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**Supporting Information**

# Syntheses, structures, and magnetic properties of three supramolecular isomeric Cu(Ⅱ) square grid networks: solvents effect on the ligand linkages

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# Contents

**Section 1 Selected Bond Distances (Å), Bond Angles (deg) and Hydrogen Bonds Datas for 1-3**

**Table S1** Selected Bond Distances (Å) and Angles (deg) for **1**.

| | | | |
|---|---|---|---|
| Cu(1)-O(1) | 1.972(4) | Cu(1)-O(2) | 1.963(3) |
| Cu(1)-O(3) | 1.975(3) | Cu(1)-O(4) | 1.964(4) |
| Cu(1)-N(1) | 2.227(3) | Cu(1)-Cu(1) #1 | 2.6980(9) |
| | | | |
| O(2)-Cu(1)-O(4) | 89.64(16) | O(2)-Cu(1)-O(1) | 88.60(15) |
| O(4)-Cu(1)-O(1) | 166.20(13) | O(2)-Cu(1)-O(3) | 166.28(13) |
| O(4)-Cu(1)-O(3) | 88.15(16) | O(1)-Cu(1)-O(3) | 90.32(16) |
| O(3)-Cu(1)-N(1) | 92.82(13) | O(4)-Cu(1)-N(1) | 103.88(13) |
| O(1)-Cu(1)-N(1) | 89.90(13) | O(2)-Cu(1)-N(1) | 100.85(13) |
| O(3)-Cu(1)-N(1) | 92.82(13) | O(4)-Cu(1)-N(1) | 103.88(13) |
| O(1)-Cu(1)-Cu(1)#1 | 82.56(9) | O(2)-Cu(1)-Cu(1)#1 | 83.36(9) |
| O(3)-Cu(1)-Cu(1)#1 | 82.94(9) | O(4)-Cu(1)-Cu(1)#1 | 83.64(9) |
| N(1)-Cu(1)-Cu(1)#1 | 171.30(10) | C(18)-N(1)-Cu(1) | 114.6(3) |
| C(1)-O(1)-Cu(1) | 124.9(3) | C(13)#1-O(3)-Cu(1) | 124.0(3) |
| C(1)#1-O(4)-Cu(1) | 124.3(3) | C(13)-O(2)-Cu(1) | 123.7(3) |
| C(19)-N(1)-Cu(1) | 128.1(3) | | |

Symmetry code: #1 -x+2,-y+1,-z+2

**Table S2** Selected Bond Distances (Å) and Angles (deg) for **2.**

| | | | |
|---|---|---|---|
| Cu(1)-O(1) | 1.961(3) | Cu(1)-O(1)#4 | 1.961(3) |
| Cu(1)-O(2) | 2.645(4) | Cu(1)-O(2) #4 | 2.645(4) |
| Cu(1)-N(1) | 2.003(3) | Cu(1)-N(1)#4 | 2.003(3) |
| | | | |
| O(1)#4-Cu(1)-O(1) | 89.10(18) | O(1)#4-Cu(1)-N(1) | 178.54(14) |
| O(1)-Cu(1)-N(1) | 89.91(14) | O(1)#4-Cu(1)-N(1)#4 | 89.91(14) |
| N(1)-Cu(1)-N(1)#4 | 91.10(19) | O(1)-Cu(1)-N(1)#4 | 178.54(14) |
| O(1)#4-Cu(1)-O(2) | 87.24(13) | O(1)-Cu(1)-O(2) | 54.80(13) |
| N(1)-Cu(1)-O(2) | 91.31(13) | N(1)#4-Cu(1)-O(2) | 126.22(13) |
| C(6)-N(1)-Cu(1) | 119.4(3) | C(7)-N(1)-Cu(1) | 122.3(3) |
| C(1)-O(1)-Cu(1) | 107.0(3) | C(1)-O(2)-Cu(1) | 75.8(3) |

Symmetry code: #4 -x, y, -z+3/2

**Table S3** Selected Bond Distances (Å) and Angles (deg) for **3**.

| | | | |
|---|---|---|---|
| Cu(1)-O(1) | 1.967(3) | Cu(1)-O(1)#4 | 1.967(3) |
| Cu(1)-O(2) | 2.515(4) | Cu(1)-O(2) #4 | 2.515(4) |
| Cu(1)-N(1) | 2.012(4) | Cu(1)-N(1)#4 | 2.012(4) |
| | | | |
| O(1)#4-Cu(1)-O(1) | 180.000(1) | O(1)#4-Cu(1)-N(1) | 88.84(15) |
| O(1)-Cu(1)-N(1) | 91.16(15) | O(1)#4-Cu(1)-N(1)#4 | 91.16(15) |
| N(1)-Cu(1)-N(1)#4 | 180.000(1) | O(1)-Cu(1)-N(1)#4 | 88.84(15) |
| O(1)#4-Cu(1)-O(2) | 122.41(13) | O(1)-Cu(1)-O(2) | 57.59(13) |
| N(1)-Cu(1)-O(2) | 88.34(15) | N(1)#4-Cu(1)-O(2) | 91.66(15) |
| C(6)-N(1)-Cu(1) | 114.2(3) | C(7)-N(1)-Cu(1) | 127.4(3) |
| C(1)-O(1)-Cu(1) | 101.7(3) | C(1)-O(2)-Cu(1) | 77.4(3) |

