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# pH and amine-induced various octamolybdate-based metal-organic complexes: assembly, structures and properties†

**Xiuli Wang,* Na Han, Hongyan Lin, Aixiang Tian, Guocheng Liu, Juwen Zhang**

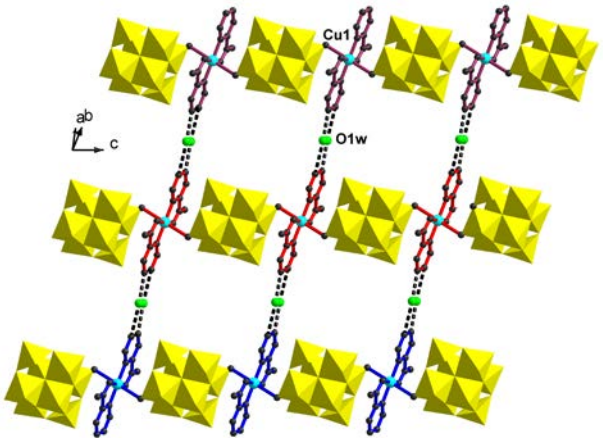


**Fig. S1** The 2D supramolecular layer of compound **1**.

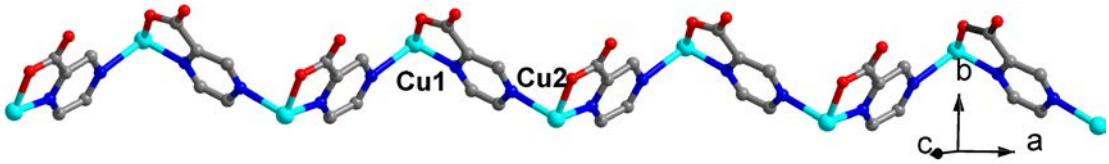


**Fig. S2** The 1D $[Cu_2(pzca)_2]_n^{2n+}$ zigzag chain in compound **2**.

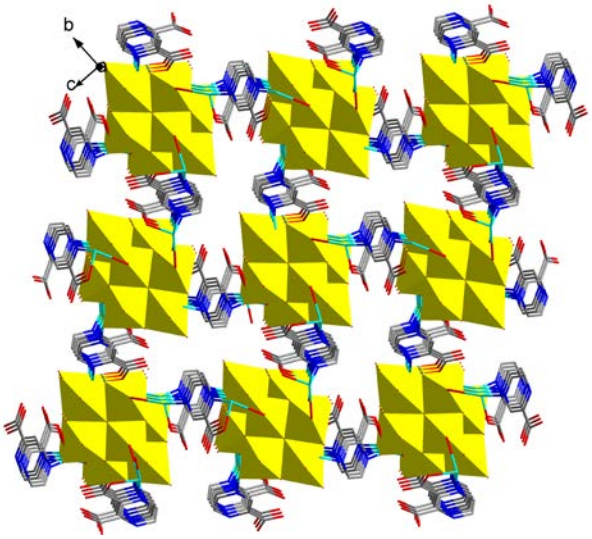


**Fig. S3** The 3D framework of **2** constructed from 1D $[Cu_2(pzca)_2]_n^{2n+}$ zigzag chains and 4–connected β–$Mo_8$ anions.

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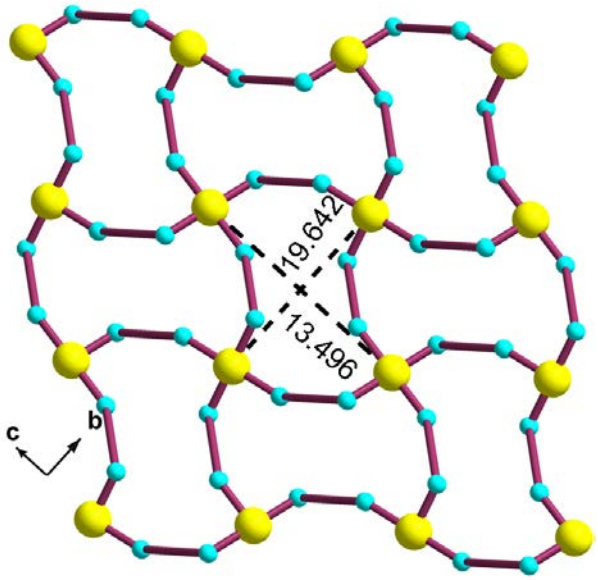



