Supporting Information for

Delicate modulated assembly of a new kind of trinuclear copper(II) motifs governed by N-contained agents

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1. ^{1}H-NMR spectrum, IR spectrum and fluorescence spectrum for H_6L.

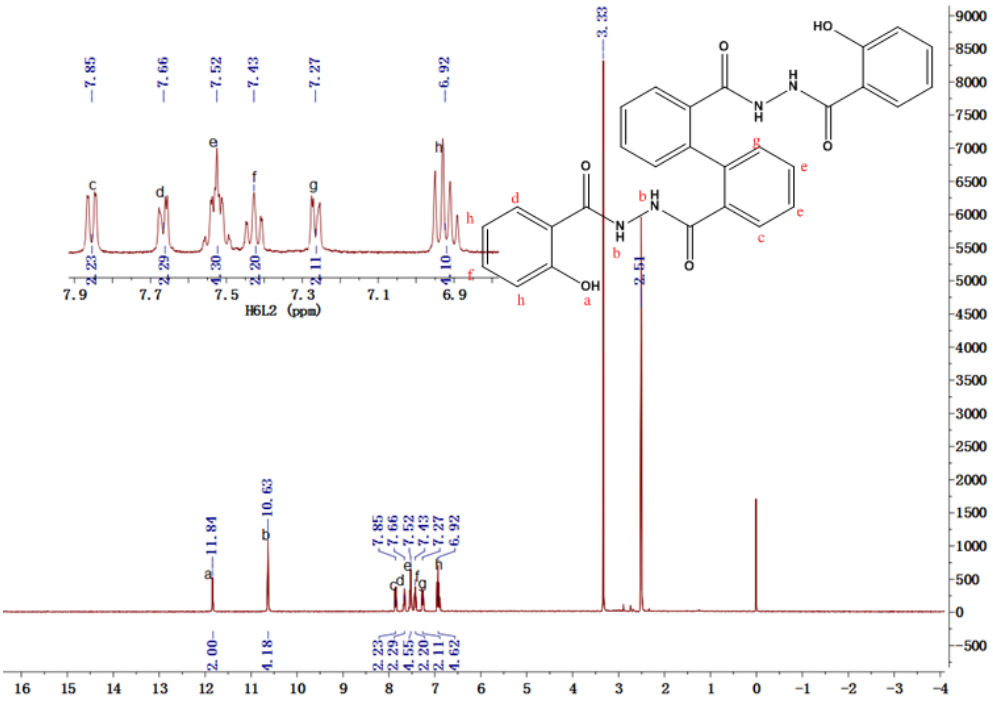

Fig. S1 ^{1}H-NMR (DMSO-d_6) spectrum for H_6**L.**

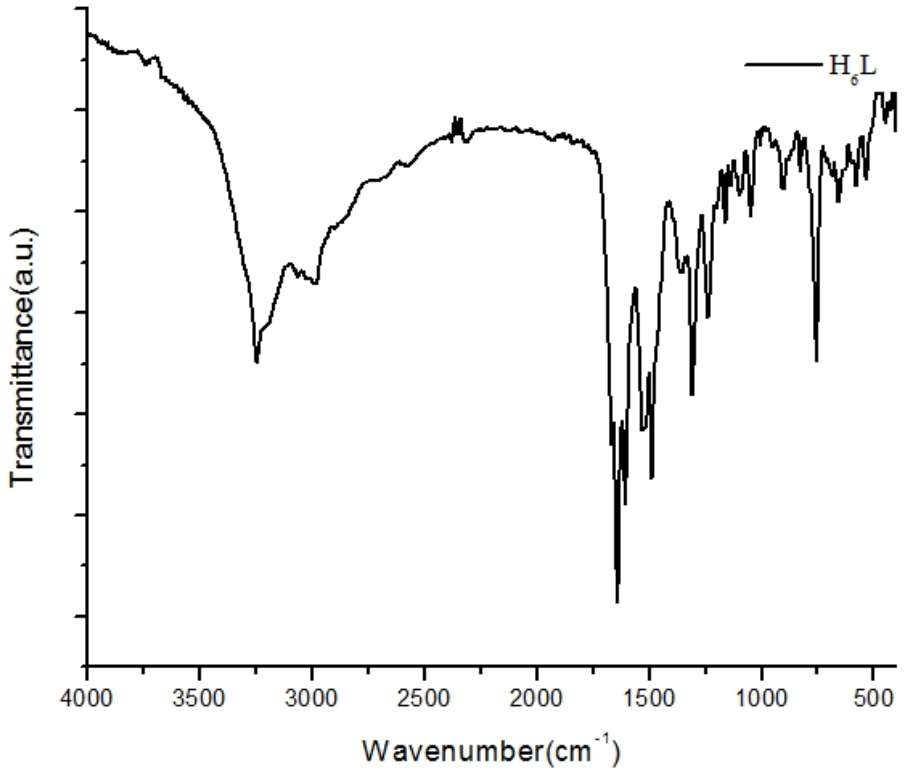

Fig. S2 IR spectrum for H_6**L** (KBr disc).