Symmetry code: #4 -x+2, -y, -z+2

**Table S4** Hydrogen Bond Lengths (Å) and Angles (˚) for **1**.

| ***D–H···A*** | ***d (D–H)*** | ***d (H···A)*** | ***∠DHA*** | ***d (D···A)*** |
|---|---|---|---|---|
| O5–H5B···O9#1 | 0.850 | 2.597 | 168.10 | 3.415 |
| O6–H6A···O5 | 0.850 | 1.948 | 141.79 | 2.669 |
| O6–H6B···N2 | 0.850 | 2.345 | 151.11 | 2.767 |
| O7–H7A···O5#2 | 0.850 | 2.145 | 138.33 | 2.835 |
| O7–H7B···O5 | 0.850 | 2.046 | 154.12 | 2.835 |
| O8–H8A···O8#3 | 0.850 | 1.678 | 142.36 | 2.408 |

Symmetry code: #1 x, -y+3/2, z+1/2 #2 -x+1/2, -y+3/2, z #3 -x+1/2, -y+1/2, z

**Table S5** Hydrogen Bond Lengths (Å) and Angles (˚) for **2**.

| ***D–H···A*** | ***d (D–H)*** | ***d (H···A)*** | ***∠DHA*** | ***d (D···A)*** |
|---|---|---|---|---|
| O3–H3A…O2#1 | 0.850 | 1.768 | 170.43 | 2.610 |
| O3–H3B…O1#2 | 0.850 | 1.901 | 170.76 | 2.743 |
| O4–H4A…O3#3 | 0.850 | 2.033 | 175.84 | 2.901 |
| O4–H4B…O6 | 0.850 | 2.140 | 178.96 | 2.986 |
| O5–H5A…O3 | 0.850 | 1.814 | 173.95 | 2.621 |
| O5–H5B…O5#1 | 0.850 | 1.892 | 173.82 | 2.739 |
| O6–H6A…O5#4 | 0.850 | 1.875 | 174.83 | 2.734 |

Symmetry code: #1-x+1/2, -y+1/2, -z+1; #2 -x+1/2, y+1/2, -z+3/2; #3 x+1/2, y+1/2, z; #4 -x+1, -y+1, -z+1