**Fig. S4** The representation of dodecagonal channels with the dimension of 13.496 × 19.642 Å$^2$ in **2**.

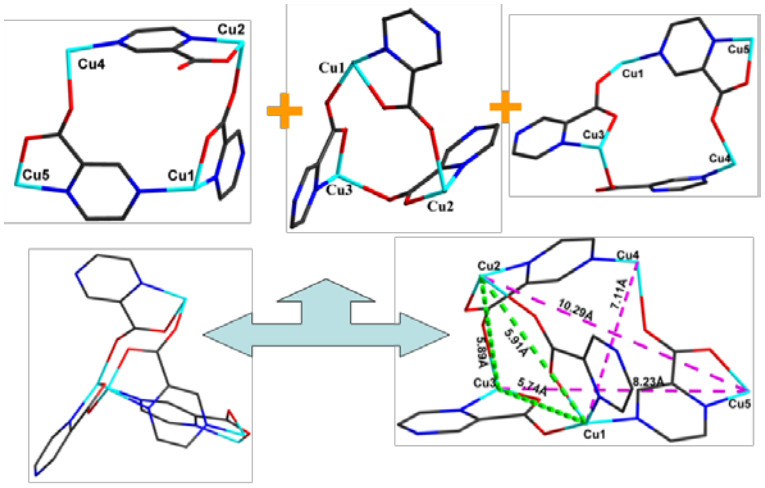



**Fig. S5** The "λ"-like submit

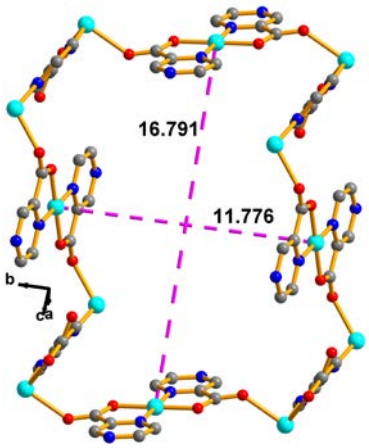



**Fig. S6** The dodecanuclear $[Cu_{12}(pzca)_{12}]$ metal–organic closed loop in compound **3**.

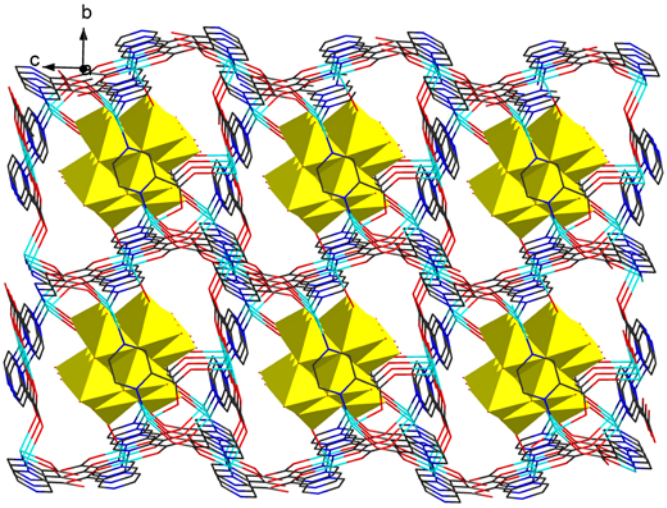
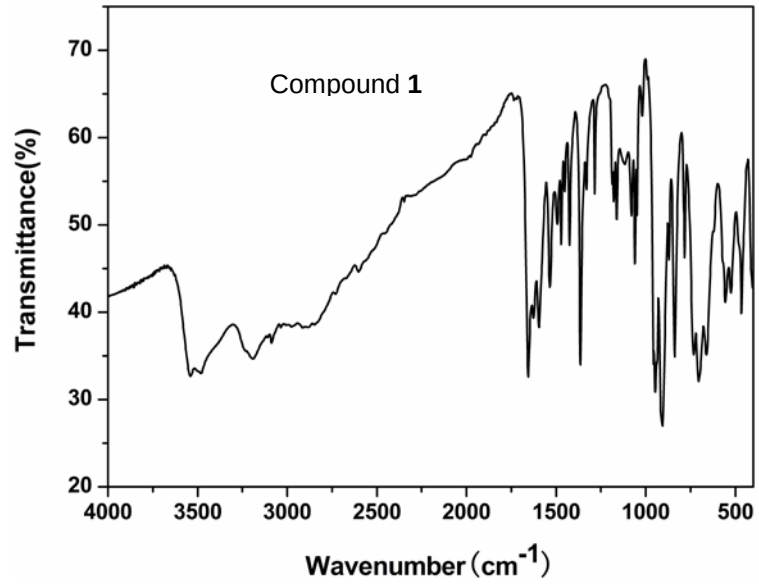
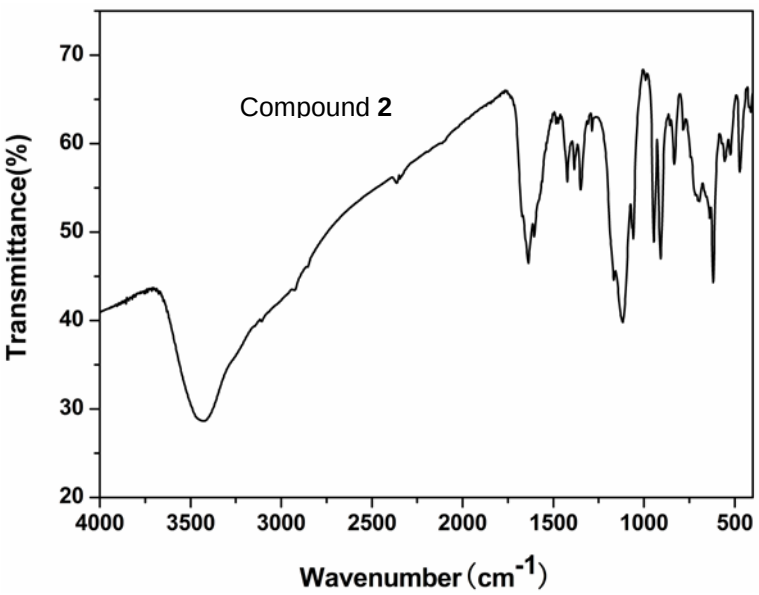



