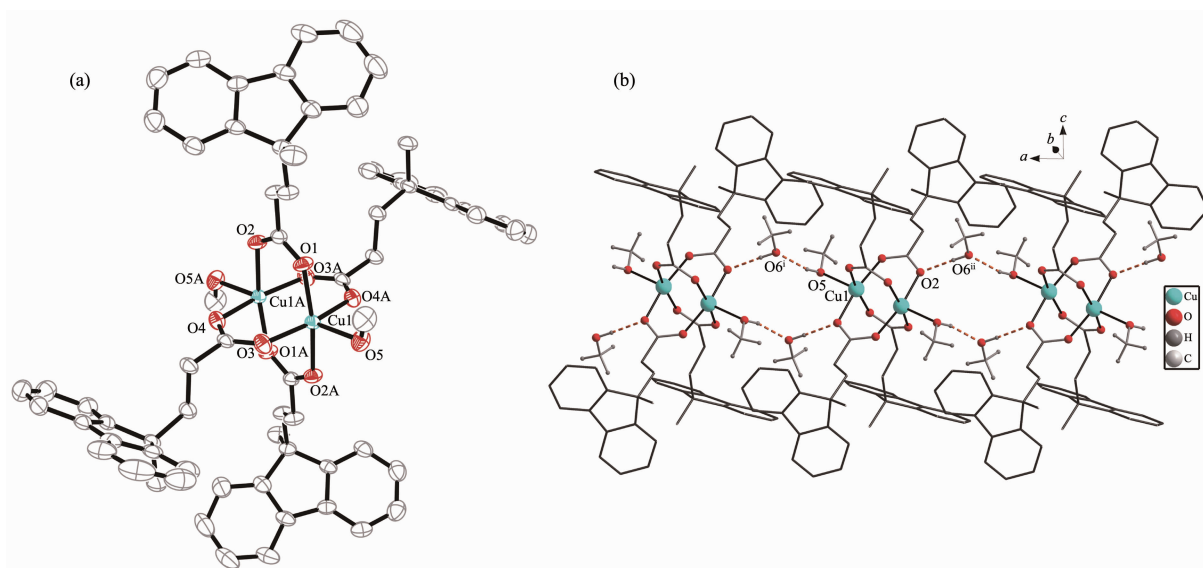
It is found that the solvent molecules can act as auxiliary ligands to coordinate with copper centers in compounds  $[\text{Cu}_2(\text{FluCO}_2)_4(\text{CH}_3\text{OH})_2]$  (**1**),  $[\text{Cu}_2(\text{FluCO}_2)_4(\text{DMF})_2]$  (**2**) and  $[\text{Cu}_2(\text{CarbCO}_2)_4(\text{CH}_3\text{CN})_2]$  (**4**). Introduction of the bridging 4,4'-bipy ligand in the reaction system afforded a 1D compound  $[\text{Cu}_2(\text{FluCO}_2)_4(4,4'\text{-bipy})_2]_n$  (**3**). This result shows that 4,4'-bipy has the stronger coordination ability than DMF. To tune the structural diversity, the chelating 2,2'-bipy ligand was employed in the reaction system. Fortunately, a new dinuclear copper carboxylate  $[\text{Cu}_2(\text{CarbCO}_2)_3(2,2'\text{-bipy})_2]\text{ClO}_4$  (**5**) was isolated.

### 2.2 Structural description

Single crystal X-ray diffraction analysis reveals that compound **1** and **2** have similar dinuclear copper structures. In the structures, the  $\text{Cu}^{\text{II}}$  atoms are bridged by four carboxylates in  $\eta':\eta':\mu$  mode into a paddle-wheel core. The cores are similar to that in  $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{CH}_3\text{OH})_2]^{[14]}$ . The axial positions are filled with  $\text{CH}_3\text{OH}$  and DMF molecules for **1** and **2**,

