Electronic Supplementary Information (ESI):

Utilizing a Copper MOF as a Reagent in a Solvent Mediated Reaction to Form a Topologically Distinct MOF

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Dalton Transactions

Experimental Section

The compound 1,2,4-triazole-1-propanenitrile[1] was prepared as described previously. All other reagents were purchased from commercial vendors and used without purification. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at ambient temperature on a Varian Mercury 300 MHz or a Varian VNMRS 500 MHz narrow-bore broadband system. ^{1}H and ^{13}C NMR chemical shifts were referenced to the residual solvent. All mass spectrometry analyses were conducted at the Mass Spectrometry Center located in the Department of Chemistry at the University of Tennessee. The DART analyses were performed using a JEOL AccuTOF-D time-of-flight (TOF) mass spectrometer with a DART (direct analysis in real time) ionization source from JEOL USA, Inc. (Peabody, MA). The ESI/MS analyses were performed using a QSTAR Elite quadrupole time-of-flight (QTOF) mass spectrometer with an electrospray ionization source from AB Sciex (Concord, Ontario, Canada). Infrared spectra were collected on a Thermo Scientific Nicolet iS10 with a Smart iTR accessory for attenuated total reflectance. Thermogravametric analysis data were collected on a TA Instruments TGA Q50 under N_2. Carbon, hydrogen, and nitrogen analyses were obtained from Atlantic Microlab, Norcross, GA.

Synthesis of 4,4'-(1,4-(*trans*-2-butene)diyl)bis-(1-(2-cyanoethyl)-1,2,4-triazolium) dibromide, 1. *Trans*-1,4-dibromo-2-butene (8.97 g, 0.0419 mol) was added to a 250 mL round bottom flask which had 1,2,4-triazole-1-propanenitrile (10.2 g, 0.0840 mol) and the mixture was diluted with acetonitrile (30 mL). The reaction was heated to reflux until a white precipitate had formed after 30 min. The reaction was cooled to rt and the precipitate was washed with diethyl ether (10 mL), and then dried under reduced pressure. The crude white solid was then washed with acetonitrile (3 x 30 mL) and dried under reduced pressure to yield the pure product (18.2 g, 89.8% yield). ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 10.47 (s, 2H), 9.41 (s, 2H), 6.17 (s, 2H), 5.07 (d, J = 3.0 Hz, 4H), 4.76 (t, J = 6.3 Hz, 4H), 3.28 (t, J = 6.3 Hz, 4H). ^{13}C{^{1}H} NMR (DMSO-d_6, 125.66 MHz): δ 144.93, 143.43, 128.94, 117.65, 48.29, 47.19, 17.35. IR (neat): 3418, 3117, 2957, 2942, 2253, 1726, 1581, 1532, 1443, 1409, 1386, 1359, 1340, 1275, 1185, 1157, 1070, 1018, 915, 878, 857, 816, 762, 670 cm^{-1}. ESI/MS (*m/z*): [M-Br]$^{+}$ 377.05, [M-2Br]$^{2+}$ 149.07. Anal. Calcd for $C_{14}H_{18}Br_2N_8$: C, 36.70; H, 3.96; N, 24.46. Found: C, 36.80; H, 3.98; N, 24.60.

Synthesis of 4,4'-(1,4-(*trans*-2-butene)diyl)bis-(1,2,4-triazole), L, 2. Potassium hydroxide (4.37 g, 0.0780 mol) and 4,4'-(1,4-(*trans*-2-butene)diyl)bis-(1-(2-cyanoethyl)-1,2,4-triazolium) dibromide (9.55 g, 0.0195 mol) were added to a 250 mL Erlenmeyer flask containing 80 mL of water and stirred for 24 h. The solution was extracted with a 1:1 ethanol:chloroform solution (5 x 100 mL) and the organic layer was subsequently evaporated under reduced pressure. The resulting white solid was washed with acetonitrile (3 x 30 mL) and dried under reduced pressure to yield the crude product (3.32 g, 89.4% yield). Soxhlet extraction using chloroform yielded 0.233 g of the analytically pure product after 6 d. Further Soxhlet extraction allows for additional product to be obtained as needed. ^{1}H NMR (DMSO-d_6, 300.1 MHz): δ 8.50 (s, 4H), 5.77 (tt, J_1 = 3.0 Hz, J_2 = 1.5 Hz, 2H), 4.70 (dd, J_1 = 3.0 Hz, J_2 = 1.4 Hz, 4H). ^{13}C{^{1}H} NMR