**Fig. S7.** The 3D framework of compound **3**.



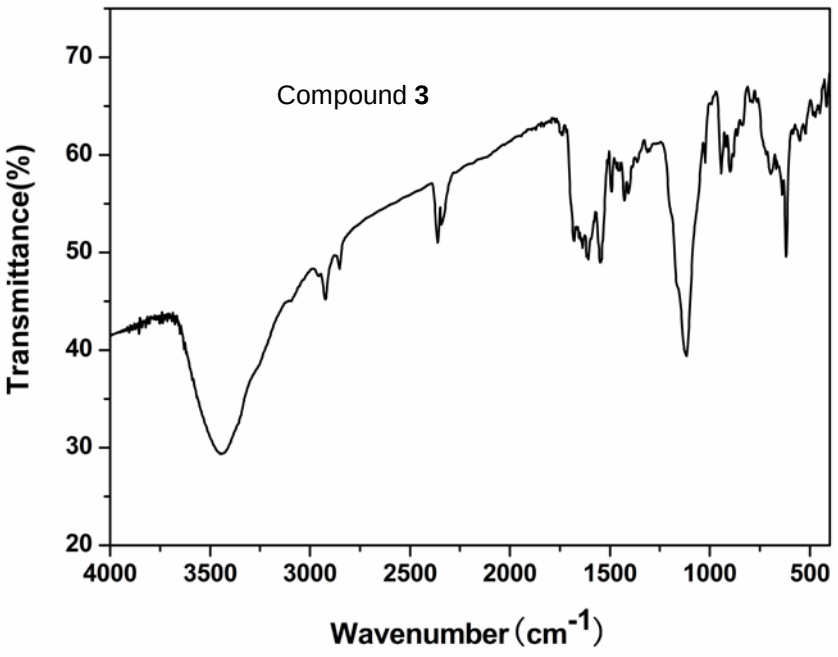



**Fig. S8.** The IR spectra of compounds **1**–**3**.

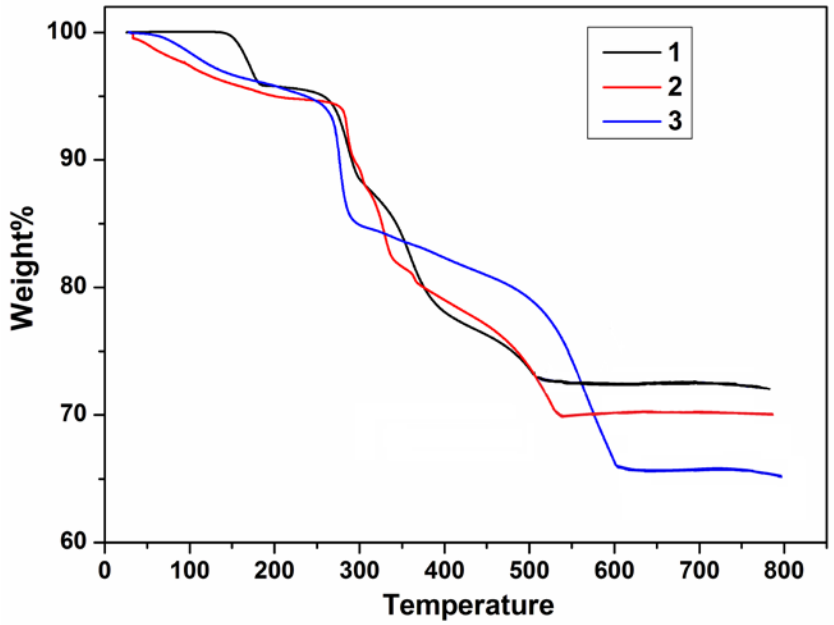



**Fig. S9.** The TG curves of compounds **1**–**3**.

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**Table S1** Selected bond distances (Å) and angles (°) for compounds **1–3**.

| | | | |
|---|---|---|---|
| Compound **1** | | | |
| Cu(1)–O(15)#2 | 1.931(3) | Cu(1)–O(15) | 1.931(3) |
| Cu(1)–N(1) | 1.989(3) | Cu(1)–N(1)#2 | 1.989(3) |
| Cu(1)–O(12)#2 | 2.597(0) | Cu(1)–O(12) | 2.597(0) |
| O(15)#2–Cu(1)–O(15) | 180.0 | O(15)–Cu(1)–N(1) | 83.68(13) |
| O(15)#2–Cu(1)–N(1) | 96.32(13) | O(15)#2–Cu(1)–N(1)#2 | 83.68(13) |
| O(15)–Cu(1)–N(1)#2 | 96.32(13) | N(1)–Cu(1)–N(1)#2 | 180.0 |
| Symmetry code for **1**: #2 –x, –y, –z | | | |
| Compound **2** | | | |
| Cu(1)–O(14) | 1.937(3) | Cu(1)–O(2W) | 1.983(3) |
| Cu(1)–N(1) | 2.319(4) | Cu(1)–N(3) | 2.011(4) |
| Cu(1)–O(1W) | 2.002(3) | Cu(1)–O10 | 2.693(7) |
| Cu(2)–O(8) | 2.772(2) | Cu(2)–O(4W) | 1.970(4) |
| Cu(2)–N(4)#3 | 2.383(4) | Cu(2)–O(3W) | 2.008(4) |
| Cu(2)–O(16) | 1.947(0) | Cu(2)–N(2)#2 | 1.992(4) |
| O(16)#2–Cu(2)–N(4)#3 | 92.55(14) | O(2W)–Cu(1)–O(1W) | 95.58(14) |
| O(14)–Cu(1)–O(2W) | 177.60(14) | N(2)#2–Cu(2)–O(3W) | 164.79(16) |
| O(14)–Cu(1)–N(3) | 82.28(15) | O(14)–Cu(1)–O(1W) | 86.63(14) |