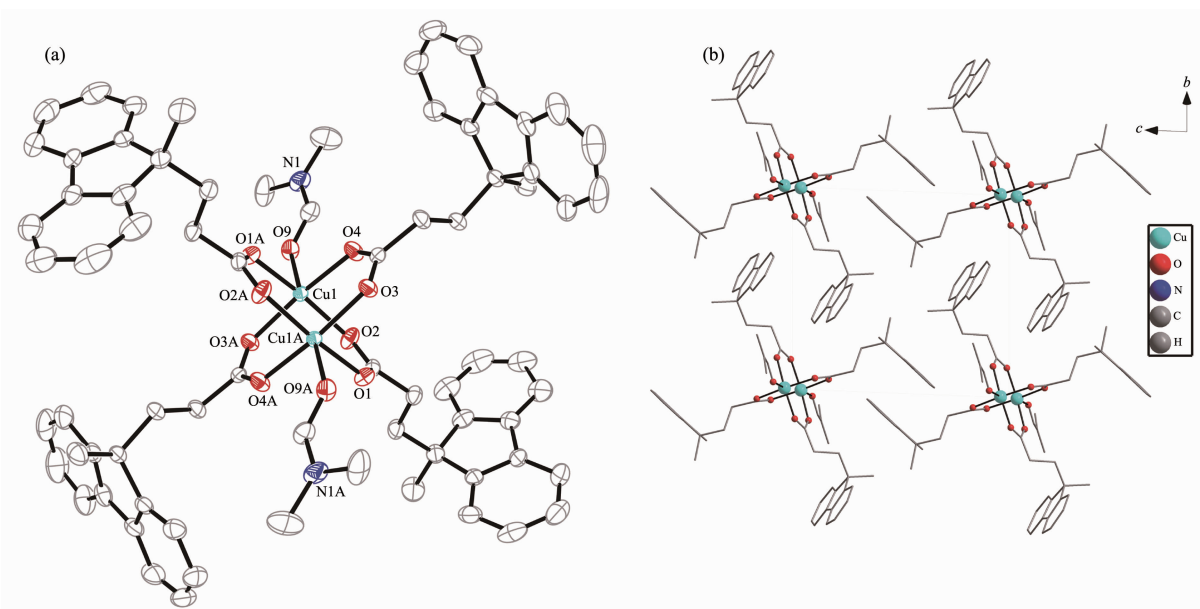
respectively. (Fig.1 and Fig.2) The  $\text{Cu}\cdots\text{Cu}$  distances are 0.261 1(1) and 0.262 4(1) nm, respectively, which are slight longer than that in  $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{CH}_3\text{OH})_2]$  0.259(1) nm. The difference seems to be attributed to the steric hindrance on the carboxyl groups. In compound **1**, the  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds ( $\text{O5}-\text{H5B}\cdots\text{O6}^{\text{i}}$  0.266 1(6) nm;  $\text{O6}^{\text{ii}}-\text{H6A}\cdots\text{O2}$  0.276 8(5) nm. Symmetry code: <sup>i</sup>  $-x+2, -y+2, -z+1$ ; <sup>ii</sup>  $-x+1, -y+2, -z+1$ ) between lattice  $\text{CH}_3\text{OH}$  and carboxylate link the dinuclear copper into one chain (Fig.1b). While in compound **2**, the molecules are packed into 3D supramolecular network through the  $\pi-\pi$  interactions (the shortest distance between the centers of benzene rings is 0.47 nm).

Compound **3** crystallizes in a monoclinic  $C2/c$  space group. The asymmetric unit contains two crystallographically independent Cu centers with 0.5 occupation, two  $\text{FluCOO}^-$  ligands, one 4,4'-bipy and one lattice DMF. The adjacent Cu atoms are bridged by four carboxylates in paddle-wheel shape (Fig.3a). The Cu-O bond lengths and the  $\text{Cu}\cdots\text{Cu}$  separation are 0.193 1(3)~0.200 3(3) nm and 0.265 1 nm, respec-



H atoms of the fluorenyl group are omitted for clarity; Symmetry codes: A:  $-x+1, -y+2, -z$ ;  
Displacement ellipsoids are drawn at the 30% probability level in (a)

Fig.1 (a) Coordination environment around the Cu atom in **1**; (b) 1D chain structure of **1** that are linked by H-bonds



H atoms are omitted for clarity; Symmetry codes: A:  $-x+1, -y, -z$ ; Displacement ellipsoids are drawn at the 30% probability level in (a)

