Effect	of	flex	xible	bis-	pyridyl-bis-	amide	ligands	and
dicarbo	xyla	tes	on	the	assembly	and	properties	of
multifu	nctio	onal	C	cu(II)	metal-or	rganic	coordina	ation
polyme	rs†							

Xiuli Wang, * Jian Luan, Hongyan Lin, Qilin Lu, Chuang Xu and Guocheng Liu

Complex 1						
Cu(1)-O(1)	1.9751(18)	Cu(1)-N(2)	2.014(2)			
Cu(1)-O(5)#1	1.9768(19)	Cu(1)-N(4)	2.027(2)			
O(5)-Cu(1)#2	1.9767(19)	Cu1–O1W	2.4513(25)			
O(1)-Cu(1)-N(2)	93.67(8)	O(1)-Cu(1)-O(5)#1	175.85(8)			
O(1)-Cu(1)-N(4)	88.00(8)	O(5)#1-Cu(1)-N(2)	90.44(9)			
N(2)-Cu(1)-N(4)	171.18(9)	O(5)#1-Cu(1)-N(4)	88.00(9)			
C(9)-N(2)-Cu(1)	119.15(18)	C(1)-O(1)-Cu(1)	124.95(18)			
C(16)-N(4)-Cu(1)	120.23(18)	C(15)-N(2)-Cu(1)	122.9(2)			
C(8)-O(5)-Cu(1)#2	128.83(19)	C(22)-N(4)-Cu(1)	122.56(19)			
Symmetry code for 1: #1 $-x$, y +	1/2, -z + 1/2; #2 -	-x, y - 1/2, -z + 1/2				
Complex 2						
Cu(1)-O(1)	1.944(2)	Cu(1)-O(1W)	2.327(3)			
Cu(1)-O(4)#1	2.001(2)	N(1)-Cu(1)#2	2.056(3)			
Cu(1)-N(2)	2.027(3)	O(4)-Cu(1)#3	2.001(2)			
Cu(1)-N(1)#2	2.056(3)	O(1)-Cu(1)-O(4)#1	147.97(11)			
O(1)-Cu(1)-N(2)	94.75(11)	C(1)-O(1)-Cu(1)	127.7(2)			
O(4)#1-Cu(1)-N(2)	92.80(11)	Cu(1)-O(1W)-H(1WA)	142(4)			
O(1)-Cu(1)-N(1)#2	90.65(12)	Cu(1)-O(1W)-H(1WB)	86(4)			
O(4)#1-Cu(1)-N(1)#2	88.17(12)	C(4)-N(1)-Cu(1)#2	116.1(2)			
N(2)-Cu(1)-N(1)#2	168.11(12)	Cu(1)#2-N(1)-H(1A)	103(4)			
O(1)-Cu(1)-O(1W)	102.11(12)	C(9)-N(2)-Cu(1)	117.4(2)			
O(4)#1-Cu(1)-O(1W)	109.53(11)	C(15)-N(2)-Cu(1)	124.5(3)			
N(2)-Cu(1)-O(1W)	85.00(12)	C(7)-O(4)-Cu(1)#3	106.1(2)			
N(1)#2-Cu(1)-O(1W)	83.51(12)					
Symmetry code for 2 : #1 x , $y + 1$, z ; #2 $-x$, $-y + 2$, $-z + 1$; #3 x , $y - 1$, z						
Complex 3						
Cu(1)-O(3)#1	1.9692(18)	Cu(1)-O(6)#2	2.220(2)			
Cu(1)-N(3)	2.027(2)	O(3)-Cu(1)#3	1.9692(18)			
Cu(1)-O(2)	2.0272(18)	O(6)-Cu(1)#2	2.220(2)			
Cu(1)-N(1)	2.035(2)	O(3)#1-Cu(1)-N(3)	90.41(8)			

Table S1 Selected bond distances (Å) and angles (°) for complexes 1–7.

