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Electronic Supplementary Information

A rare cationic building block that generates a new type of polyhedral network with “cross-linked” pto topology network.

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Materials and Methods

All reagents were purchased commercially in analytical grade and employed without further purification. The chemical reagents for this work were all purchased from Sigma Aldrich and include: copper(II) tetrafluoroborate hydrate, $Cu(BF_4)_2.xH_2O$, ammonium hexafluorostannate, $(NH_4)_2SnF_6$, ammonium hexafluorogermanate(IV), $(NH_4)_2GeF_6$, ammonium hexafluorosilicate, $(NH_4)_2SiF_6$, potassium hexafluorotitanate(IV), K_2TiF_6, potassium hexafluorozirconate, K_2ZrF_6, chloroform ($CHCl_3$) and methanol (CH_3OH).

2,4,6-tris(4-pyridyl)pyridine (Tripp) was prepared by the cyclization reaction of 4-acetylpyridine and 4-pyridinecarbaldehyde according to Constable *et al.*.[1]

Synthesis of Compounds 1-5

$[Cu_6(Tripp)_8(ZrF_6)_3]X$ (1): $Cu(BF_4)_2.xH_2O$ (2.40 mg, 0.010 mmol) and K_2ZrF_6 (2.9 mg, 0.010 mmol) dissolved in 6 mL of chloroform was carefully layered over an solution (6 mL) of Tripp (4.2 mg, 0.013 mmol) in a long thin test tube (h = 15 cm; Ø = 1.5 cm). The tube was sealed with parafilm and left undisturbed at room temperature. After 2-3 weeks, purple single crystals were harvested. FT-IR (solid, ν_{max} in cm^{-1}): 3410, 3251, 3106, 1596, 1636, 1561, 1536, 1501, 1436, 1403, 1326, 1265, 1225, 1095, 1067, 1033, 1006, 988, 899, 821, 716.

$[Cu_6(Tripp)_8(SnF_6)_3]X$ (2): Crystals of **2** were prepared in a similar manner as **1,** except that $(NH_4)_2SnF_6$ (2.7 mg, 0.010 mmol) was used instead of K_2ZrF_6. After 2-3 weeks, purple single crystals were harvested. FT-IR (solid, ν_{max} in cm^{-1}): 3400, 3311, 3108, 1637, 1597, 1559, 1538, 1505, 1436, 1402, 1324, 1270, 1222, 1133, 1100, 1066, 1032, 1006, 988, 823, 717, 693, 667.

$[Cu_6(Tripp)_8(GeF_6)_3]X$ (3): Crystals of **3** were prepared in a manner similar to **1,** except that $(NH_4)_2GeF_6$ (2.25 mg, 0.010 mmol) was used instead of K_2ZrF_6. After 2-3 weeks, purple single crystals were harvested. FT-IR (solid, ν_{max} in cm^{-1}): 3390, 3252, 3106, 1635, 1618, 1597, 1560, 1538, 1505, 1436, 1325, 1268, 1223, 1094, 1065, 1033, 1009, 989, 898, 873, 822, 713, 667.

$[Cu_6(Tripp)_8(TiF_6)_3]X$ (4): Crystals of **4** were prepared in the same way as **1** except that K_2TiF_6 (2.43 mg, 0.010 mmol) was used instead of K_2ZrF_6. After 2-3 weeks, purple single crystals were harvested. FT-IR (solid, ν_{max} in cm^{-1}): 3407, 3248, 3106, 1637, 1618, 1597, 1560, 1538, 1505, 1436, 1402, 1324, 1267, 1223, 1065, 1033, 1007, 900, 821, 718, 668.

$[Cu_6(Tripp)_8(SiF_6)_3]X$ (5): Crystals of **5** were prepared in the same way as **1** except that $(NH_4)_2SiF_6$ (1.8mg, 0.010 mmol) was used instead of K_2ZrF_6. After 2-3 weeks, purple single crystals were harvested. FT-IR (solid, ν_{max} in cm^{-1}): 3386, 3245, 3104, 1637, 1616, 1596, 1561, 1538, 1507, 1435, 1400, 1320, 1221, 1134, 1096, 1064, 1031, 1009, 898, 821, 693, 669.

Single Crystal X-Ray Diffraction

SCXRD data were collected at 100 K on a Bruker D8 Quest difractometer equipped with Cukα microfocus X-ray generator, Photon 100 detector and Oxford Cryosystem 700 series. The data were integrated, and empirically corrected for X-ray absorption with Sadabs,[2] in the Bruker APEX II software suite. The structures were solved by direct methods and refined against F_o, with the ShelX software[2] interfaced by X-Seed.[3]

Table 1: Summary of Crystallographic data for crystals **1** to **5**.