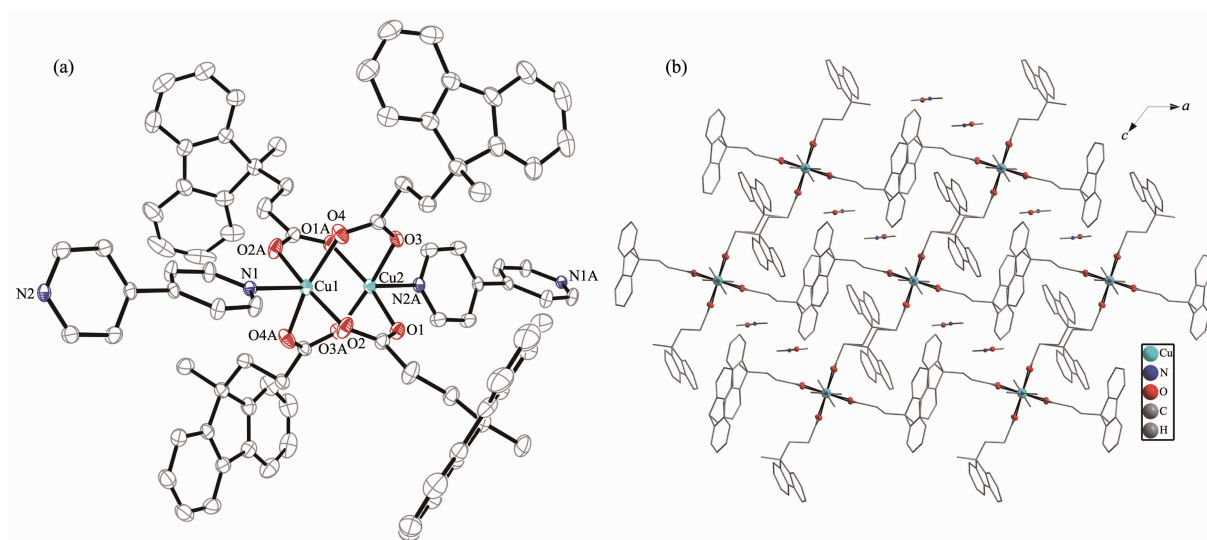
Fig.2 (a) Coordination environment around the Cu atom in **2**; (b) Packing diagram of **2** viewed along the *a* axis

ctively, which are similar to that in **1** and **2**. The dimers are bridged by the 4,4'-bipy ligands into one-dimensional chain along the *b* axis (Fig.3b). The 1D polymeric chains are further packed together through  $\pi$ - $\pi$  interactions (the shortest distance between the centers of benzene rings is 0.44 nm) into 3D supramolecular network.

Compound **4** crystallizes in a triclinic  $P\bar{1}$  space group and the asymmetric unit contains of one Cu<sup>II</sup>

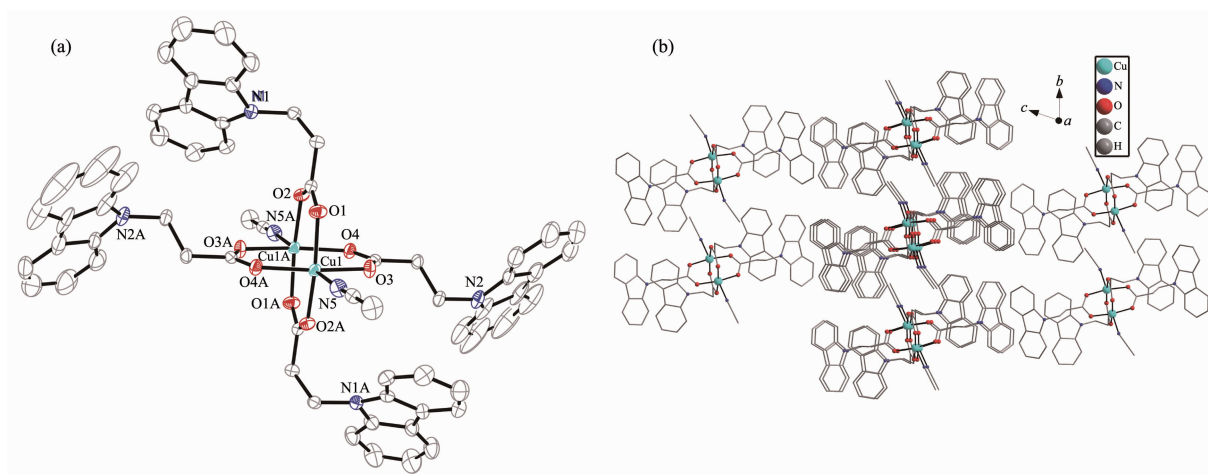
center, two CarbCOO<sup>-</sup> ligands and one CH<sub>3</sub>CN molecule. It has a dinuclear structure similar to compound **1**, but the outer bulky aryl groups are carbazolyl group and the axial positions are filled with CH<sub>3</sub>CN (Fig.4a). The Cu-O bond lengths are similar to that in compounds **1**~**3**. The Cu...Cu distance is 0.263 0(1) nm, close to that in [Cu<sub>2</sub>(Cabo)<sub>4</sub>(dmf)<sub>2</sub>]·2dmf (Cabo = carbazolyl acetate)<sup>[15]</sup>. The dinuclear molecules are packed together through  $\pi$ - $\pi$  (the shortest distance