## Section 2 Structural Information for 1, 2 and 3

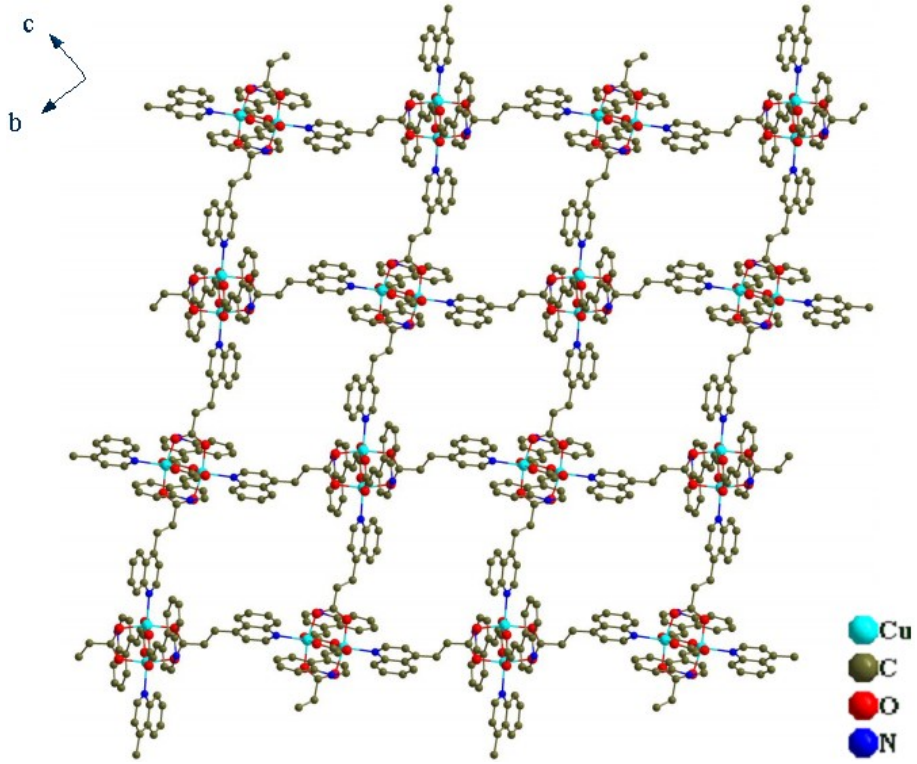


**Fig. S1** The 2D undulated layer structure of **1** viewed down from *a* axis.

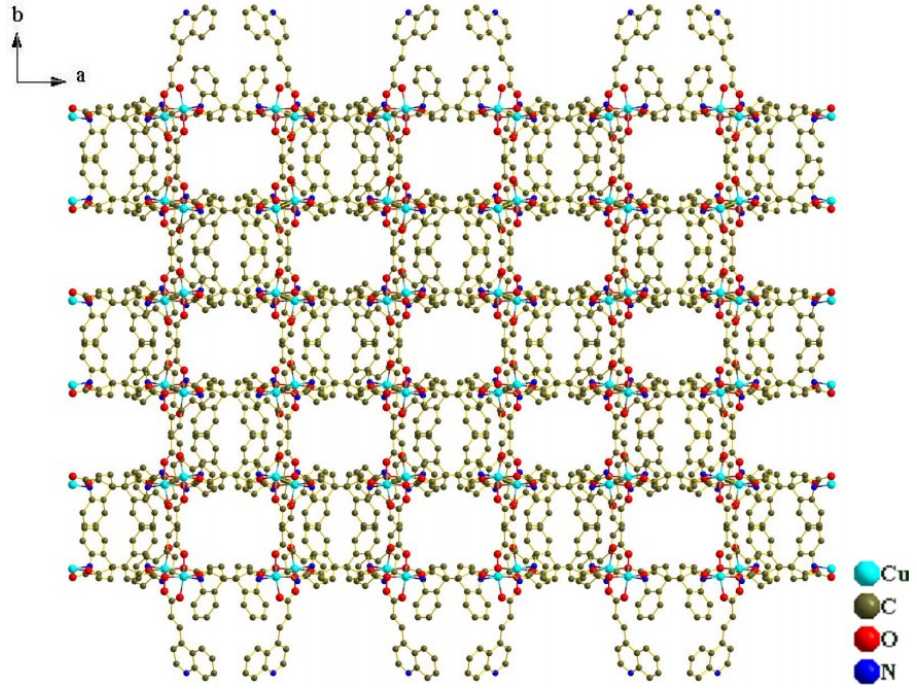


**Fig. S2** The 3D stacking picture of **1** viewed down from *c* axis.

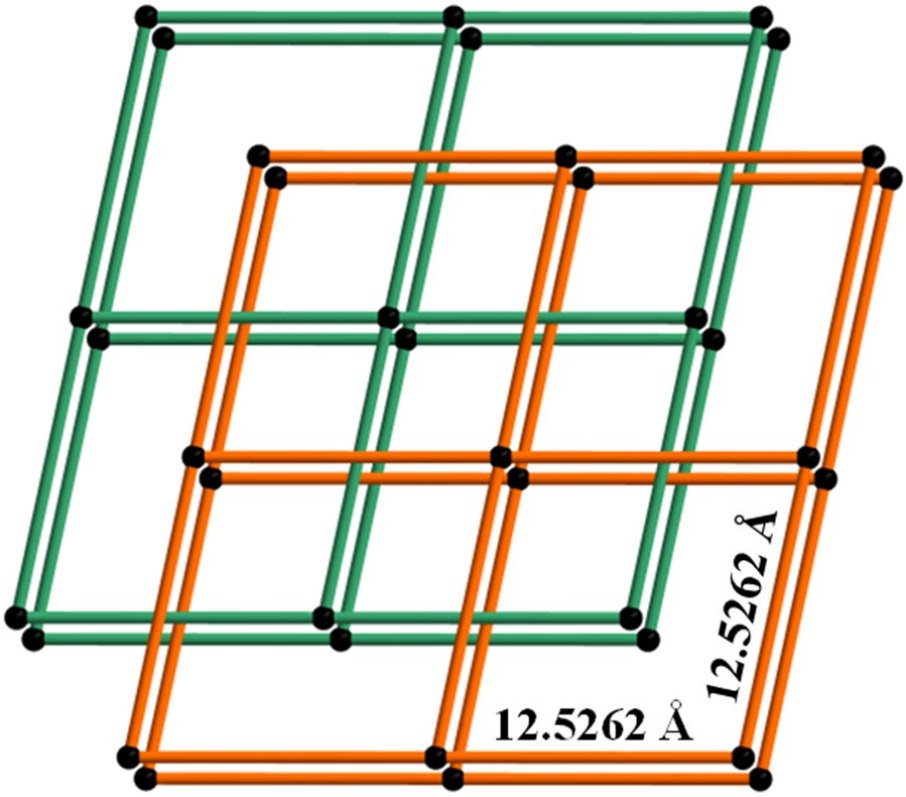


**Fig. S3** Schematic representation of the ABAB stacking structure of **1**, in which the balls represent the paddle-wheel dinuclear Cu(II) secondary building units.

