Electronic Supplementary Information (ESI)

Supramolecular interactions induced distortion of BTB ligands: breaking convention to reproduce the unusual (3, 4, 4)-connected MOF topology

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Section 1. Materials and Methods

All of the chemicals were obtained from commercial channels and used without further purification. Powder X-ray diffraction (PXRD) data was tested on a Rigaku D/max-2550 diffractometer (Cu-Kα radiation, λ = 1.5418 Å). Elemental analyses (C, H, and N) were collected by a vario MICRO (Elementar, Germany). The thermal gravimetric analyses (TGA) were performed on a TGA Q500 thermogravimetric analyzer (air, heating rate of 10 ^{o}C min^{-1}).

Synthesis of JLU-MOF59

A solid mixture of H_3BTB (0.015 g, 0.034 mmol), $CuCl_2{\cdot}2H_2O$ (0.01 g, 0.059 mmol), NMF (5 mL), EtOH (2.5 mL), and HNO_3 (1.5 mL) (2.2 mL HNO_3 in 10 mL DMF) were sealed in a 20 mL vial and then heated at 85 °C for 12 h. Green block crystals were collected and washed with NMF (62% yield based on $CuCl_2{\cdot}2H_2O$). Elemental analysis (wt %) for **JLU-MOF59**: calculated: C, 55.40; H, 4.750; N, 5.580, found: C, 54.96; H, 4.872; N, 5.641.

Section 2. Supporting structure information of JLU-MOF59

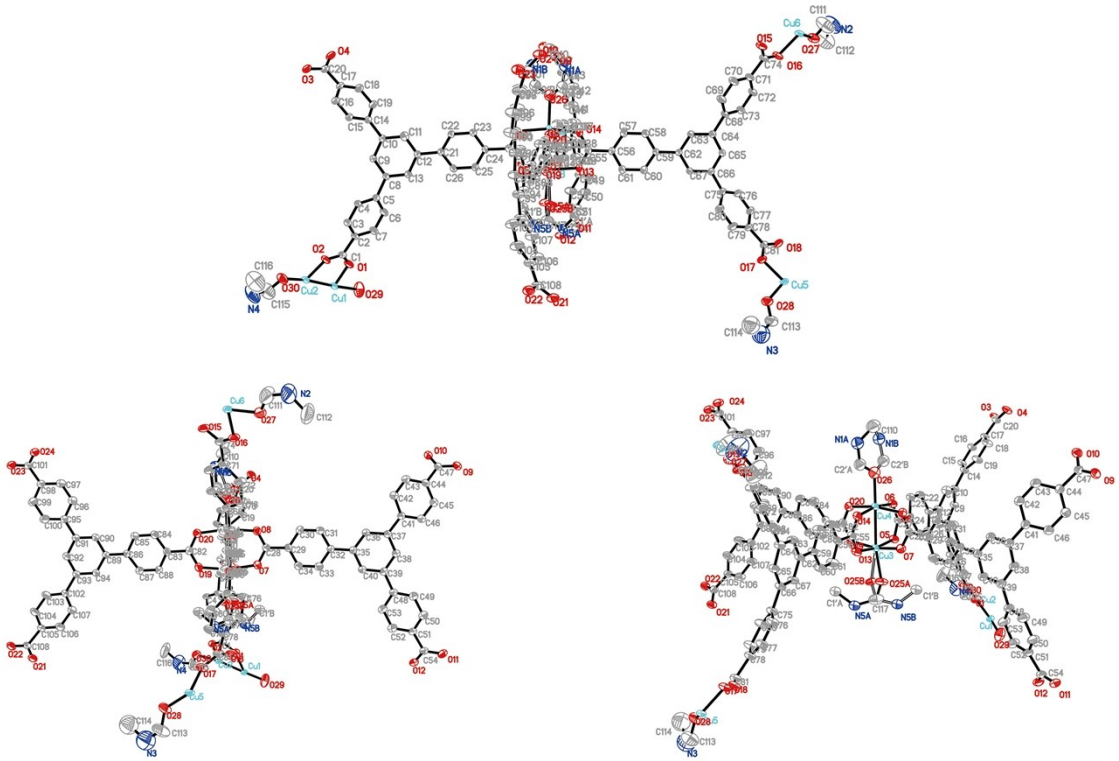

Figure S1 Thermal ellipsoid (30%) plot of the non-hydrogen bonded framework of **JLU-MOF59** via three different directions.