| N(3)–Cu(1)–N(1) | 101.42(15) | O(2W)–Cu(1)–N(1) | 85.97(15) |
| O(1W)–Cu(1)–N(1) | 94.82(14) | O(1W)–Cu(1)–N(3) | 161.00(16) |
| O(14)–Cu(1)–N(1) | 94.78(15) | O(2W)–Cu(1)–N(3) | 95.35(16) |
| O(3W)–Cu(2)–N(4)#3 | 88.19(14) | O(4W)–Cu(2)–N(4)#3 | 93.37(14) |
| O(16)#2–Cu(2)–O(3W) | 89.20(16) | O(4W)–Cu(2)–N(2)#2 | 94.00(16) |
| O(16)#2–Cu(2)–N(2)#2 | 81.25(15) | O(16)#2–Cu(2)–O(4W) | 173.16(15) |
| N(2)#2–Cu(2)–N(4)#3 | 103.95(14) | O(4W)–Cu(2)–O(3W) | 94.40(17) |
| Symmetry code for **2**: #2 x, –y – 1/2, z + 1/2; #3 x + 1, –y – 1/2, z + 1/2. | | | |
| Compound **3** | | | |
| Cu(1)-N(5) | 1.847(6) | Cu(1)-O(3W) | 2.094(5) |
| Cu(1)-N(6) | 1.883(5) | Cu(1)-O(12) | 2.237(11) |
| Cu(1)-O(7) | 2.255(9) | Cu(1')-O(7) | 1.933(8) |
| Cu(1')-C(3') | 1.97(15) | Cu(1')-O(12') | 1.975(8) |
| Cu(1')-O(3W) | 2.094(5) | Cu(1')-N(5) | 2.128(6) |
| Cu(1')-N(6) | 2.327(5) | Cu(2)-O(9)#2 | 1.945(4) |
| Cu(2)-N(3) | 1.988(4) | Cu(2)-O(9) | 1.945(4) |
| Cu(2)-N(3)#2 | 1.988(4) | Cu(3)-N(1)#3 | 1.971(4) |
| Cu(3)-O(10)#3 | 2.350(4) | Cu(3)-O(10) | 2.350(4) |
| Cu(3)-O(11)#3 | 1.983(4) | Cu(3)-O(11) | 1.983(4) |
| N(1)-Cu(3) | 1.971(4) | N(4)-Cu(4)#4 | 1.940(4) |
| Cu(4)-N(4)#5 | 1.940(4) | Cu(4)-O(13) | 2.146(4) |
| Cu(4)-O(15)#5 | 2.248(4) | O(15)-Cu(4)#4 | 2.248(4) |
| Cu(5)-O(14) | 1.950(4) | Cu(5)-O(14)#6 | 1.950(4) |
| Cu(5)-N(7)#6 | 1.965(5) | Cu(5)-N(7) | 1.965(5) |