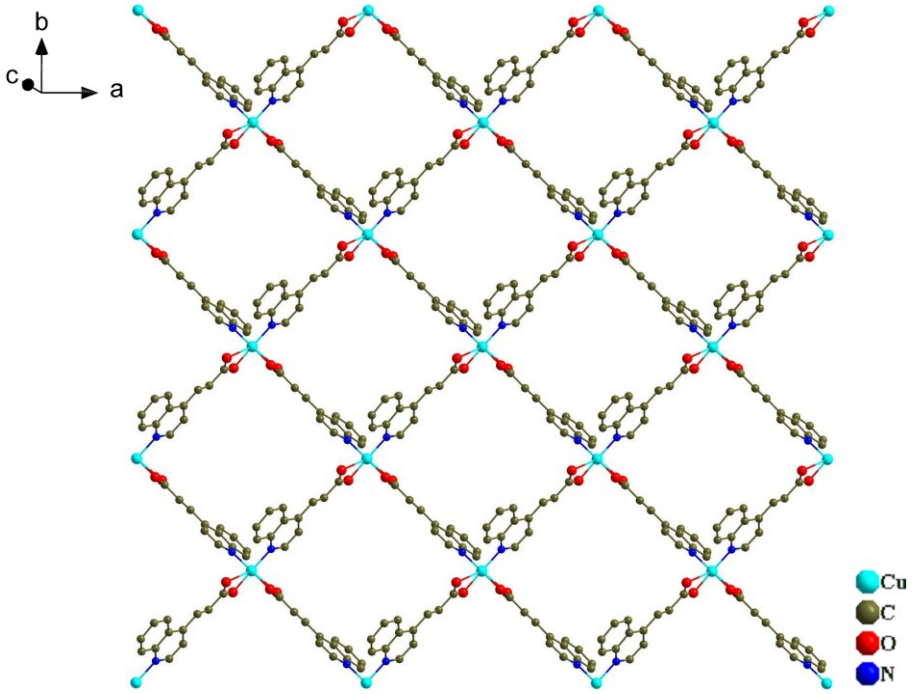


**Fig. S4** The 2D layer structure picture of **2**.

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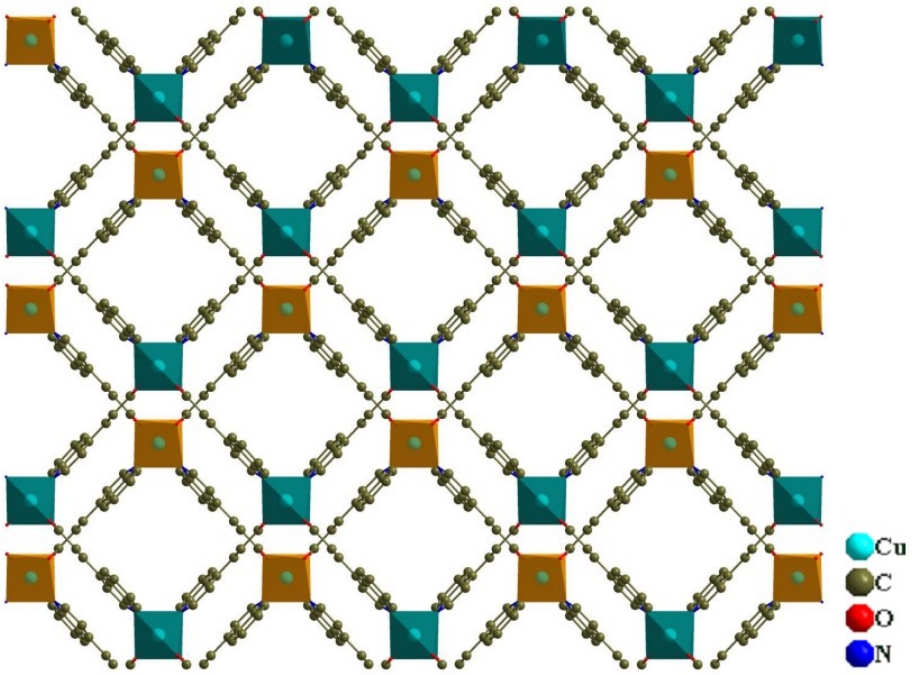


