

Supporting Information

Four tetrazolate-based 3D frameworks with diverse subunits directed by inorganic anions or azido coligand: hydrothermal syntheses, crystal structures, and magnetic behaviors

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Table S1 Selected bond lengths /Å and angles /° for **1**^a

Cu(1)–N(6)	1.991(3)	Cu(1)–O(5)	2.056(2)
Cu(1)–O(3)	2.252(2)	Cu(2)–O(1)	1.968(2)
Cu(2)–O(5)	2.004(2)	Cu(2)–N(8) ^{#2}	2.009(3)
Cu(2)–N(4) ^{#3}	2.013(3)	Cu(2)–N(7) ^{#1}	2.414(3)
Cu(2)–N(2)	2.434(3)	Cu(3)–N(1)	1.946(3)
Cu(3)–N(5)	1.958(3)	Cu(3)–O(2) ^{#4}	1.991(2)
Cu(3)–O(5)	2.028(2)	Cu(3)–O(2)	2.256(2)
N(6)–Cu(1)–O(5)	88.01(10)	N(6) ^{#1} –Cu(1)–O(5)	91.99(10)
N(6)–Cu(1)–O(5) ^{#1}	91.99(10)	N(6) ^{#1} –Cu(1)–O(5) ^{#1}	88.01(10)
N(6)–Cu(1)–O(3)	89.69(10)	N(6) ^{#1} –Cu(1)–O(3)	90.30(10)
O(5)–Cu(1)–O(3)	85.94(8)	O(5) ^{#1} –Cu(1)–O(3)	94.06(8)
N(6)–Cu(1)–O(3) ^{#1}	90.31(10)	N(6) ^{#1} –Cu(1)–O(3) ^{#1}	89.70(10)
O(5)–Cu(1)–O(3) ^{#1}	94.06(8)	O(5) ^{#1} –Cu(1)–O(3) ^{#1}	85.94(8)
O(1)–Cu(2)–O(5)	92.24(9)	O(1)–Cu(2)–N(8) ^{#2}	85.70(10)
O(5)–Cu(2)–N(4) ^{#3}	94.13(10)	O(1)–Cu(2)–N(7) ^{#1}	89.37(9)
N(8) ^{#2} –Cu(2)–N(4) ^{#3}	88.13(11)	N(8) ^{#2} –Cu(2)–N(7) ^{#1}	95.11(10)
O(5)–Cu(2)–N(7) ^{#1}	87.77(9)	O(1)–Cu(2)–N(2)	98.08(10)
N(4) ^{#3} –Cu(2)–N(7) ^{#1}	87.12(10)	N(8) ^{#2} –Cu(2)–N(2)	90.97(10)
O(5)–Cu(2)–N(2)	86.45(9)	N(4) ^{#3} –Cu(2)–N(2)	86.08(10)
N(5)–Cu(3)–O(5)	90.32(10)	N(1)–Cu(3)–O(2) ^{#4}	92.37(10)
N(5)–Cu(3)–O(2) ^{#4}	88.11(10)	N(1)–Cu(3)–O(5)	91.72(10)
N(1)–Cu(3)–O(2)	103.01(10)	N(5)–Cu(3)–O(2)	92.59(10)
O(2) ^{#4} –Cu(3)–O(2)	78.91(9)	O(5)–Cu(3)–O(2)	91.68(8)

^a Symmetry codes: ^{#1} 1 – x, – y, 1 – z; ^{#2} x – 1, y, z; ^{#3} 1/2 – x, y – 1/2, 3/2 – z; ^{#4} 1 – x, 1 – y, 1 – z.