| | | | |
|---|---|---|---|
| N(5)-Cu(1)-N(6) | 127.8(3) | N(5)-Cu(1)-O(3W) | 104.7(2) |
| N(5)-Cu(1')-N(6) | 97.4(2) | O(12')-Cu(1')-N(6) | 93.1(2) |
| O(3W)-Cu(1')-N(6) | 90.00(18) | C(3')-Cu(1')-N(6) | 102(4) |
| O(7)-Cu(1')-N(6) | 104.8(3) | O(3W)-Cu(1')-N(5) | 95.5(2) |
| O(12')-Cu(1')-N(5) | 166.0(3) | C(3')-Cu(1')-N(5) | 113(7) |
| O(7)-Cu(1')-N(5) | 81.4(3) | O(12')-Cu(1')-O(3W) | 93.8(3) |
| C(3')-Cu(1')-O(3W) | 147(7) | O(7)-Cu(1')-O(3W) | 165.2(3) |
| C(3')-Cu(1')-O(12') | 55(7) | O(7)-Cu(1')-O(12') | 86.9(3) |
| O(7)-Cu(1')-C(3') | 32(7) | O(12)-Cu(1)-O(7) | 40.2(4) |
| O(3W)-Cu(1)-O(7) | 133.3(3) | N(6)-Cu(1)-O(7) | 109.4(3) |
| N(5)-Cu(1)-O(7) | 79.9(3) | O(3W)-Cu(1)-O(12) | 104.9(4) |
| N(6)-Cu(1)-O(12) | 96.7(3) | N(5)-Cu(1)-O(12) | 116.6(4) |
| N(6)-Cu(1)-O(3W) | 103.7(2) | O(9)-Cu(2)-N(3) | 83.48(18) |
| O(9)#2-Cu(2)-O(9) | 180.000(2) | O(9)#2-Cu(2)-N(3) | 96.52(18) |
| N(3)-Cu(2)-N(3)#2 | 179.999(2) | O(9)-Cu(2)-N(3)#2 | 96.52(18) |
| O(9)#2-Cu(2)-N(3)#2 | 83.48(18) | N(1)#3-Cu(3)-O(11) | 96.70(17) |
| N(1)-Cu(3)-N(1)#3 | 180.0 | N(1)-Cu(3)-O(11) | 83.30(17) |
| O(10)#3-Cu(3)-O(10) | 180.0(2) | O(11)-Cu(3)-O(10) | 91.25(18) |
| O(11)#3-Cu(3)-O(10) | 88.75(18) | N(1)#3-Cu(3)-O(10) | 95.58(16) |
| N(1)-Cu(3)-O(10) | 84.42(16) | O(11)#3-Cu(3)-O(10)#3 | 91.25(18) |
| O(11)-Cu(3)-O(10)#3 | 88.75(18) | N(1)#3-Cu(3)-O(10)#3 | 84.42(16) |
| N(1)-Cu(3)-O(10)#3 | 95.58(16) | O(11)-Cu(3)-O(11)#3 | 179.999(1) |
| N(1)#3-Cu(3)-O(11)#3 | 83.30(17) | N(1)-Cu(3)-O(11)#3 | 96.70(17) |
| N(2)-Cu(4)-N(4)#5 | 150.7(2) | N(2)-Cu(4)-O(13) | 100.63(17) |
| O(13)-Cu(4)-O(15)#5 | 90.95(16) | N(4)#5-Cu(4)-O(15)#5 | 95.78(18) |
| N(2)-Cu(4)-O(15)#5 | 106.81(19) | N(4)#5-Cu(4)-O(13) | 97.36(17) |
| O(14)-Cu(5)-O(14)#6 | 180.0(2) | O(14)-Cu(5)-N(7) | 83.73(18) |
| N(7)-Cu(5)-N(7)#6 | 180.0 | O(14)#6-Cu(5)-N(7)#6 | 83.73(18) |
| O(14)-Cu(5)-N(7)#6 | 96.27(18) | O(14)#6-Cu(5)-N(7) | 96.27(18) |