O(3)#1-Cu(1)-O(2)	147.83(8)	N(1)-Cu(1)-O(6)#2	90.50(8)		
N(3)-Cu(1)-O(2)	90.56(8)	C(1)-O(2)-Cu(1)	104.53(15)		
O(3)#1-Cu(1)-N(1)	87.38(8)	C(9)-N(1)-Cu(1)	117.13(18)		
N(3)-Cu(1)-N(1)	177.62(8)	C(15)-N(1)-Cu(1)	125.07(18)		
O(2)-Cu(1)-N(1)	91.78(8)	C(5)-O(3)-Cu(1)#3	125.45(17)		
O(3)#1-Cu(1)-O(6)#2	124.16(8)	C(16)-N(3)-Cu(1)	121.22(18)		
N(3)-Cu(1)-O(6)#2	89.99(8)	C(22)-N(3)-Cu(1)	120.34(18)		
O(2)-Cu(1)-O(6)#2	87.99(7)	C(5)-O(6)-Cu(1)#2	162.00(18)		
Symmetry code for 3 : #1 x + 1, y	y, z; #2 - x + 1, -y,	-z + 1; #3 x - 1, y, z			
	Compl	ex 4			
Cu(1)-O(6)#1	1.895(2)	Cu(2)-O(6)	1.882(2)		
Cu(1)-O(6)	1.895(2)	Cu(2)-O(3)#2	1.964(2)		
Cu(1)-O(1)	1.941(3)	Cu(2)-O(2)	1.973(2)		
Cu(1)-O(1)#1	1.941(3)	O(3)-Cu(2)#2	1.964(2)		
N(1)-Cu(2)	2.070(3)	Cu(2)-O5	2.4613(29)		
O(6)#1-Cu(1)-O(1)	86.73(11)	O(6)#1-Cu(1)-O(6)	180		
O(6)-Cu(1)-O(1)	93.26(11)	O(6)-Cu(2)-O(2)	89.83(10)		
O(6)#1-Cu(1)-O(1)#1	93.27(11)	O(3)#2-Cu(2)-O(2)	161.49(12)		
O(6)-Cu(1)-O(1)#1	86.74(11)	O(6)-Cu(2)-N(1)	177.32(11)		
O(1)-Cu(1)-O(1)#1	180	O(3)#2-Cu(2)-N(1)	86.63(10)		
C(1)-O(1)-Cu(1)	131.1(2)	O(2)-Cu(2)-N(1)	87.71(10)		
C(10)-N(1)-Cu(2)	122.0(2)	C(1)-O(2)-Cu(2)	128.5(2)		
C(9)-N(1)-Cu(2)	121.1(2)	C(8)-O(3)-Cu(2)#2	131.1(2)		
O(6)-Cu(2)-O(3)#2	95.40(10)	Cu(2)-O(6)-Cu(1)	136.37(14)		
Symmetry code for 4: $\#1 - x + 1$,	-y, -z; #2 -x + 2,	-y, -z			
	Compl	ex 5			
Cu(1)-O(6)	1.8834(18)	Cu(2)-O(6)#3	1.8677(18)		
Cu(1)-O(4)#1	1.9820(18)	Cu(2)-O(6)	1.8677(18)		
Cu(1)-O(2)	1.9901(18)	Cu(2)-O(3)	1.954(2)		
Cu(1)-N(1)	2.055(2)	Cu(2)-O(3)#3	1.954(2)		
Cu(1)-O(1)#2	2.384(2)	O(4)-Cu(1)#1	1.9820(18)		
O(1)-Cu(1)#2	2.383(2)	O(6)-Cu(1)-O(4)#1	91.91(8)		
O(6)-Cu(1)-O(2)	90.71(8)	C(5)-N(1)-Cu(1)	122.03(18)		
O(4)#1-Cu(1)-O(2)	163.33(8)	O(6)#3-Cu(2)-O(6)	179.999(2)		
O(6)-Cu(1)-N(1)	176.51(9)	O(6)#3-Cu(2)-O(3)	88.16(8)		
O(4)#1-Cu(1)-N(1)	87.56(8)	O(6)-Cu(2)-O(3)	91.84(8)		
O(2)-Cu(1)-N(1)	88.82(8)	O(6)#3-Cu(2)-O(3)#3	91.84(8)		
O(6)-Cu(1)-O(1)#2	94.75(8)	O(6)-Cu(2)-O(3)#3	88.16(8)		
O(4)#1-Cu(1)-O(1)#2	103.78(8)	O(3)-Cu(2)-O(3)#3	180		
O(2)-Cu(1)-O(1)#2	92.40(8)	C(10)-O(2)-Cu(1)	130.28(17)		
N(1)-Cu(1)-O(1)#2	88.72(8)	C(10)-O(3)-Cu(2)	134.19(19)		
C(6)-O(1)-Cu(1)#2	123.38(18)	C(17)-O(4)-Cu(1)#1	125.89(17)		
C(1)-N(1)-Cu(1)	120.70(18)	Cu(2)-O(6)-Cu(1)	126.51(10)		
Symmetry code for 5: #1 $-x$, $-y + 1$, $-z + 1$; #2 $-x$, $-y + 2$, $-z + 1$; #3 $-x - 1$, $-y + 1$, $-z + 1$					