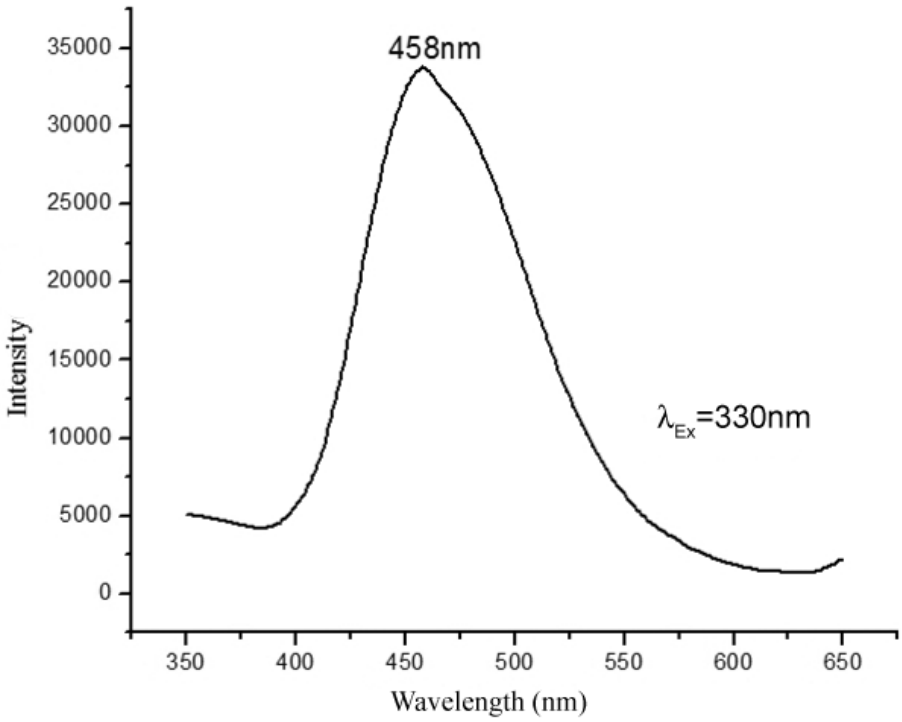

Fig. S3 Solid-state fluorescence spectrum for H_6**L.**

2. XRPD patterns of complex 3-5.

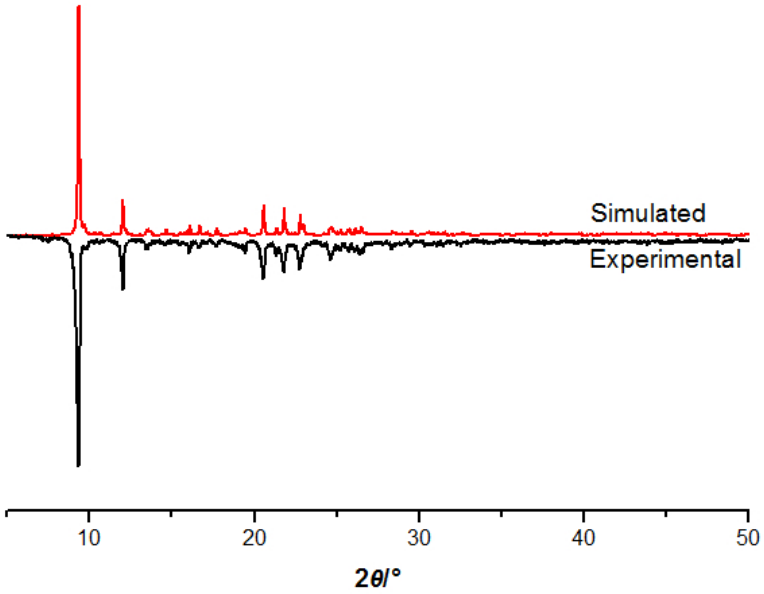

Fig. S4 XRPD patterns of complex **3.**

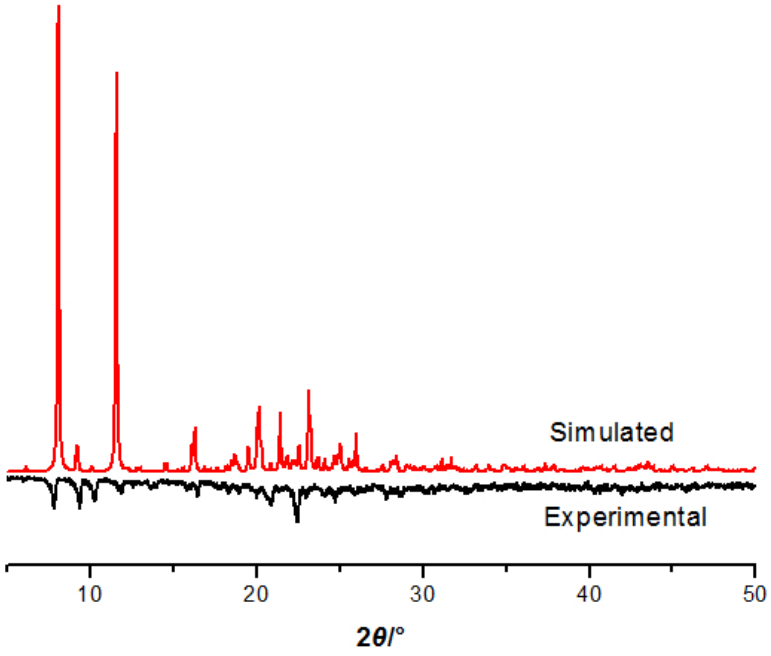

Fig. S5 XRPD patterns of complex **4**. It is worth to mention that there are some minor disagreements in the degree of 20-25°, which suggest the crystal structure of **4** with *EqAx* assembly style might not be the only structure that existed in the synthesis, however, still the major one. Based on this XRPD result, thermal gravimetric analysis and magnetic measurement wasn't taken for **4**.