(DMSO-d_6, 125.66 MHz): δ 143.08, 128.88, 45.05. IR (neat): 3368, 3103, 2940, 2253, 1660, 1590, 1530, 1510, 1453, 1436, 1382, 1337, 1277, 1176, 1080, 1066, 995, 970, 948, 873, 833, 743, 682 cm^{-1}. DART/MS (*m/z*): 191.1 $[M+H]^+$. Anal. Calcd for $C_8H_{10}N_6$: C, 50.52; H, 5.30; N, 44.18. Found: C, 49.93; H, 5.22; N, 43.70.

Synthesis of $[Cu_4(L)_4(SO_4)_4]•4[Cu(H_2O)_6(SO_4)]$, 3. Copper(II) sulphate pentahydrate (0.0367 g, 0.147 mmol) and **2** (0.0140 g, 0.0735 mmol) were added to separate 4 mL scintillation vials and dissolved with 1 mL and 2 mL of water, respectively. The vials were heated to 85 °C for 30 min in an aluminum heating block. The solutions were mixed and heated for an additional 1 h until large blue crystalline needles had formed. The needles were collected using a Buchner funnel and filter paper and the crystals were washed with water (2 x 5 mL) and ether (3 x 5 mL) (0.0216 g, 47.5% yield). IR (neat): 3114, 1636, 1566, 1450, 1402, 1377, 1215, 1048, 974, 891, 746 cm^{-1}. Anal. Calcd for $C_{32}H_{88}Cu_8N_{24}O_{56}S_8$: C, 15.56; H, 3.59; N, 13.61. Found: C, 15.94; H, 3.59; N, 13.53.

Synthesis of $[Cu_6(L)_3(SO_4)_5(OH)_2(H_2O)_6]•13H_2O$, 4. Copper(II) sulphate pentahydrate (0.0918 g, 0.367 mmol) and **2** (0.0035 g, 0.018 mmol) were added to separate 4 mL scintillation vials and dissolved with 1 mL and 2 mL of water, respectively. The vials were heated to 85 °C for 30 min in an aluminum heating block. The solutions were mixed and heated for 24 h until large blue block crystals had formed. The block crystals were collected using a Buchner funnel and filter paper and the crystals were washed with water (2 x 5 mL) and ether (3 x 5 mL) (0.0069 g, 73% yield). IR (neat): 3369, 3109, 1635, 1553, 1449, 1400, 1083, 1023, 964 cm^{-1}. Anal. Calcd for $C_{24}H_{44}Cu_6N_{18}O_{28}S_5•13H_2O$: C, 15.94; H, 3.90; N, 13.94. Found: C, 15.97; H, 3.55; N, 13.68.

Synthesis of 4 utilizing the same reaction conditions as 3. Copper(II) sulphate pentahydrate (0.0367 g, 0.147 mmol) and **2** (0.0140 g, 0.0735 mmol) were added to separate 4 mL scintillation vials and dissolved with 1 mL and 2 mL of water, respectively. The vials were heated to 85 °C for 30 min in an aluminum heating block. The solutions were mixed and heated for an additional 48 h until large blue block crystals had formed. The block crystals were collected using a Buchner funnel and filter paper and the crystals were washed with water (2 x 5 mL) and ether (3 x 5 mL) (0.0065 g, 15% yield).

Synthesis of 4 from 3. **3** (10.0 mg, 0.00405 mmol) was added to a 4 mL scintillation vial containing 0.5 mL of water and heated to 85 °C in an aluminum heating block. After heating the mixture for 48 h, single crystals of **4** were separated under a microscope utilizing their distinct shape and color. These collected crystals yielded 2.8 mg of **4**. (33% yield). Single crystal and powder X-ray diffraction measurements were collected on the separated crystals. The structure of the separated **4** was confirmed by single crystal X-ray diffraction and PXRD.

Time dependent reactions of 4 from 3. **3** (10.0 mg, 0.00405 mmol) was added to a 4 mL scintillation vial containing 0.5 mL of water. The mixture was then heated to 85 °C in an aluminum heating block and powder X-ray diffraction pattern were taken at specific time intervals to monitor the reaction as shown in Figure 3.