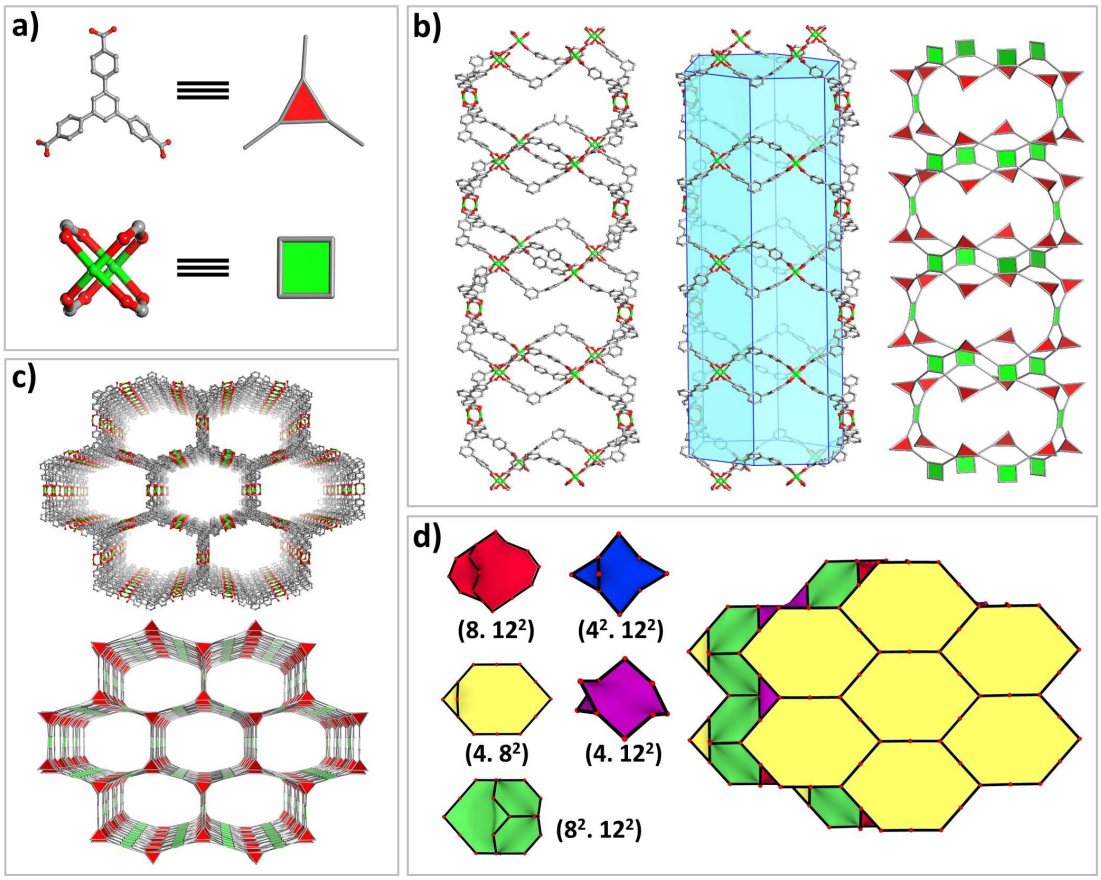

Figure S2 Description of the non-interpenetrated structure of **JLU-MOF59:** (a) Cu paddlewheel SBUs viewed as a 4-c node, and organic BTB^{3-} ligand viewed as a 3-c node; (b) hexagonal 1D straight channel; (c) ball and stick model of the 3D framework and polyhedral view of the net; (d) topological features of the compound displayed by tiling.