Complex 6					
Cu(1)-O(4)#1	1.941(3)	Cu(1)-Cu(1)#2	2.8042(11)		
Cu(1)-O(1)	1.952(3)	O(2)-Cu(1)#2	1.979(2)		
Cu(1)-O(2)#2	1.979(2)	O(4)-Cu(1)#1	1.941(3)		
Cu(1)-N(1)	1.993(3)	O(4)#1-Cu(1)-O(1)	87.44(11)		
O(4)#1-Cu(1)-O(2)#2	90.91(10)	O(2)#2-Cu(1)-Cu(1)#2	84.00(8)		
O(1)-Cu(1)-O(2)#2	161.98(11)	N(1)-Cu(1)-Cu(1)#2	136.11(9)		
O(4)#1-Cu(1)-N(1)	163.07(12)	C(1)-O(1)-Cu(1)	128.0(2)		
O(1)-Cu(1)-N(1)	92.64(11)	C(16)-N(1)-Cu(1)	121.5(2)		
O(2)#2-Cu(1)-N(1)	94.09(11)	C(20)-N(1)-Cu(1)	121.1(3)		
O(4)#1-Cu(1)-Cu(1)#2	60.51(8)	C(1)-O(2)-Cu(1)#2	121.1(2)		
O(1)-Cu(1)-Cu(1)#2	79.58(8)	C(8)-O(4)-Cu(1)#1	119.5(2)		
Symmetry code for 6 : $\#1 - x + 2, -y, -z + 1$; $\#2 - x + 1, -y, -z + 1$					
Complex 7					
Cu(1)-O(1)	1.944(4)	Cu(1)-N(1)	2.042(5)		
Cu(1)-O(3)#1	2.047(4)	Cu(1)-N(2)#2	2.070(4)		
Cu(1)-O(1W)	2.377(4)	N(2)-Cu(1)#2	2.070(4)		
O(3)-Cu(1)#3	2.047(4)	O(1)-Cu(1)-N(1)	93.06(17)		
O(1)-Cu(1)-O(3)#1	151.17(16)	N(1)-Cu(1)-O(3)#1	94.06(17)		
O(1)-Cu(1)-N(2)#2	88.25(17)	N(1)-Cu(1)-N(2)#2	172.82(17)		
O(3)#1-Cu(1)-N(2)#2	88.13(17)	O(1)-Cu(1)-O(1W)	118.72(16)		
N(1)-Cu(1)-O(1W)	89.32(17)	O(3)#1-Cu(1)-O(1W)	89.29(16)		
N(2)#2-Cu(1)-O(1W)	83.86(16)	C(10)-O(1)-Cu(1)	124.0(4)		
C(5)-N(1)-Cu(1)	120.4(4)	C(1)-N(1)-Cu(1)	122.3(4)		
C(16)-N(2)-Cu(1)#2	116.5(3)	C(14)-O(3)-Cu(1)#3	102.7(3)		
Symmetry code for 7 : #1 x , $y + 1$, z ; #2 $-x + 1$, $-y$, $-z + 1$; #3 x , $y - 1$, z					