H atoms are omitted for clarity; Symmetry codes: A:  $-x, y, -z+1/2$ ; B:  $x, y-1, z$ ;  
Displacement ellipsoids are drawn at the 30% probability level in (a)

Fig.3 (a) Coordination environment around the Cu atom in **3**; (b) Packing diagram of **3** viewed along the *b* axis



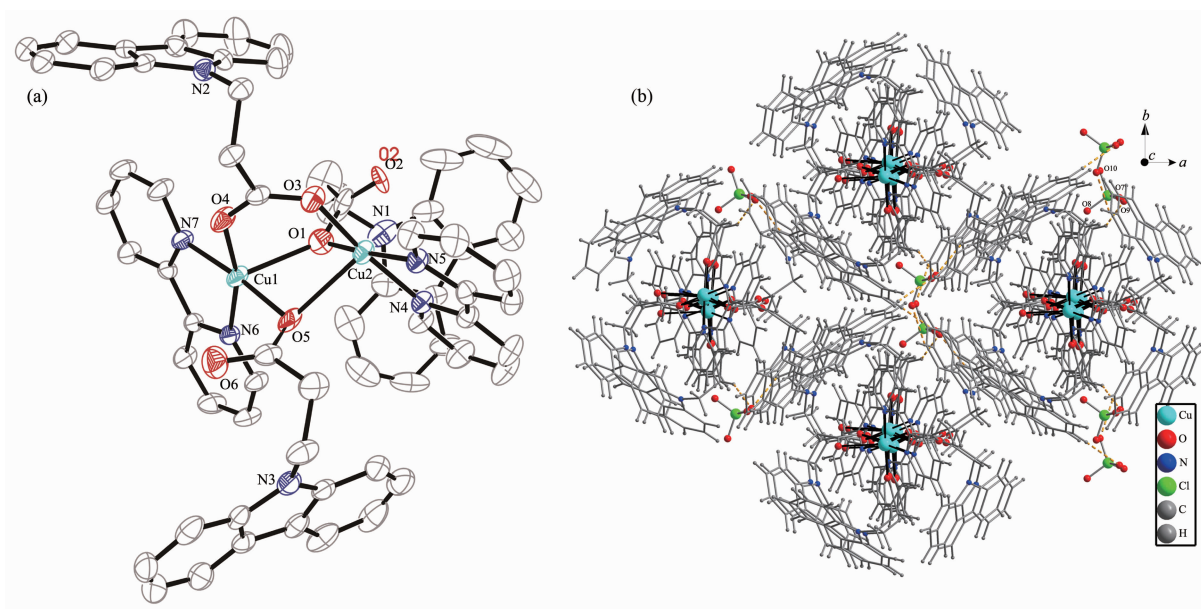
Displacement ellipsoids are drawn at the 30% probability level (a)

Fig.4 (a) Coordination environment around the Cu atom in **4**; (b) Packing diagram of **4** viewed along the *a* axis

between the centers of benzene rings is 0.46 nm) and Van der Waals interactions into 3D supramolecular network.