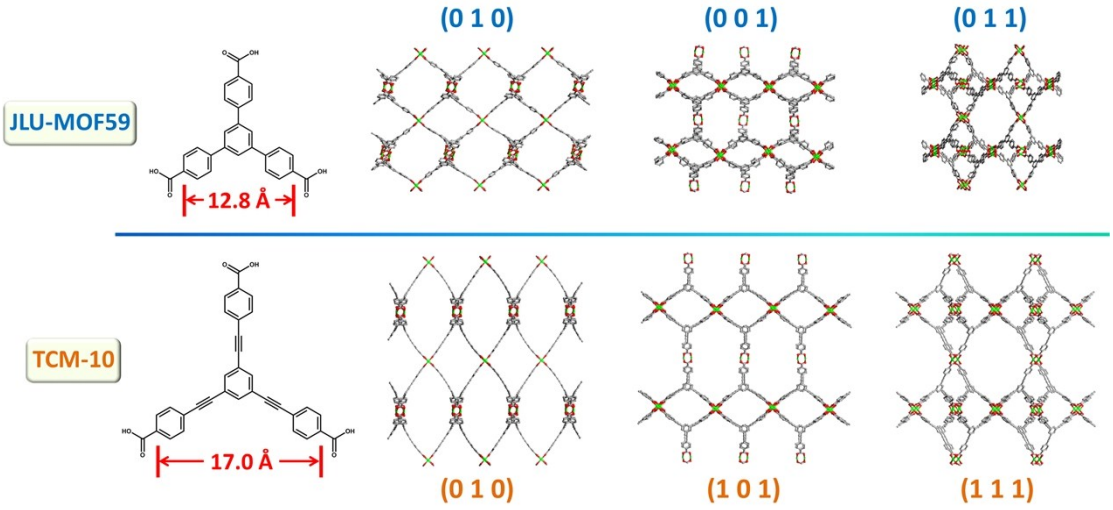

Figure S3 Comparison of **JLU-MOF59** and TCM-10 in ligand size and different directions.[1]

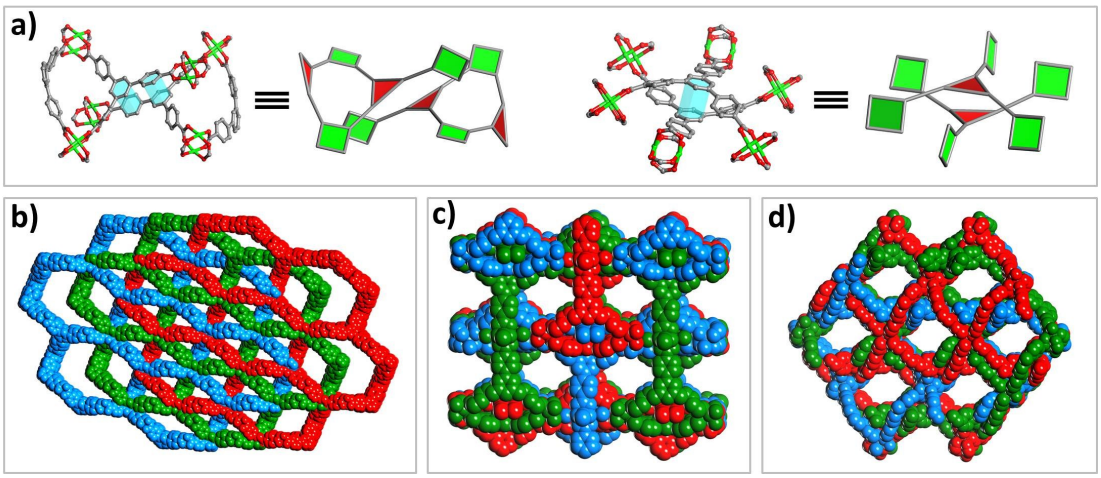

Figure S4 Description of the interpenetrated structure of **JLU-MOF59:** (a) polyhedral view of the two different π-π interactions; (b, c, d) CPK models in three different directions.

Section 3. PXRD and TGA data

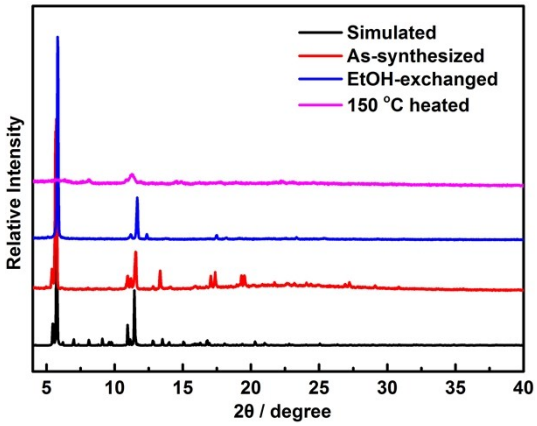

Figure S5 PXRD patterns of **JLU-MOF59** for simulated, as-synthesized, EtOH-exchanged and 150 °C heated samples.