	Tripp-Cu-ZRFSIX (1)	**Tripp-Cu-SNFSIX (2)**	**Tripp-Cu-GEFSIX (3)**	**Tripp-Cu-TIFSIX (4)**	**Tripp-Cu-SIFSIX (5)**
Formula*	$C_{160}H_{112}Cu_6F_{18}Zr_3N_{32}$	$C_{160}H_{112}Cu_6F_{18}Sn_3N_{32}$	$C_{160}H_{112}Cu_6F_{18}Ge_3N_{32}$	$C_{160}H_{112}Cu_6F_{18}Ti_3N_{32}$	$C_{160}H_{112}Cu_6F_{18}Si_3N_{32}$
Formula weight* /g	3479.71	3562.12	3423.82	3349.75	3290.32
Temp. /K	100(2)	100(2)	100(2)	100(2)	100(2)
Cryst. system	cubic	cubic	cubic	cubic	cubic
Space group	*Pm*-3	*Pm*-3	*Pm*-3	*Pm*-3	*Pm*-3
a, b, c /Å	21.165(2)	21.2379(10)	21.2111(8)	21.2174(8)	21.1882(4)
α, β, γ /°	90	90	90	90	90
V/Å^3	9481(3)	9579.3(14)	9543.1(11)	9551.6(11)	9512.2(5)
Z'	1/24	1/24	1/24	1/24	1/24
D_c* /g cm^{-3}	0.609	0.617	0.596	0.582	0.574
reflns coll.	17481	23379	52384	13544	37996
unique reflns	1090	2542	1867	1796	1866
R_{int}	0.2043	0.1930	0.1026	0.0968	0.1166
R_1 [$I > 2\sigma(I)$]	0.2289	0.1508	0.1513	0.1732	0.1621
wR_2 [$I > 2\sigma(I)$]	0.4225	0.3811	0.4423	0.4334	0.3851
R_1 (all data)	0.2351	0. 1653	0.1590	0.2601	0. 1719
wR_2 (all data)	0.5336	0.4436	0.4511	0.4642	0.4090
GOF	2.388	1.195	2.098	1.490	1.060

* the reported values are based on the assigned electron density only.

Powder X-ray Diffraction

PXRD pattern were collected on a Panalytical Empyrean diffractometer at 40 kV, 40 mA for Cu_{α} (λ = 1.5418 Å), equipped with a X'cellerator detector. The measurement where performed at room temperature with a scan speed of 0.5 s/step (6°/min) and a step size of 0.05° in 2θ. Graphics were generated in the Panalytical X'Pert Highscore Plus v 3.0 for Windows.

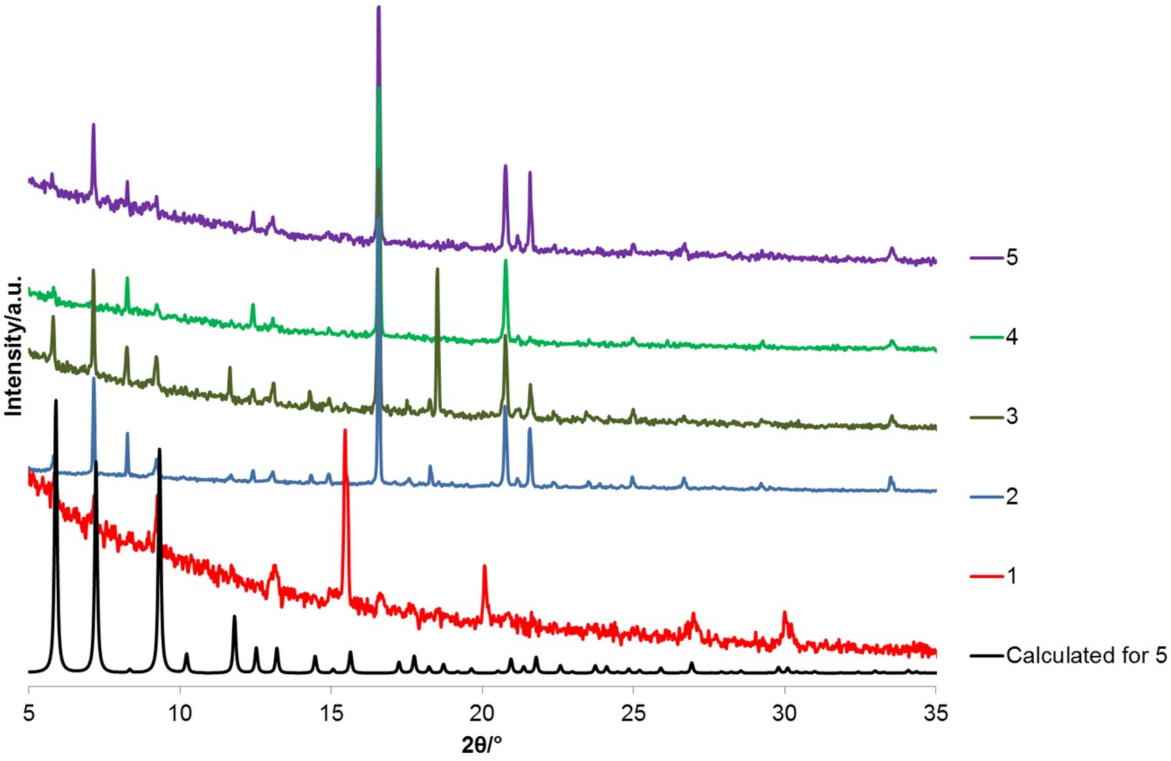

Figure S1: Comparison of PXRD patterns: calculated for **5** (black) and the experimental ones for **1** (red), **2** (blue), **3** (dark green), **4** (light green) and **5** (purple).