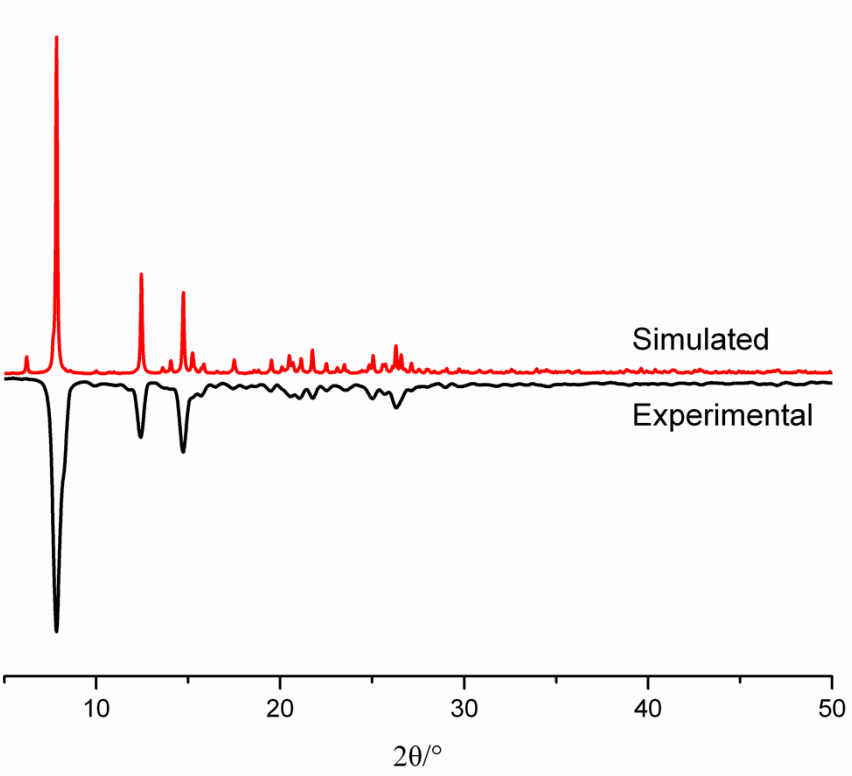

Fig. S6 XRPD patterns of complex **5.**

3. Lists of bond lengths and hydrogen bonds for complex 1-5 (Table S1-S9).

Table S1 List of Bond lengths for complex **1** involved Cu^{II} centers (Å).

Cu(1)-O(1)	1.902(4)	Cu(1)-N(1)	1.907(5)
Cu(1)-O(3)	1.971(4)	Cu(1)-N(8)#1	2.043(5)
Cu(1)-O(1S)	2.6367(83)	Cu(1)-O(2S)	2.5011(57)
Cu(2)-O(5)	1.924(4)	Cu(2)-O(2)	1.943(4)
Cu(2)-N(2)	1.961(5)	Cu(2)-N(3)	1.967(5)
Cu(3)-O(6)	1.901(4)	Cu(3)-N(4)	1.910(5)
Cu(3)-O(4)	1.957(4)	Cu(3)-N(7)	2.036(4)
Cu(3)-O(3S)	2.388(4)		

Symmetry codes: #1, x, -y+2, z+1/2.

Table S2 List of hydrogen bond lengths and angles for complex **1**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<D−H···A (°)
O1W-H1WC...O1_#1	0.809(10)	1.965(16)	2.767(6)	171(7)
O1W-H1WD...N6	0.806(10)	2.020(17)	2.817(6)	170(6)
O2W-H2WC...O3S_#2	0.809(10)	2.09(2)	2.852(6)	156(5)
O2W-H2WD...O1W	0.803(10)	1.97(2)	2.759(7)	166(6)
O3W-H3WD...O2S_#3	0.809(10)	2.287(13)	3.094(8)	176(7)
O3W-H3WC...O2W	0.808(10)	2.08(3)	2.843(7)	156(7)

Symmetry codes: #1, x, -y+1, z-1/2; #2, x, y-1, z; #3, -x+1/2, y-1/2, -z+1/2.

Table S3 List of Bond lengths for complex **2** involved Cu^{II} centers (Å).

Cu(1)-O(1)	1.910(4)	Cu(1)-N(1)	1.919(5)
Cu(1)-O(2)	1.984(4)	Cu(1)-N(5)	2.024(5)
Cu(2)-O(3)	1.926(4)	Cu(1)-O(1S)	2.7237(44)
Cu(2)-O(4)	1.940(4)	Cu(2)-N(2)	1.946(5)
Cu(2)-N(3)	1.957(5)	Cu(3)-N(4)	1.898(5)
Cu(3)-O(6)	1.901(4)	Cu(3)-O(1W)	1.920(4)
Cu(3)-O(5)	1.955(4)	Cu(3)-O(7)#1	2.5597(44)

Symmetry codes: #1, x, -y+2, z-1/2.

Table S4 List of hydrogen bond lengths and angles for complex **2**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<D−H···A (°)
O1W-H1WA...O1S_#2	0.839(10)	1.876(18)	2.704(7)	169(6)
O1W-H1WB...O6_#3	0.839(10)	1.788(12)	2.626(6)	178(7)

Symmetry codes: #1, -x+1/2, -y+3/2, -z+1; #2, -x+1/2, y-1/2, -z+1/2; #3, -x+1/2, -y+3/2, -z.

Table S5 List of Bond lengths for complex **3** involved Cu^{II} centers (Å).