**Fig. S5** The 3D stacking picture of **2** viewed down from *c* axis.

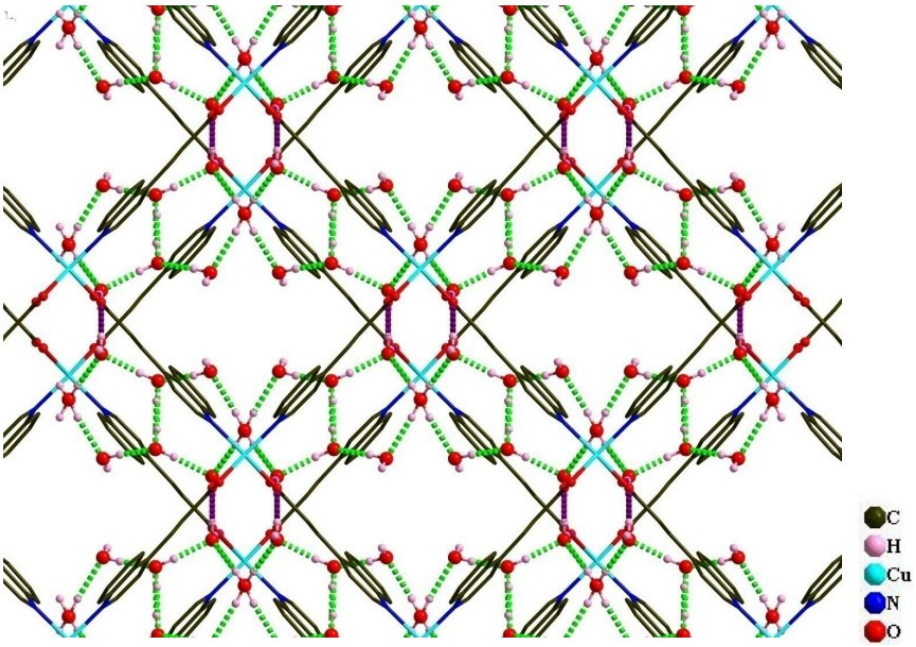


**Fig. S6** The 3D supramolecular structure picture of **2** assembled form hydrogen bond interactions.

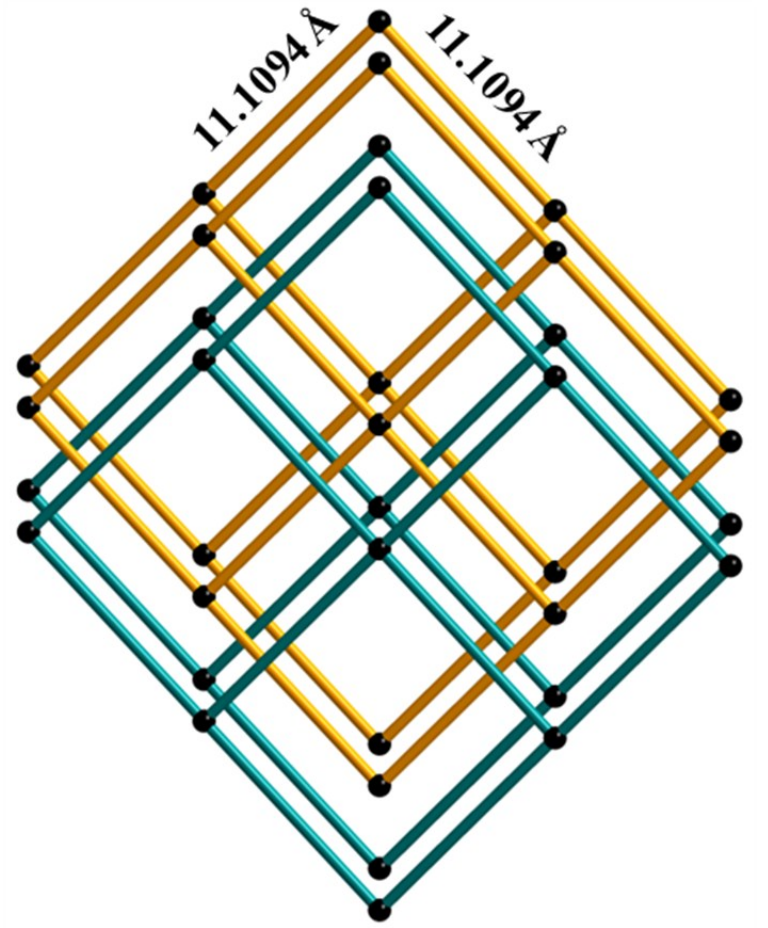


**Fig. S7** Schematic representation of the ABAB stacking structure of **2**, in which the black balls represent the mononuclear Cu(II) centers.