X-ray Structure Determinations. Data was collected on a Bruker SMART APEXII three circle diffractometer equipped with a CCD area detector and operated at 1,800 W power (45 kV, 40 mA) to generate Mo Kα radiation (λ = 0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur focusing optics. A single crystal of **3** was mounted on nylon CryoLoops (Hampton Research) with Paratone-N (Hampton Research) frozen at -173 ºC, while a single crystal of **4** was mounted in a glass capillary (Hampton Research) and flame sealed and cooled to 5 ºC. Initial scans of each specimen were taken to obtain preliminary unit cell parameters and to assess the mosaicity (i.e. breadth of spots between frames) of the crystal to select the required frame width for data collection. For all cases frame widths of 0.5º were judged to be appropriate and full hemispheres of data were collected using the *Bruker APEX2* software suite to carry out overlapping ϕ and ω scans at detector setting of $2\theta = 28^{o}$. Following data collection, reflections were sampled from all regions of the Ewald sphere to re-determine unit cell parameters for data integration. Following exhaustive review of collected frames the resolution of the dataset was judged, and, if necessary, regions of the frames where no coherent scattering was observed were removed from consideration for data integration using the *Bruker SAINTplus* program.[2] Data was integrated using a narrow frame algorithm and were subsequently corrected for absorption. Absorption corrections were performed for both samples using the SADABS program.[2] Space group determination and tests for merohedral twinning were carried out using *XPREP*.[2] In all cases, the highest possible space group was chosen.

Final models were refined anisotropically (with the exception of H atoms). In the case of **3**, hydrogen atoms on the linker were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.5 times U_{eq} of the attached C atoms; water hydrogens were located by Fourier electron density map and with isotropic displacement parameters 1.5 times U_{eq} of the attached O atoms. In the case of **4**, the crystal loses solvent very quickly, even at -173.15°C. Therefore, the crystal was mounted in a capillary and flame sealed to prevent the loss of solvent during the collection. The data was collected at 5°C. Position disorder of the third sulphate anion (SO_4) was present in the structure. In the final least-squares refinement this disorder was taken into account by two parts of SO_4 anions: Part 1 contains S2', O33', O30', O31', and O32' with 0.652 occupancy and Part 2 contains S2'', O33'', O30'', O31'', and O32'' with 0.348 occupancy. Disordered water molecules were present in the structure. SQUEEZE routine was used to simplify and improve the refinement. The presence of large solvent accessible volume and relative poor data quality prevents the anisotropic refinement for all non-hydrogen atoms. Atoms O31, O32 and O33 as well as O30', O31', O32' and O33' were refined iostropically. All structures were examined using the *Addsym* subroutine of PLATON[3] to assure that no additional symmetry could be applied to the models.

Powder X-ray experiments. Powder X-ray diffraction (PXRD) data were collected using a Panalytical Empyrean θ-2θ diffractometer in reflectance Bragg-Brentano geometry. Cu-Kα radiation (λ = 1.5406 Å; 1,800 W, 45kV, 40 mA) was focused using a planar Gobel Mirror riding the Kα line. A 0.25 mm divergence slit was used for all measurements. Diffracted radiation was detected using a PIXcel^{3d} detector [(6° 2θ sampling width) equipped with a Ni monochrometer]. All samples were mounted onto a zero background quartz plate fixed on a sample holder by dropping powders and then leveling the sample surface. The best counting statistics were achieved by using a 0.0131º 2θ step scan from 4 – 50° with an exposure time of 81.6 s per step and a revolution spin rate of 4 s.

TGA data for 3 and 4.

Figure S1: TGA for **3**.