Table S2 Selected bond lengths /Å and angles /° for **2**^a

Cu(1)–N(2)	2.022(3)	Cu(1)–Cl(1)	2.6050(16)
Cu(2)–N(4) ^{#4}	2.009(4)	Cu(2)–N(1)	2.056(4)
Cu(2)–Cl(1)	2.4743(16)		
N(2) ^{#1} –Cu(1)–N(2)	87.6(2)	N(2)–Cu(1)–N(2) ^{#2}	92.4(2)
N(2) ^{#1} –Cu(1)–N(2) ^{#3}	92.4(2)	N(2) ^{#2} –Cu(1)–N(2) ^{#3}	87.6(2)
N(2) ^{#1} –Cu(1)–Cl(1)	87.79(10)	N(2)–Cu(1)–Cl(1)	87.79(10)
N(2) ^{#2} –Cu(1)–Cl(1)	92.21(10)	N(2) ^{#3} –Cu(1)–Cl(1)	92.21(10)
N(2) ^{#1} –Cu(1)–Cl(1) ^{#3}	92.21(10)	N(2)–Cu(1)–Cl(1) ^{#3}	92.21(10)
N(2) ^{#2} –Cu(1)–Cl(1) ^{#3}	87.79(10)	N(2) ^{#3} –Cu(1)–Cl(1) ^{#3}	87.79(10)
N(4) ^{#4} –Cu(2)–N(4) ^{#5}	91.3(2)	N(4) ^{#4} –Cu(2)–N(1)	89.68(15)
N(4) ^{#5} –Cu(2)–N(1) ^{#1}	89.68(15)	N(1)–Cu(2)–N(1) ^{#1}	87.7(2)
N(4) ^{#4} –Cu(2)–Cl(1)	96.72(10)	N(4) ^{#5} –Cu(2)–Cl(1)	96.72(10)
N(1)–Cu(2)–Cl(1)	92.67(10)	N(1) ^{#1} –Cu(2)–Cl(1)	92.67(10)

^a Symmetry codes: ^{#1} $x, y, 1 - z$; ^{#2} $1 - x, 1 - y, z$; ^{#3} $1 - x, 1 - y, 1 - z$; ^{#4} $3/2 - x, y + 1/2, 1/2 - z$; ^{#5} $3/2 - x,$

y + $1/2,$ z + $1/2.$

Table S3 Selected bond lengths /Å and angles /° for **3**^a

Cu(1)–N(4) ^{#1}	1.981(3)	Cu(1)–N(3) ^{#2}	1.986(3)
Cu(1)–N(5)	1.991(3)	Cu(1)–N(5) ^{#3}	2.000(2)
Cu(1)–N(1)	2.204(3)		
N(4) ^{#1} –Cu(1)–N(5)	86.53(11)	N(3) ^{#2} –Cu(1)–N(5)	93.10(11)
N(4) ^{#1} –Cu(1)–N(5) ^{#3}	91.38(11)	N(3) ^{#2} –Cu(1)–N(5) ^{#3}	86.07(10)
N(4) ^{#1} –Cu(1)–N(1)	99.92(11)	N(3) ^{#2} –Cu(1)–N(1)	93.13(11)
N(5)–Cu(1)–N(1)	96.04(12)	N(5) ^{#3} –Cu(1)–N(1)	96.82(12)

^a Symmetry codes: ^{#1} $1/2 - x, 1 - y, z - 1/2$; ^{#2} $-x, y + 1/2, 1/2 - z$; ^{#3} $x - 1/2, 3/2 - y, -z$.

Table S4 Selected bond lengths /Å and angles /° for **4**^a

Cu(1)–N(5) ^{#1}	2.100(7)	Cu(2)–N(6)	2.096(7)
Cu(1)–N(7)	2.134(6)	Cu(2)–N(4)	2.120(6)
Cu(1)–N(3)	2.142(6)		
N(5) ^{#1} –Cu(1)–N(7)	89.8(3)	N(5) ^{#2} –Cu(1)–N(7)	90.2(3)
N(5) ^{#1} –Cu(1)–N(7) ^{#3}	90.2(3)	N(5) ^{#2} –Cu(1)–N(7) ^{#3}	89.8(3)
N(5) ^{#1} –Cu(1)–N(3) ^{#3}	89.8(2)	N(5) ^{#2} –Cu(1)–N(3) ^{#3}	90.2(2)
N(7)–Cu(1)–N(3) ^{#3}	89.9(3)	N(7) ^{#3} –Cu(1)–N(3) ^{#3}	90.1(3)
N(5) ^{#1} –Cu(1)–N(3)	90.2(2)	N(5) ^{#2} –Cu(1)–N(3)	89.8(2)
N(7)–Cu(1)–N(3)	90.1(3)	N(7) ^{#3} –Cu(1)–N(3)	89.9(3)
N(6) ^{#4} –Cu(2)–N(6) ^{#2}	88.4(3)	N(6) ^{#4} –Cu(2)–N(6)	88.4(3)
N(6) ^{#2} –Cu(2)–N(6)	88.4(3)	N(6) ^{#4} –Cu(2)–N(4) ^{#4}	90.5(2)
N(6) ^{#2} –Cu(2)–N(4) ^{#4}	90.0(3)	N(6) ^{#2} –Cu(2)–N(4) ^{#2}	90.5(3)
N(6)–Cu(2)–N(4) ^{#2}	90.0(3)	N(4) ^{#4} –Cu(2)–N(4) ^{#2}	91.1(2)
N(6) ^{#4} –Cu(2)–N(4)	90.0(3)	N(6)–Cu(2)–N(4)	90.5(3)
N(4) ^{#4} –Cu(2)–N(4)	91.1(2)	N(4) ^{#2} –Cu(2)–N(4)	91.1(2)