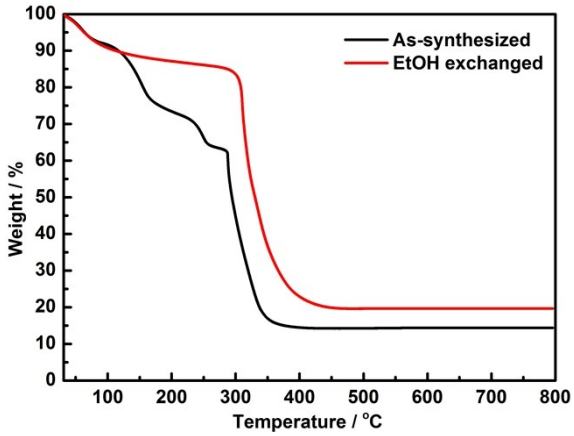

Figure S6 TGA curves of **JLU-MOF59** for the as-synthesized and EtOH-exchanged samples.

Section 4. Gas sorption measurements

BET surface area was measured by N_2 adsorption isotherms at 77 K with a Micrometrics ASAP 2420 instrument. MOF supercritical CO_2 activation was performed using a Tousimis™ Samdri® PVT-3D critical point dryer (Tousimis, Rockville, MD, USA).

Activation procedures:

Fresh absolute EtOH was used to exchange the NMF molecules with EtOH. The solvent exchange was repeated three times daily for three days. This sample was subjected to supercritical carbon dioxide drying procedure.[2] Liquid CO_2 was used to exchange the EtOH, the system was vented 6 times over the course of 18 hours to fully exchange the EtOH with CO_2. The system was then bled at the rate of 0.2 cc/s. Subsequently the samples were transferred into a sorption tube and dried on an activation port of an ASAP 2420 under dynamic vacuum at 50 ˚C for 10 h.

BET calculation:

The conditions for calculating the BET surface area are satisfied at five points between P/P_0 = 0.05 to 0.13 before the occurrence of the sudden increase. As shown in Figure S7, the 5 points showed an excellent linear relationship (R2>0.999).

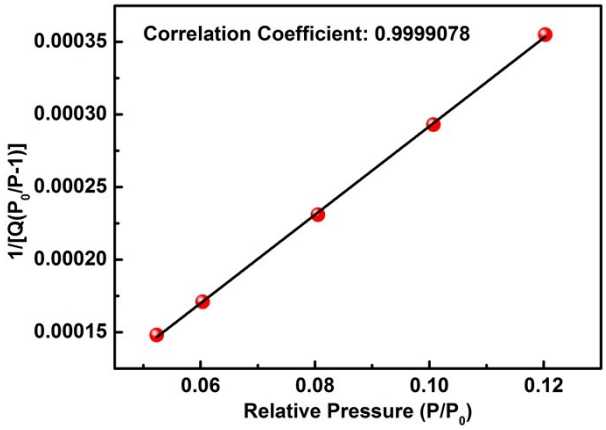

Figure S7 The linear fitting curve for calculating BET surface areas of **JLU-MOF59**.

Section 4. X-ray crystallography and structure information

JLU-MOF59 was collected on a Bruker D8 Venture diffractometer using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation at room temperature to obtain the crystallographic data. The structure of **JLU-MOF59** was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-2014.[3] All the metal atoms were located first, and then the oxygen, carbon and nitrogen of the compound were subsequently found in difference Fourier maps. The hydrogen atoms of the ligand were placed geometrically. All non-hydrogen atoms were refined anisotropically. For

there were lots of disordered solvent molecules in the structure, the PLATON/SQUEEZE was applied to remove their diffraction contribution.[4] The final formula was derived from crystallographic data combined with elemental and thermogravimetric analysis data. The detailed crystallographic data and selected bond lengths and angles for **JLU-MOF59** are listed in Table S2-S3, respectively. Topology information for **JLU-MOF59** was calculated by TOPOS 4.0.[5]