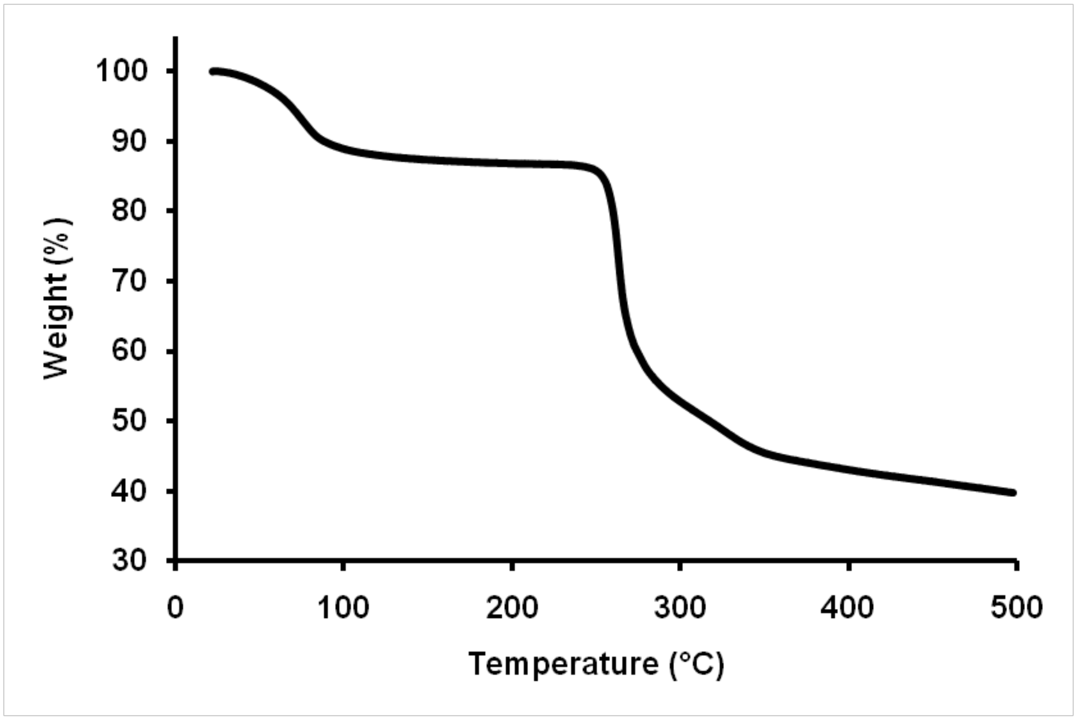
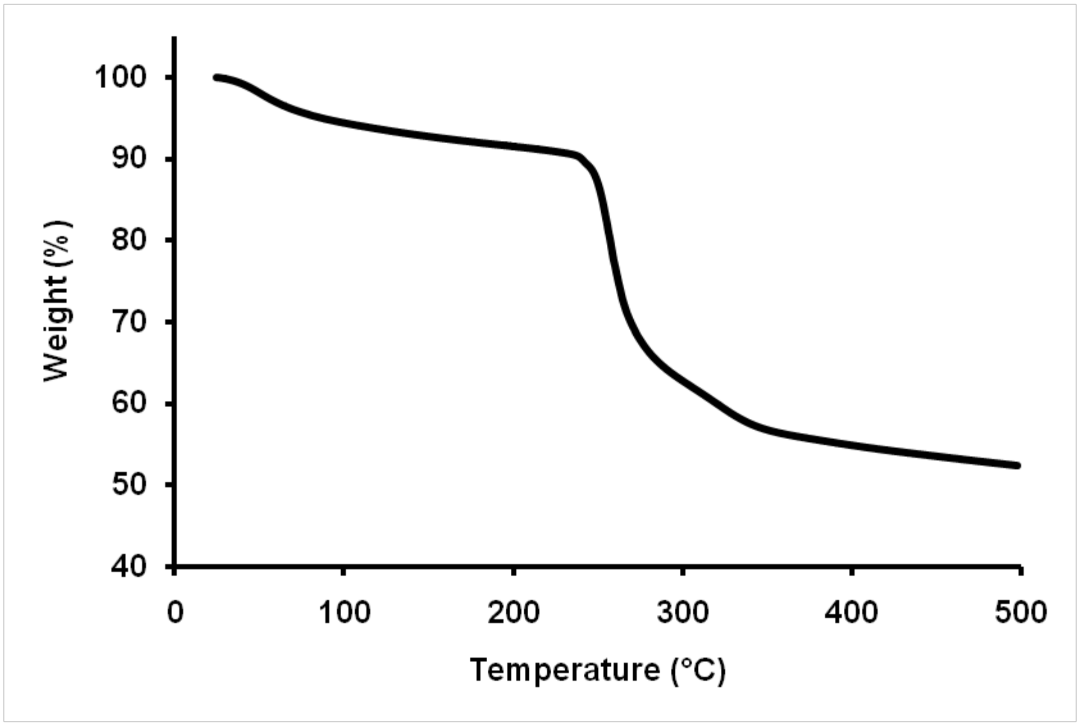


Figure S2: TGA for **4**.