Table S2. Selected hydrogen-bonding geometry (Å, °) for complex 1

D–H···A	D–H	Н•••А	D•••A	D–H•••A			
O(1W)–H(1WA)····O(7)	0.79	1.97	2.7486	166			
Table S3. Selected hydrogen-bonding geometry (Å, °) for complex 2							
D–H…A	D–H	Н•••А	D•••A	D–H•••A			
N(3)–H(3B)…O(3)	0.86	2.52	3.3684	169			
Table S4. Selected hydrogen-bonding geometry (Å, °) for complex 6							
D–H…A	D–H	Н•••А	D•••A	D–H•••A			
O(1W)-H(1WA)····O(9)	0.89	2.05	2.8592	151			
O(1W)–H(1WA)····O(3)	0.83	1.90	2.7340	177			



Scheme S1 Coordination modes of the polycarboxylates in complexes 1–7.



Fig.S1 View of the 3D supramolecular network in complex 1.



Fig.S2 View of the 3D supramolecular network in complex 2.



Fig.S4 ORTEP drawings of complex **5** with thermal ellipsoids at 50% probability. The lattice water molecules and H atoms have been omitted for clarity. Symmetry code: #1 - x, -y + 1, -z + 1.



(0)

Fig. S5 The $[Cu_6(3-dpye)_2(\mu_2-OH)_4]$ loop in **4** (a) and $[Cu_6(3-dpyb)_2(\mu_2-OH)_4]$ loop in **5** (b) tuned by the spacer length of ligands.



Fig.S6 View of the 3D network in complex 4.



Fig.S7 View of the 3D supramolecular network in complex 6.



Fig.S8 ORTEP drawings of complex **7** with thermal ellipsoids at 50% probability. The lattice water molecules and H atoms have been omitted for clarity.



Fig.S9 The simplified representation of 2D layer in complex 7.





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Fig.S10 (a–g) The IR spectra of complexes 1–7. (h–n) The IR spectra of complexes 1–7 after the photocatalysis experiments.









Fig.S11 The simulated (black line) and experimental (red line) powder X-ray diffraction patterns for complexes 1–7.



Fig.S12 The TG curves of complexes 1–7.







Fig.S13 Cyclic voltammograms of **2**-CPE (+550 to 150 mV), **3**-CPE (-450 to 500 mV), **4**-CPE (+600 to 250 mV), **5**-CPE (+600 to 250 mV), **6**-CPE (-450 to 500 mV), and **7**-CPE (+600 to 200 mV) in 0.01 M H₂SO₄-0.5 M Na₂SO₄ aqueous solution. Scan rate: 100 mV s⁻¹, respectively.







Fig.S14 Cyclic voltammograms of the **2**-, **3**-, **4**-, **5**-, **6**-, **7**-CPE in 0.01 M H_2SO_4 -0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280 mV s⁻¹ for **2**-, **3**-, **6**-, **7**-CPE, and 20, 40, 60, 80, 100, 120, 140, 160, 180, 200 mV s⁻¹ for **4**-CPE and **5**-CPE). The inset shows the plots of the anodic and cathodic peak currents against scan rates.





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Fig.S15 Cyclic voltammograms of the bare CPE in 0.01 M H_2SO_4 -0.5 M Na_2SO_4 aqueous solution containing 1.0 mmol/L KNO₂, **1**-CPE, **2**-CPE and **4**-CPE in 0.01 M H_2SO_4 -0.5 M Na_2SO_4 aqueous solution containing: 0.0 (a), 2.0 (b), 4.0 (c), 6.0 (d) and 8.0 (e) mmol/L KNO₂. **5**-CPE and **7**-CPE in 0.01 M H_2SO_4 -0.5 M Na_2SO_4 aqueous solution containing: 0.0 (a), 2.0 (b), 4.0 (c) and 6.0 (d) mmol/L KNO₂. Scan rate: 100 mV s⁻¹, respectively.





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Fig. S16 Absorption spectra of the MB solution during the decomposition reaction under UV light irradiation with the use of **1**, **2**, **4**, **5**, **7**, and without catalyst.