Table S2. Crystal data and structure refinements for **JLU-MOF59.**

Compound	**JLU-MOF59**
Formula	$C_{139}H_{143}Cu_6N_{12}O_{40.5}$
Mw	3010.89
Temp (K)	297(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
a (Å)	32.634(4)
b (Å)	30.916(3)
c (Å)	39.284(4)
α (°)	90
β (°)	109.930(4)
γ (°)	90
V (Å^3)	37260(7)
Z, D_C (Mg/m^3)	8, 1.073
F(000)	12472
θ range (deg)	2.335 - 25.087
reflns collected/unique	198375 / 32937
R_{int}	0.0793
data/restraints/params	32937 / 2862 / 1458
GOF on F^2	1.087
R^1, wR^2 (I>2σ(I))	0.0662, 0.1999
R^1, wR^2 (all data)	0.1009, 0.2217

Due to the presence of a highly disordered NMF molecule, we were unable to accurately add hydrogen atoms to it, so there is “Alert level B” about “H-atoms Missing” appeared. However, the number of hydrogen atoms is calculated into the molecular formula.

Table S3. Selected bond lengths [A] and angles [o] for **JLU-MOF59**.

JLU-MOF59			
Cu(1)-O(11)#1	1.950(4)	O(19)-Cu(3)-O(25B)	88.3(3)
Cu(1)-O(10)#2	1.957(4)	O(5)-Cu(3)-O(25B)	99.8(4)
Cu(1)-O(3)#3	1.971(3)	O(7)-Cu(3)-O(25B)	103.9(3)
Cu(1)-O(1)	1.983(3)	O(13)-Cu(3)-O(25B)	90.9(4)
Cu(1)-O(29)	2.169(4)	O(19)-Cu(3)-Cu(4)	84.38(10)
Cu(1)-Cu(2)	2.6218(8)	O(5)-Cu(3)-Cu(4)	83.94(9)
Cu(4)-O(20)	1.970(3)	O(7)-Cu(3)-Cu(4)	83.37(10)
Cu(4)-O(14)	1.974(3)	O(13)-Cu(3)-Cu(4)	85.27(10)
Cu(4)-O(8)	1.985(3)	O(25A)-Cu(3)-Cu(4)	171.1(3)
Cu(4)-O(6)	1.989(3)	O(25B)-Cu(3)-Cu(4)	171.8(3)
Cu(4)-O(26)	2.134(5)	O(2)-Cu(2)-O(4)#3	170.95(15)
Cu(4)-Cu(3)	2.6250(7)	O(2)-Cu(2)-O(12)#1	91.63(16)
Cu(3)-O(19)	1.950(3)	O(4)#3-Cu(2)-O(12)#1	87.87(17)
Cu(3)-O(5)	1.950(3)	O(2)-Cu(2)-O(9)#2	87.45(15)
Cu(3)-O(7)	1.952(3)	O(4)#3-Cu(2)-O(9)#2	90.73(16)
Cu(3)-O(13)	1.957(3)	O(12)#1-Cu(2)-O(9)#2	165.23(16)
Cu(3)-O(25A)	2.170(11)	O(2)-Cu(2)-O(30)	94.70(15)
Cu(3)-O(25B)	2.176(8)	O(4)#3-Cu(2)-O(30)	94.35(16)
Cu(2)-O(2)	1.961(3)	O(12)#1-Cu(2)-O(30)	91.75(18)
Cu(2)-O(4)#3	1.967(3)	O(9)#2-Cu(2)-O(30)	103.02(17)
Cu(2)-O(12)#1	1.970(4)	O(2)-Cu(2)-Cu(1)	87.90(10)
Cu(2)-O(9)#2	1.975(3)	O(4)#3-Cu(2)-Cu(1)	83.08(11)
Cu(2)-O(30)	2.133(4)	O(12)#1-Cu(2)-Cu(1)	81.79(12)
Cu(6)-O(16)	1.954(3)	O(9)#2-Cu(2)-Cu(1)	83.45(11)
Cu(6)-O(23)#4	1.960(4)	O(30)-Cu(2)-Cu(1)	173.11(13)
Cu(6)-O(24)#5	1.970(4)	O(16)-Cu(6)-O(23)#4	87.12(17)
Cu(6)-O(15)#6	1.971(3)	O(16)-Cu(6)-O(24)#5	89.84(17)
Cu(6)-O(27)	2.155(4)	O(23)#4-Cu(6)-O(24)#5	168.26(16)
Cu(6)-Cu(6)#6	2.6237(12)	O(16)-Cu(6)-O(15)#6	168.77(15)
Cu(5)-O(21)#4	1.959(4)	O(23)#4-Cu(6)-O(15)#6	91.82(17)
Cu(5)-O(17)	1.969(3)	O(24)#5-Cu(6)-O(15)#6	88.96(17)
Cu(5)-O(22)#7	1.969(3)	O(16)-Cu(6)-O(27)	97.43(15)
Cu(5)-O(18)#8	1.974(3)	O(23)#4-Cu(6)-O(27)	100.16(17)
Cu(5)-O(28)	2.159(4)	O(24)#5-Cu(6)-O(27)	91.47(17)
Cu(5)-Cu(5)#8	2.6188(12)	O(15)#6-Cu(6)-O(27)	93.76(15)
O(18)-Cu(5)#8	1.974(3)	O(16)-Cu(6)-Cu(6)#6	87.30(11)
O(15)-Cu(6)#6	1.971(3)	O(23)#4-Cu(6)-Cu(6)#6	87.11(11)
O(23)-Cu(6)#4	1.960(4)	O(24)#5-Cu(6)-Cu(6)#6	81.42(12)
O(24)-Cu(6)#9	1.970(4)	O(15)#6-Cu(6)-Cu(6)#6	81.48(11)
O(21)-Cu(5)#4	1.959(4)	O(27)-Cu(6)-Cu(6)#6	171.48(12)