PXRD patterns for 3 and 4.

Figure S3: PXRD pattern for **3**: experimental (red) and simulated (black).

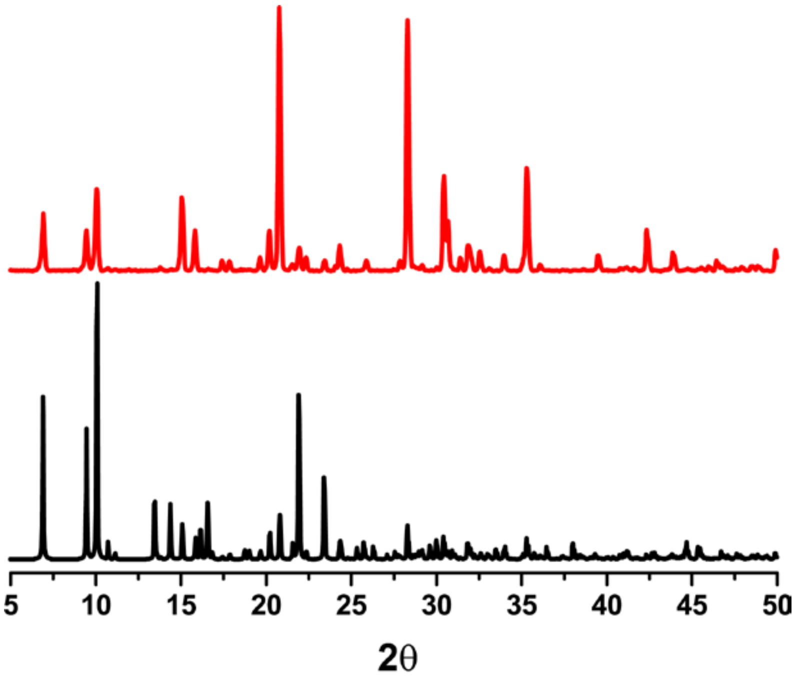
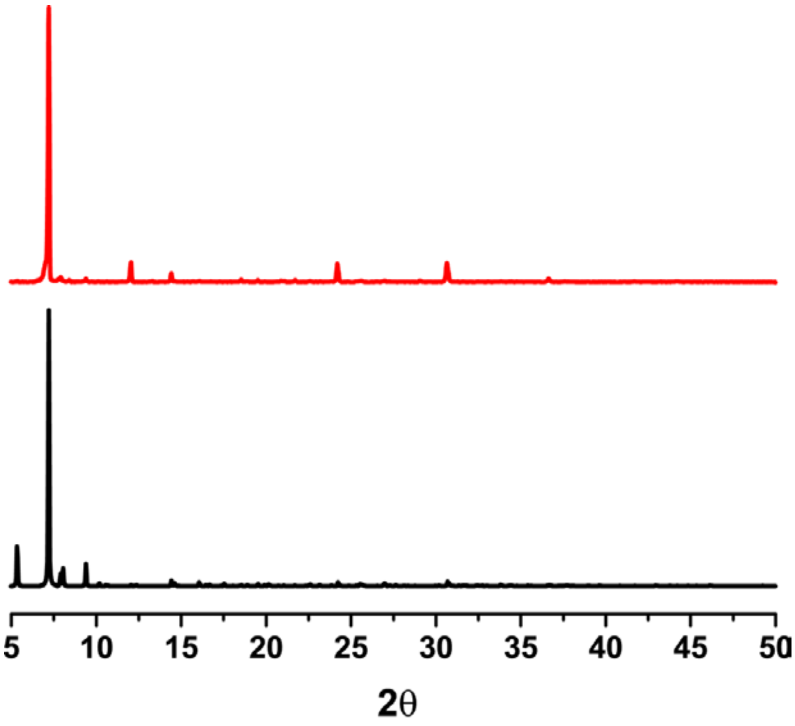


Figure S4: PXRD pattern for **4**: experimental (red) and simulated (black).



IR spectra for 1 and 2.

Figure S5: IR spectrum for **1**.