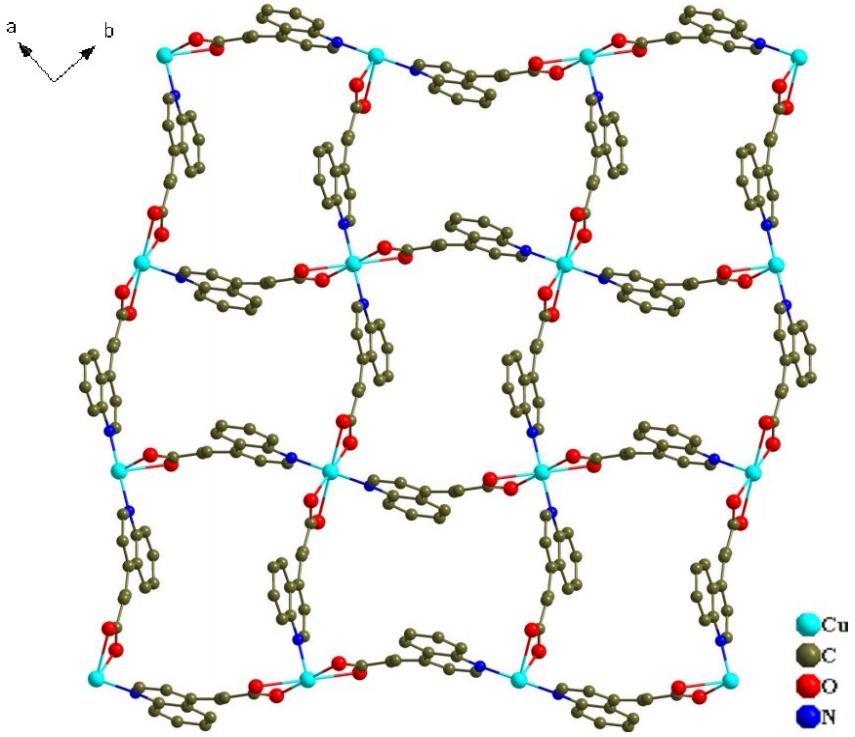


**Fig. S8** The 2D layer structure picture of **3**.

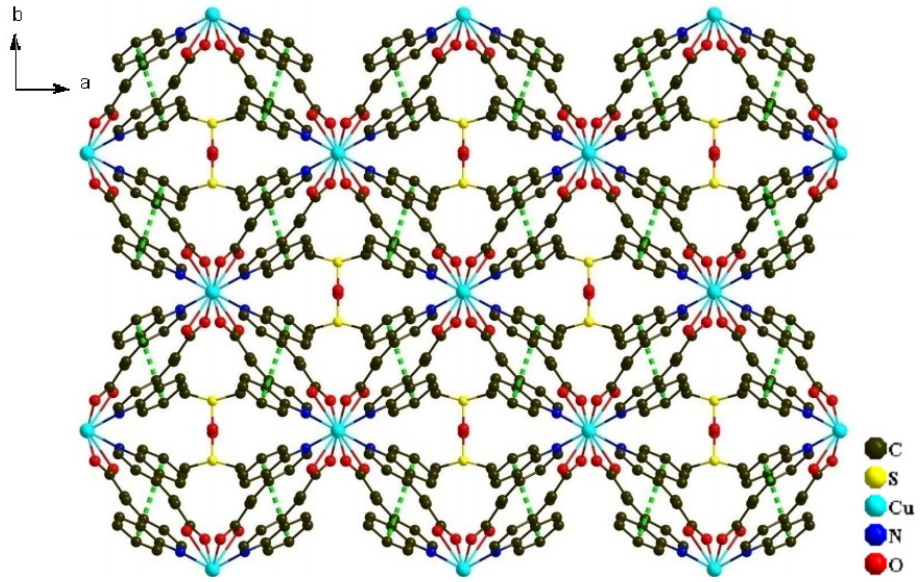


**Fig. S9** View of the 2D layered structure formed by π–π stacking and H-bonding interactions of **3**.

## Section 3 IR spectrum, TGA Curves and PXRD Patterns for 1, 2 and 3

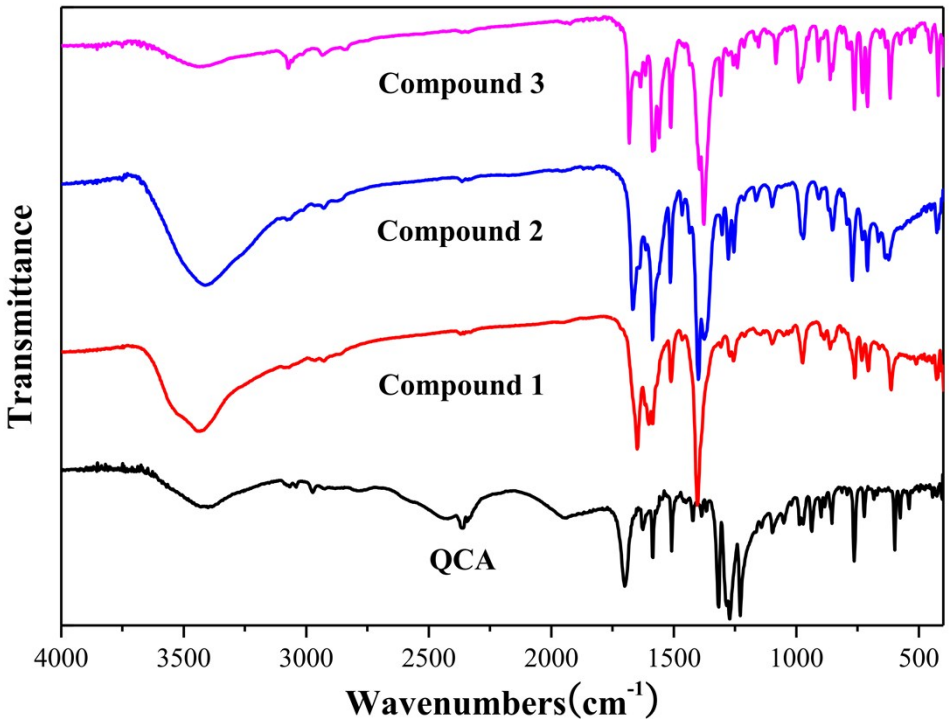