O(22)-Cu(5)#1	1.969(3)	O(21)#4-Cu(5)-O(17)	88.14(17)
O(3)-Cu(1)#10	1.971(3)	O(21)#4-Cu(5)-O(22)#7	168.88(16)
O(4)-Cu(2)#10	1.967(3)	O(17)-Cu(5)-O(22)#7	90.37(16)
O(10)-Cu(1)#2	1.957(4)	O(21)#4-Cu(5)-O(18)#8	90.63(16)
O(9)-Cu(2)#2	1.975(3)	O(17)-Cu(5)-O(18)#8	168.82(15)
O(11)-Cu(1)#7	1.950(4)	O(22)#7-Cu(5)-O(18)#8	88.69(16)
O(12)-Cu(2)#7	1.970(4)	O(21)#4-Cu(5)-O(28)	101.05(17)
O(11)#1-Cu(1)-O(10)#2	171.55(16)	O(17)-Cu(5)-O(28)	96.70(15)
O(11)#1-Cu(1)-O(3)#3	87.43(15)	O(22)#7-Cu(5)-O(28)	90.07(17)
O(10)#2-Cu(1)-O(3)#3	89.28(16)	O(18)#8-Cu(5)-O(28)	94.43(15)
O(11)#1-Cu(1)-O(1)	92.31(16)	O(21)#4-Cu(5)-Cu(5)#8	85.82(11)
O(10)#2-Cu(1)-O(1)	88.95(16)	O(17)-Cu(5)-Cu(5)#8	85.35(11)
O(3)#3-Cu(1)-O(1)	165.60(15)	O(22)#7-Cu(5)-Cu(5)#8	83.07(11)
O(11)#1-Cu(1)-O(29)	91.5(2)	O(18)#8-Cu(5)-Cu(5)#8	83.48(11)
O(10)#2-Cu(1)-O(29)	96.78(19)	O(28)-Cu(5)-Cu(5)#8	172.86(13)
O(3)#3-Cu(1)-O(29)	100.24(19)	C(28)-O(7)-Cu(3)	125.7(3)
O(1)-Cu(1)-O(29)	94.16(18)	C(27)-O(5)-Cu(3)	124.2(3)
O(11)#1-Cu(1)-Cu(2)	86.71(12)	C(55)-O(13)-Cu(3)	122.0(3)
O(10)#2-Cu(1)-Cu(2)	85.26(11)	C(82)-O(19)-Cu(3)	123.4(3)
O(3)#3-Cu(1)-Cu(2)	85.08(10)	C(1)-O(2)-Cu(2)	118.9(3)
O(1)-Cu(1)-Cu(2)	80.54(10)	C(55)-O(14)-Cu(4)	124.2(3)
O(29)-Cu(1)-Cu(2)	174.30(15)	C(82)-O(20)-Cu(4)	122.5(3)
O(20)-Cu(4)-O(14)	89.23(14)	C(1)-O(1)-Cu(1)	126.7(3)
O(20)-Cu(4)-O(8)	169.04(14)	C(28)-O(8)-Cu(4)	121.5(3)
O(14)-Cu(4)-O(8)	89.47(14)	C(74)-O(16)-Cu(6)	119.4(3)
O(20)-Cu(4)-O(6)	89.22(13)	C(111)-O(27)-Cu(6)	121.0(6)