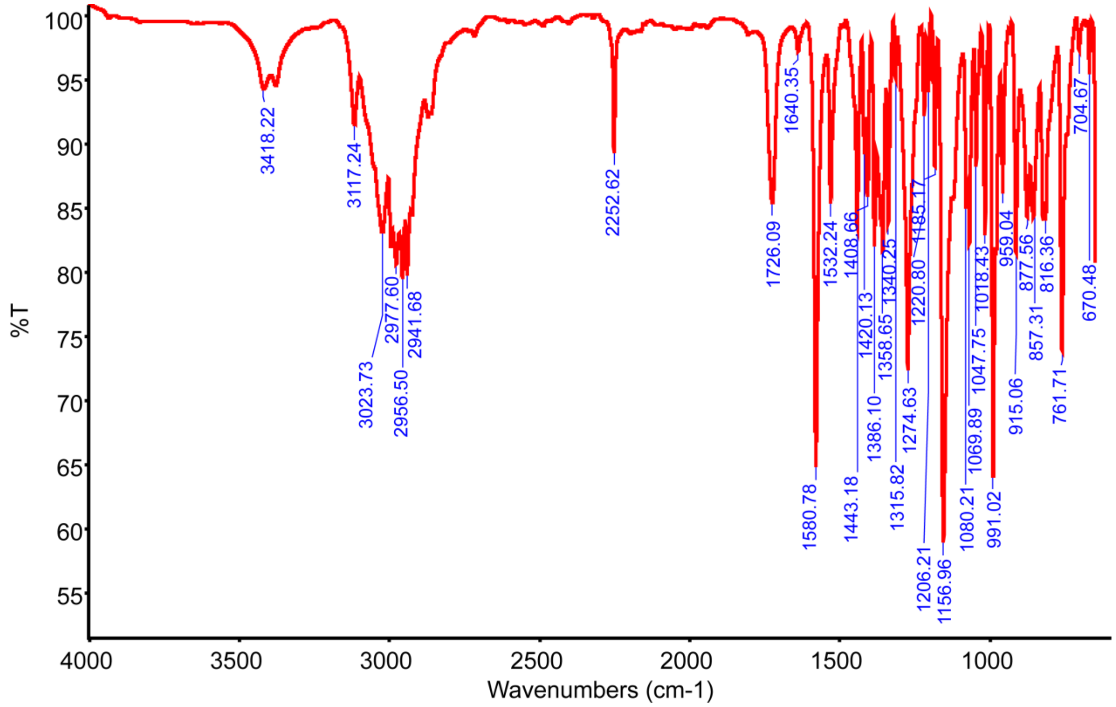
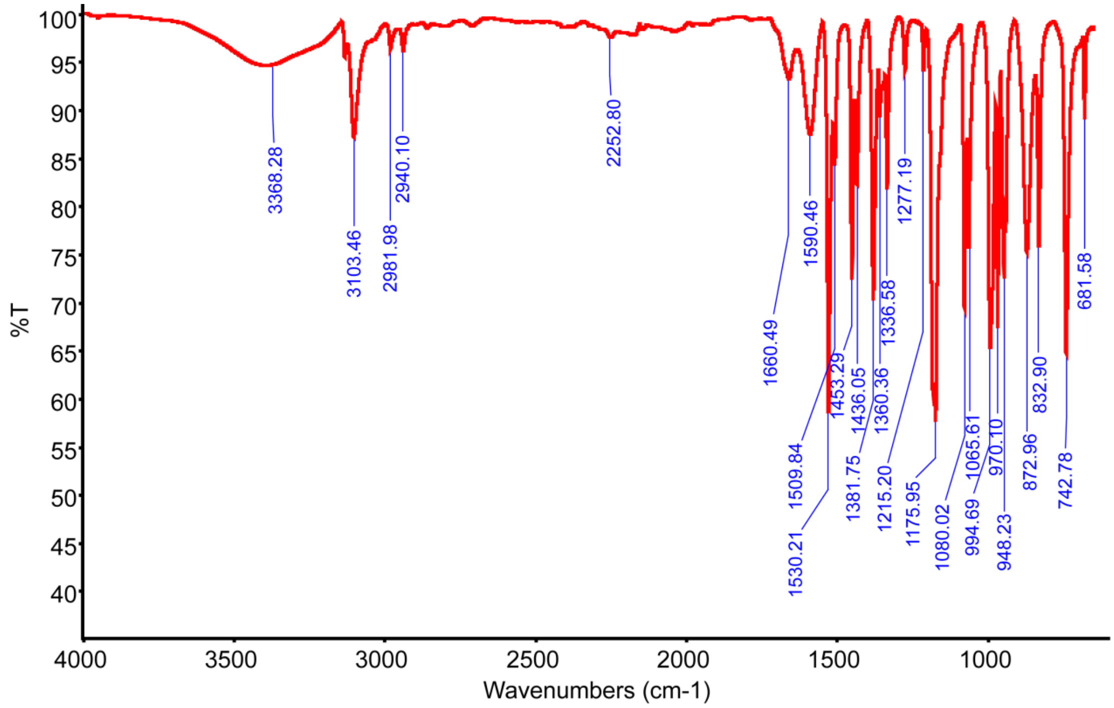