Symmetry code for **3**: #2 –x + 2, –y + 4, –z; #3 –x + 2, –y + 3, –z; #5 x + 1, y, z; #6 –x + 1, –y + 3, –z + 1; #7 –x + 2, –y + 4, –z + 1; #8 x – 1, y – 1, z.

**Table S2** Selected hydrogen–bonding geometry (Å, °) for compound **1**

| D–H···A | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| N3–H(3D)···O9 | 0.89 | 2.57 | 3.0949 | 119 |
| N4–H(4D)···O8 | 0.89 | 2.38 | 2.8983 | 118 |
| C(4)–H(4A)···O(1W) | 0.93 | 2.49 | 3.3138 | 148 |
| N(2)–H(2A)···O(1W) | 0.86 | 2.06 | 2.8760 | 158 |

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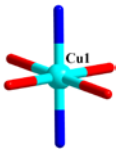
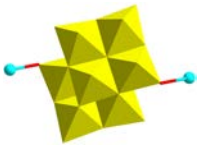
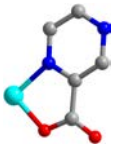
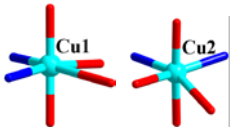
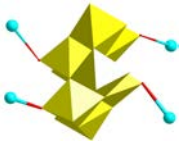
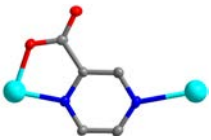
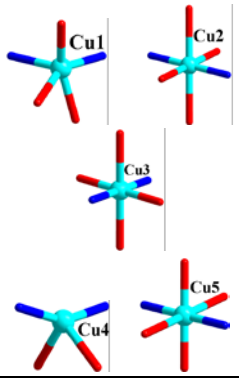
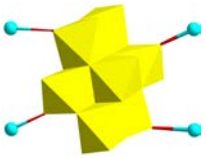
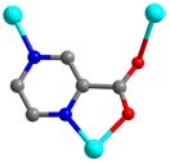
**Table S3** The bond valence calculations of the Cu ions in compound **3**.

| Cu ions | Cu1 | Cu2 | Cu3 | Cu4 | Cu5 |
|---|---|---|---|---|---|
| Bond Valence | 1.97 | 2.07 | 2.11 | 1.48 | 2.03 |

**Table S4** The coordination modes of the Cu(II) ions, $\beta$-$Mo_8$ anions and pzca ligands in compounds **1**–**3**.

| Compound | Cu(II) ions | $\beta$-$Mo_8$ anions | pzca ligands |
|---|---|---|---|
| **1** |  |  |  A |
| **2** |  |  |  B |
| **3** |  |  |  C |