**Fig. S10** IR spectrum picture of QCA ligand and compounds **1-3**.

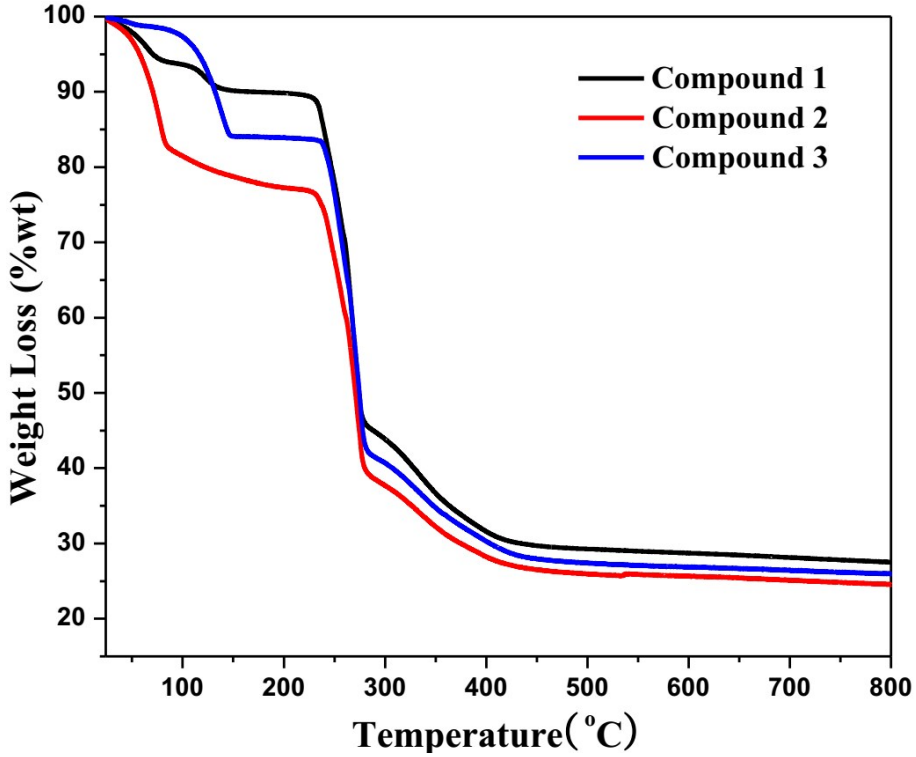


**Fig. S11** TGA curve for compounds **1-3**.

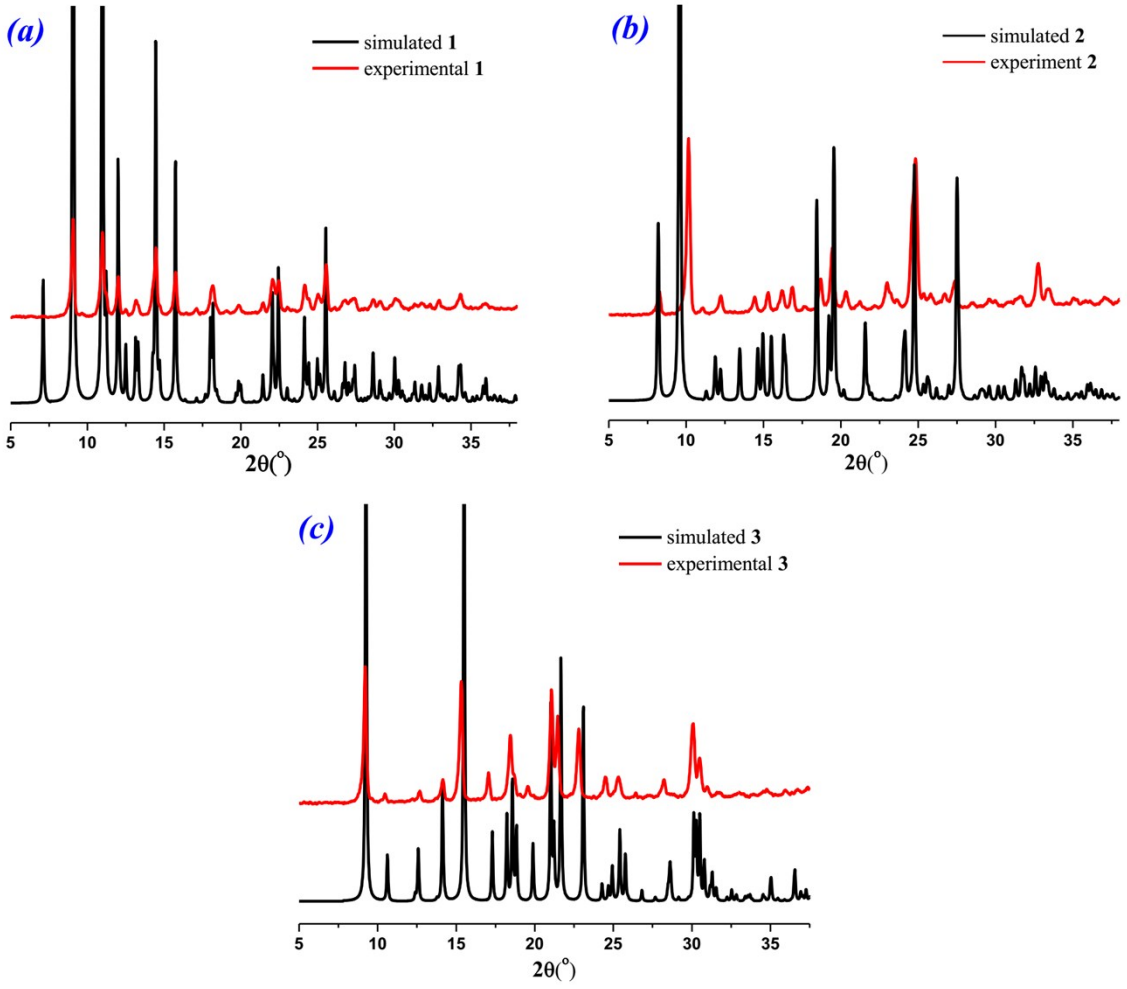


**Fig. S12** Experimental and simulated PXRD pattern for (a) **1**, (b) **2** and (c) **3**.

## Section 4 Magnetic Properties Curves for 1 and 2

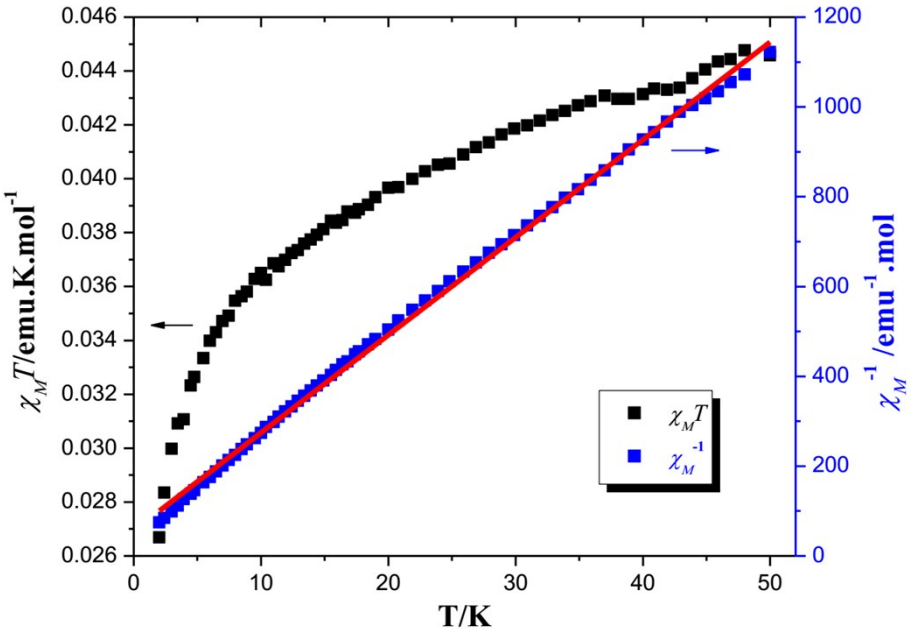