O(14)-Cu(4)-O(6)	167.96(13)	C(27)-O(6)-Cu(4)	121.2(3)
O(8)-Cu(4)-O(6)	89.79(14)	C(81)-O(17)-Cu(5)	121.4(3)
O(20)-Cu(4)-O(26)	95.71(16)	C(115)-O(30)-Cu(2)	119.6(6)
O(14)-Cu(4)-O(26)	95.69(16)	C(2'A)-O(26)-Cu(4)	122.8(7)
O(8)-Cu(4)-O(26)	95.25(16)	C(2'B)-O(26)-Cu(4)	120.7(10)
O(6)-Cu(4)-O(26)	96.35(16)	C(113)-O(28)-Cu(5)	115.8(5)
O(20)-Cu(4)-Cu(3)	84.12(10)	C(81)-O(18)-Cu(5)#8	123.8(3)
O(14)-Cu(4)-Cu(3)	83.00(9)	C(74)-O(15)-Cu(6)#6	125.6(3)
O(8)-Cu(4)-Cu(3)	84.92(10)	C(101)-O(23)-Cu(6)#4	119.5(4)
O(6)-Cu(4)-Cu(3)	84.96(9)	C(101)-O(24)-Cu(6)#9	125.1(4)
O(26)-Cu(4)-Cu(3)	178.68(14)	C(108)-O(21)-Cu(5)#4	120.7(3)
O(19)-Cu(3)-O(5)	88.88(15)	C(108)-O(22)-Cu(5)#1	123.5(4)
O(19)-Cu(3)-O(7)	167.75(15)	C(20)-O(3)-Cu(1)#10	122.2(3)
O(5)-Cu(3)-O(7)	89.75(15)	C(20)-O(4)-Cu(2)#10	124.7(3)
O(19)-Cu(3)-O(13)	89.80(15)	C(47)-O(10)-Cu(1)#2	120.9(3)
O(5)-Cu(3)-O(13)	169.21(14)	C(47)-O(9)-Cu(2)#2	122.7(4)
O(7)-Cu(3)-O(13)	89.26(16)	C(54)-O(11)-Cu(1)#7	119.4(4)
O(19)-Cu(3)-O(25A)	103.0(4)	C(54)-O(12)-Cu(2)#7	124.5(4)

O(5)-Cu(3)-O(25A)	91.3(6)	C(117)-O(25A)-Cu(3)	154.5(10)
O(7)-Cu(3)-O(25A)	89.2(4)	C(117)-O(25B)-Cu(3)	157.1(8)
O(13)-Cu(3)-O(25A)	99.4(6)		

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,-y+1/2,z-1/2 #2 -x,-y,-z+1 #3 -x-1/2,y+1/2,-z+1/2 #4 -x+1,y,-z+1/2
#5 x+1/2,-y-1/2,z+1/2 #6 -x+3/2,-y-1/2,-z+1 #7 x+1/2,-y+1/2,z+1/2
#8 -x+3/2,-y+1/2,-z+1 #9 x-1/2,-y-1/2,z-1/2 #10 -x-1/2,y-1/2,-z+1/2

Section 4. References

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