^a Symmetry codes: ^{#1} $x - y, x, 2 - z$; ^{#2} $1 - x + y, 1 - x, z$; ^{#3} $1 - x, 1 - y, 2 - z$; ^{#4} $1 - y, x - y, z$.

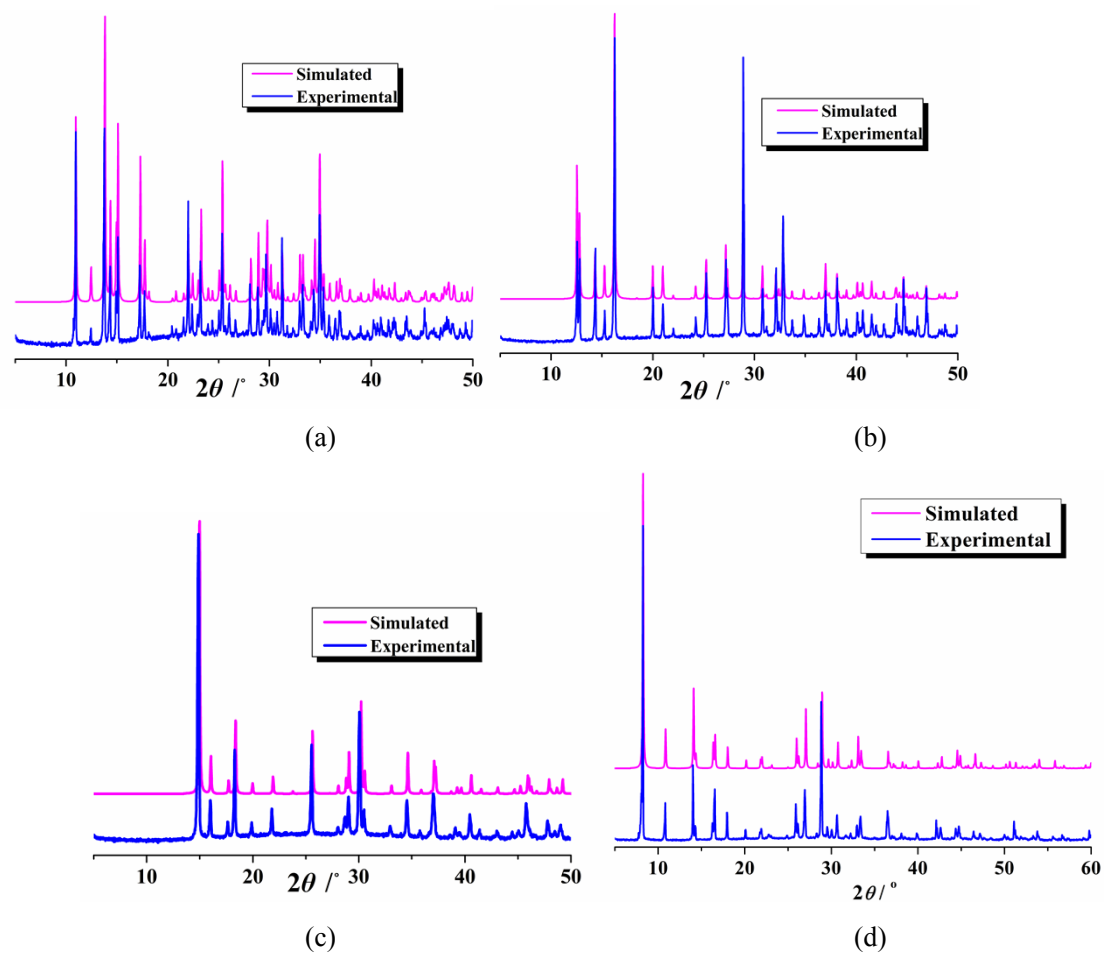


Fig. S1. Simulated (purple) and experimental (blue) PXRD patterns for **1** (a)–**4** (d).