**Fig. S13** Temperature dependence of $\chi_M$T and $\chi_M^{-1}$of **1** at H = 1 kOe from 2 to 50 K. The red line represents the best fit to the Curie-Weiss law.

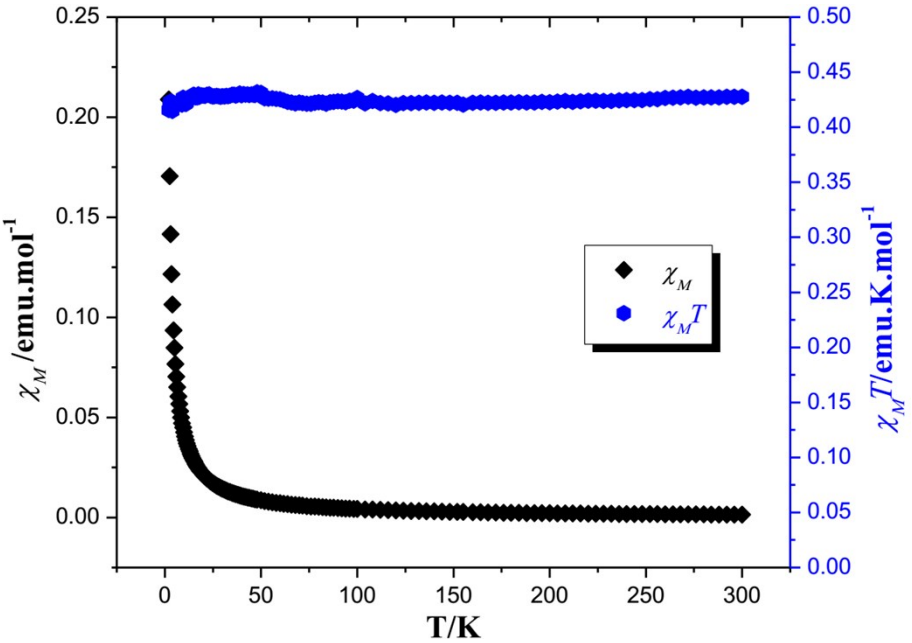


**Fig. S14** Temperature dependence of $\chi_M$T and $\chi_M$ of **2** at H = 1 kOe from 2 to 300 K.