Cu(1)-N(1)	1.904(2)	Cu(1)-O(1)	1.909(2)
Cu(1)-O(2)	1.981(2)	Cu(1)-N(5)	2.014(3)
Cu(1)-O(1)#1	2.5368(26)	Cu(1)-Cu(1)#1	3.4107(9)
Cu(2)-O(3)	1.920(2)	Cu(2)-O(4)	1.922(2)
Cu(2)-N(2)	1.941(2)	Cu(2)-N(3)	1.959(2)
Cu(3)-O(6)	1.903(2)	Cu(3)-N(4)	1.909(2)
Cu(3)-O(5)	1.963(2)	Cu(3)-N(6)	2.006(3)
Cu(3)-O(6)#2	2.4543(22)	Cu(3)-Cu(3)#2	3.2429(9)

Symmetry codes: #1, -x+1, -y+1, -z; #2, –x+2, -y+1, -z+1.

Table S6 List of Bond lengths for complex **4** involved Cu^{II} centers (Å).

Cu(1)-N(1)	1.888(5)	Cu(1)-O(1)	1.943(4)
Cu(1)-O(1)#1	1.976(4)	Cu(1)-O(2)	1.984(4)
Cu(1)-O(1W)	2.313(5)	Cu(1)-Cu(1)#1	2.9969(15)
Cu(2)-O(4)	1.912(4)	Cu(2)-O(3)	1.918(4)
Cu(2)-N(2)	1.950(5)	Cu(2)-N(3)	1.952(5)
Cu(3)-N(4)	1.891(4)	Cu(3)-O(6)	1.903(5)
Cu(3)-O(5)	1.950(4)	Cu(3)-O(1S)	1.960(4)
Cu(3)-O(6)#2	2.5585(48)	Cu(3)-Cu(3)#2	3.4072(13)

Symmetry codes: #1, -x+1, -y+1, -z+1; #2, -x, -y+1, -z+2.

Table S7 List of hydrogen bond lengths and angles for complex **4**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<D−H···A (°)
O1W-H1WA...O2S_#1	0.88(9)	1.97(9)	2.839(9)	172(9)
O1W-H1WB...O3S_#1	0.96(9)	1.83(9)	2.789(9)	174(8)

Symmetry codes: #1, x+1, y, z.

Table S8 List of Bond lengths for complex **5** involved Cu^{II} centers (Å).

Cu(1)-N(1)	1.900(4)	Cu(1)-O(1)	1.936(4)
Cu(1)-O(2)	1.940(4)	Cu(1)-O(6)#1	1.964(3)
Cu(1)-O(1S)	2.404(5)	Cu(1)-Cu(3)#1	2.9899(11)
Cu(2)-O(3)	1.906(4)	Cu(2)-O(4)	1.911(4)
Cu(2)-N(3)	1.944(4)	Cu(2)-N(2)	1.965(4)
Cu(3)-N(4)	1.906(4)	Cu(3)-O(6)	1.926(4)
Cu(3)-O(5)	1.953(4)	Cu(3)-O(1)#2	1.977(3)
Cu(3)-O(1W)	2.306(8)	Cu(3)-Cu(1)#2	2.9899(10)
Cu(4)-N(5)	1.891(5)	Cu(4)-O(7)	1.933(4)
Cu(4)-O(9)	1.952(4)	Cu(4)-O(12)#1	1.991(3)
Cu(4)-O(2W)	2.221(5)	Cu(4)-Cu(6)#1	2.9964(11)

Cu(5)-O(8)	1.926(4)	Cu(5)-O(10)	1.941(4)
Cu(5)-N(7)	1.943(5)	Cu(5)-N(6)	1.949(4)
Cu(6)-N(8)	1.900(4)	Cu(6)-O(11)	1.951(4)
Cu(6)-O(12)	1.951(4)	Cu(6)-O(7)#2	1.958(4)
Cu(6)-O(2S)	2.5416(74)	Cu(6)-Cu(4)#2	2.9964(11)

Symmetry codes: #1, -x+1/2, y-1/2, z; #2, -x+1/2, y+1/2, z.

Table S9 List of hydrogen bond lengths and angles for complex **5**.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<D−H···A (°)
O2W-H2WC...O3S	0.86(2)	1.98(4)	2.788(10)	156(6)
O2W-H2WD...O1S	0.85(2)	2.00(4)	2.766(7)	151(6)
O1W-H1WB...O2S_#1	0.89(2)	1.83(8)	2.619(11)	146(12)

Symmetry codes: #1, x, y, z-1.