Figure S6: IR spectrum for **2**.



IR Spectra for 3 and 4.

Figure S7: IR spectrum for **3**.

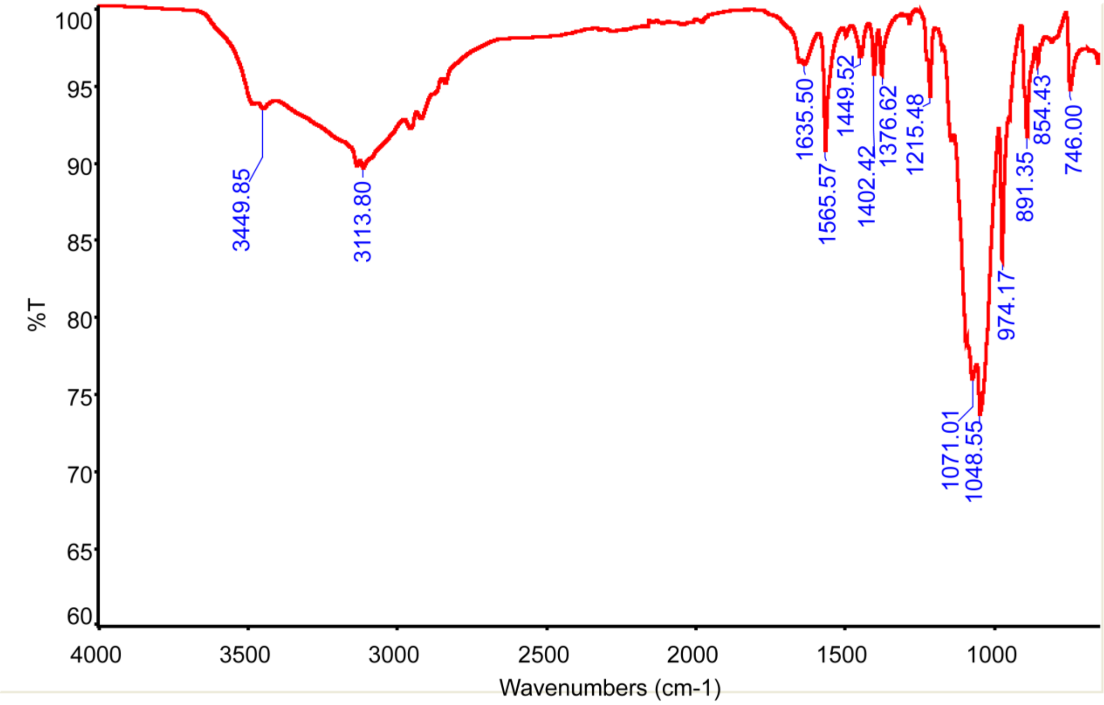


Figure S8: IR spectrum for **4**.