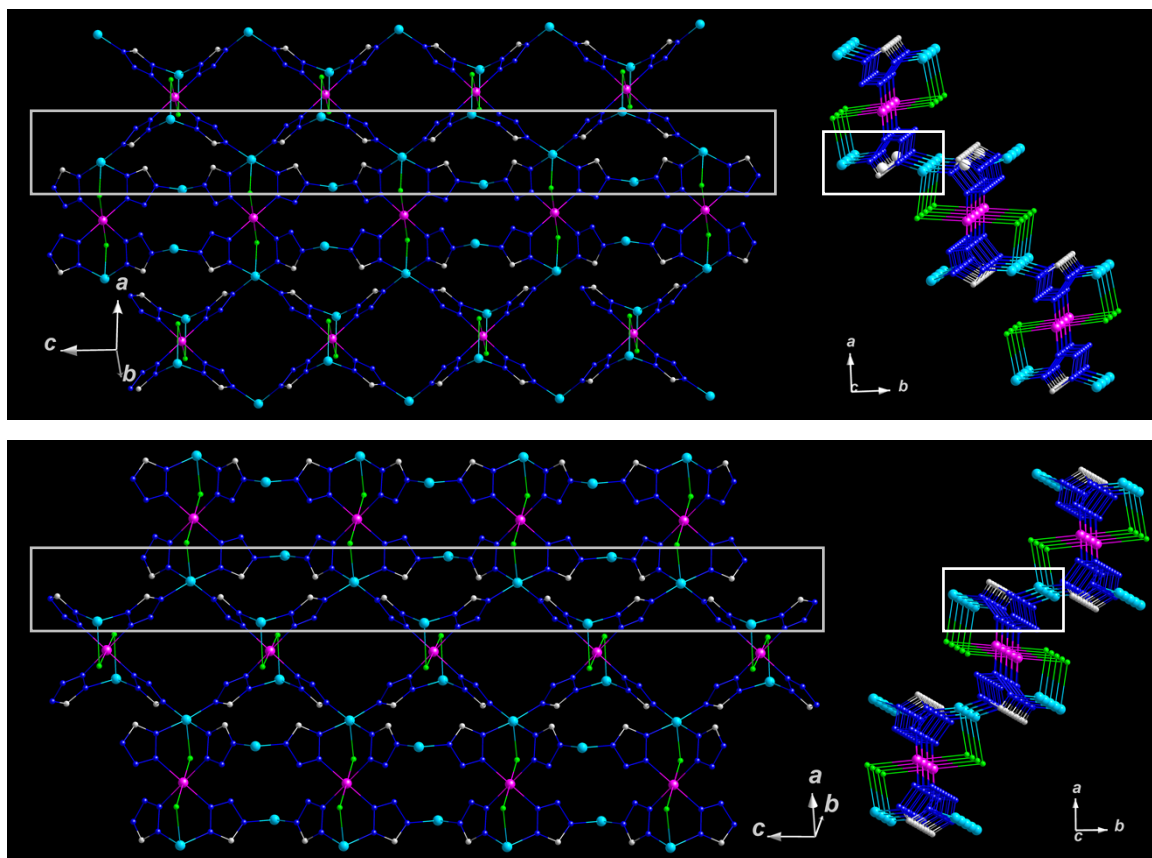


Fig. S2. The connection modes of tz^- ligand and Cu_2 ion in the two different planes of **2**.

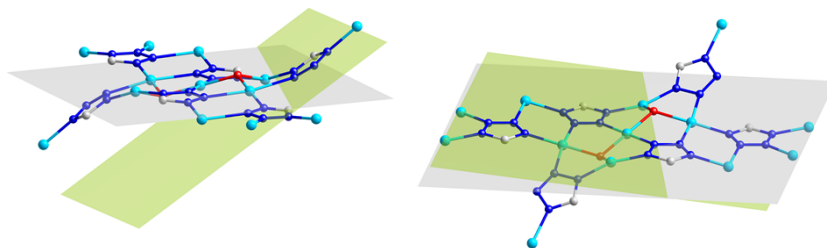


Fig. S3. The dihedral angles between the Cu^{II}_5 plane and the μ_3 -/ μ_4 - tz^- planes in **1**.