Single crystal X-ray diffraction analysis reveals that complex **5** crystallizes in a monoclinic *Cc* space group and consists of a dinuclear  $[\text{Cu}_2(\text{CarbCO}_2)_3(2,2'\text{-bipy})_2]^+$  cation and a well-separated  $\text{ClO}_4^-$  anion. The  $\text{Cu}^{\text{II}}$  atoms are bridged by three carboxylate groups. Two of the *N*-carbazolylpropionates are in the monoatomic bridging mode, while the third is in the bidentate  $\eta':\eta':\mu$  bridging mode; a terminal 2,2'-bipy molecule completes the five coordination at each  $\text{Cu}^{\text{II}}$  ion. Fig.5a shows that the copper atoms are

orthogonally bridged to the monodentate bridging carboxylates and equatorially bridged to the bidentate carboxylate and have similar Cu-O bond distances (Cu1-O1 0.227 3(6) nm, Cu2-O1 0.206 2(7) nm) to those of  $[\text{Cu}_2(\text{Cabo})_3(\text{phen})_2](\text{ClO}_4) \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}^{[15]}$ . The C-H...O hydrogen bond interactions exist between adjacent carbazolyl rings and perchlorate anions (C18-H18...O9<sup>i</sup> 0.327 (1) nm; C22-H22...O7<sup>ii</sup> 0.342(1) nm; C29-H29A...O9<sup>iii</sup> 0.330(1) nm; C32-H32...O10<sup>iv</sup> 0.322 8(2) nm. Symmetry code: <sup>i</sup>  $x-1/2, y-1/2, z$ ; <sup>ii</sup>  $x, y-1, z$ ; <sup>iii</sup>  $x, -y+1, z+1/2$ ; <sup>iv</sup>  $x, -y+2, z+1/2$ ). Moreover, the  $\pi$ - $\pi$  (the shortest distance between the centers of benzene rings is 0.46 nm) interactions further help the



H atoms are omitted for clarity

Fig.5 (a) Coordination environment around the Cu atom in **5**; (b) Packing diagram of **5** viewed along the *c* axis

packing of the dinuclear molecules (Fig.5b).

### 3 Conclusions

Five new copper carboxylates were synthesized by using bulky monocarboxylates 3-(9-methyl-9-*H*-fluorene-9-yl)-propionate and *N*-carbazolylpropionate as ligands. Compounds **1**, **2** and **4** have the typical paddle-wheel  $[\text{Cu}_2(\mu\text{-O}_2\text{C-R})_4]$  core. Compound **3** has a 1D chain structure, in which the paddle-wheel dimers are bridged by 4,4'-bipy. Compound **5** has a different dimeric core from **1**~**4**, in which the copper atoms are bridged by three carboxylates. The  $\pi$ - $\pi$  interactions between the benzene rings in **2**~**5** stabilized the compounds. Further work is in progress to construct multi-dimensional compounds based on the bulky carboxylic acids.

### References:

- [1] Maurer C, Baumgartner B, Pabisch S, et al. *Dalton Trans.*, **2014**,43:950-957
- [2] Cook T R, Vajpayee V, Lee M H, et al. *Acc. Chem. Res.*, **2013**,46:2464-2474
- [3] Corma A, García H, Llabrés i Xamena F X. *Chem. Rev.*, **2010**,110:4606-4655
- [4] Bagai R, Christou G. *Chem. Soc. Rev.*, **2009**,38:1011-1026
- [5] Derikvand Z, Bruno G, Rudbari H A, et al. *Inorg. Chim. Acta*, **2014**,410:221-229
- [6] (a) Chui S S Y, Lo S M F, Charmant J P H, et al. *Science*, **1999**,283:1148-1150  
(b) Yaghi O M, Li H L, Eddaoudi M, et al. *Nature*, **1999**,402:276-279  
(c) Li J, Zhang Z J, Zhao Y G, et al. *Chem. Commun.*, **2013**,49:653-661
- [7] Stamatatos T C, Teat S J, Wernsdorfer W, et al. *Angew. Chem. Int. Ed.*, **2009**,48:521-524
- [8] Chen Z L, Ma Y S, Liang F P, et al. *Eur. J. Inorg. Chem.*, **2007**:2040-2045
- [9] Ma Y S, Tang X Y, Xue F F, et al. *Eur. J. Inorg. Chem.*, **2012**:1243-1249
- [10] Zhang X J, Tian Y P, Li S L, et al. *Polyhedron*, **2003**,22:397-402
- [11] Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. New York: John Wiley and Sons, **1986**:233
- [12] CrystalClear, Rigaku Corporation, Tokyo, Japan, **2005**.
- [13] Sheldrick G M. *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **2008**,64:112
- [14] Rao V M, Manohar H. *Inorg. Chim. Acta*, **1979**,34:L213
- [15] Tian Y P, Zhang X J, Wu J Y, et al. *New J. Chem.*, **2002**,26:1468-1473