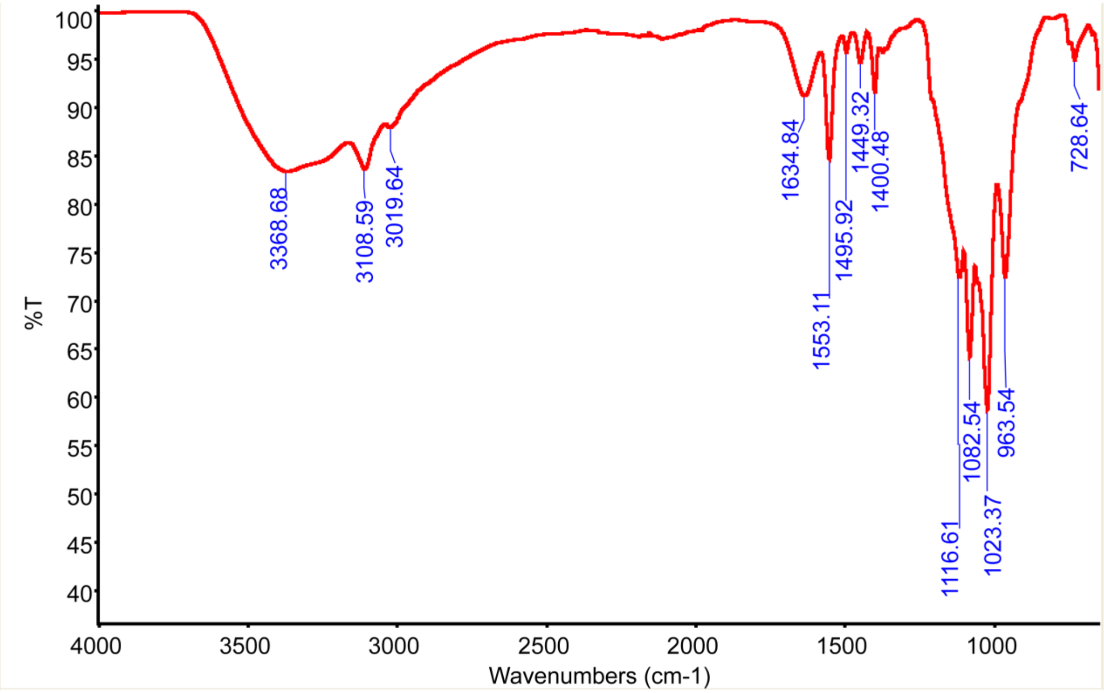


Table **S1**. Crystal data and structure refinement for **3**.

Identification code	**3**	
Empirical formula	C8 H28 Cu2 N6 O17 S2	
Formula weight	671.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	p 21 21 21	
Unit cell dimensions	a = 6.9676(3) Å	α= 90°.
	b = 17.4113(8) Å	β= 90°.
	c = 18.6278(9) Å	γ = 90°.
Volume	2259.83(18) $Å^3$	
Z	4	
Density (calculated)	1.974 Mg/m^3	
Absorption coefficient	2.160 mm^{-1}	
F(000)	1376	
Crystal size	0.13 x 0.03 x 0.03 mm^3	
Theta range for data collection	1.60 to 28.32°.	
Index ranges	-8<=h<=7, -22<=k<=23, -22<=l<=24	
Reflections collected	15324	
Independent reflections	4532 [R(int) = 0.0463]	
Completeness to theta = 25.00°	96.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9380 and 0.7665	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4532 / 2 / 371	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0674	
R indices (all data)	R1 = 0.0297, wR2 = 0.0692	
Absolute structure parameter	0.157(9)	
Largest diff. peak and hole	0.499 and -0.926 e.$Å^{-3}$	

Table **S2**. Crystal data and structure refinement for **4**.

Identification code	**4**	
Empirical formula	C24 H30 Cu6 N18 O28 S5	
Formula weight	1560.20	
Temperature	278(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	p n n a	
Unit cell dimensions	a = 24.569(4) Å	α= 90°.
	b = 14.682(2) Å	β= 90°.
	c = 22.399(3) Å	γ = 90°.
Volume	8080(2) $Å^3$	
Z	4	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	1.747 mm^{-1}	
F(000)	3112	
Crystal size	0.50 x 0.40 x 0.20 mm^3	
Theta range for data collection	1.66 to 23.39°.	
Index ranges	-27<=h<=27, -16<=k<=16, -24<=l<=24	
Reflections collected	64167	
Independent reflections	5881 [R(int) = 0.0647]	
Completeness to theta = 23.39°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7213 and 0.4753	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5881 / 20 / 382	
Goodness-of-fit on F^2	1.231	
Final R indices [I>2sigma(I)]	R1 = 0.0997, wR2 = 0.2924	
R indices (all data)	R1 = 0.1204, wR2 = 0.3151	
Largest diff. peak and hole	3.748 and -0.984 e.$Å^{-3}$	

References.

1. A. Horáth, *Synthesis*, 1995, **9**, 1183.
2. Bruker, *SAINT-Plus* (Version 7.03). Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
3. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2005.