Infrared Spectroscopy

IR spectra were carried out on a PerkinElmer Spectrum 100 FT-IR Spectrometer with a Universal ATR sampling accessory. The spectra were recorded in the wave number region of 4000–650 cm^{-1} and with a resolution setting of 2 and 16 scans per sample.

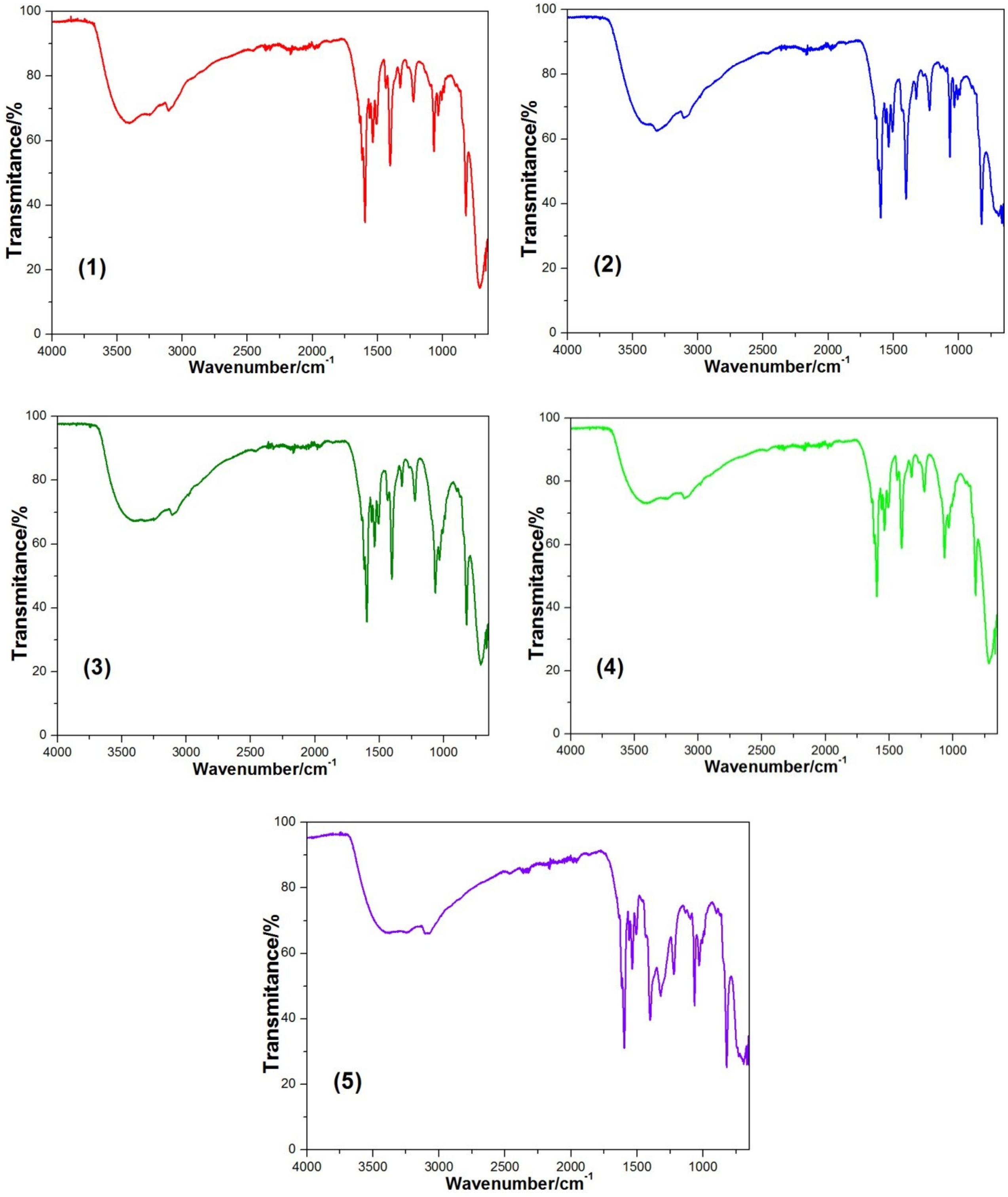

Figure S2: FT-IR of the samples **1**, **2**, **3**, **4** and **5**.

Thermogravimetric analysis

TGA was performed under 50 ml/L stream of nitrogen on a TA Instrument Q50 from 30 °C to 500 °C at the heating rate of 10 °C/min.

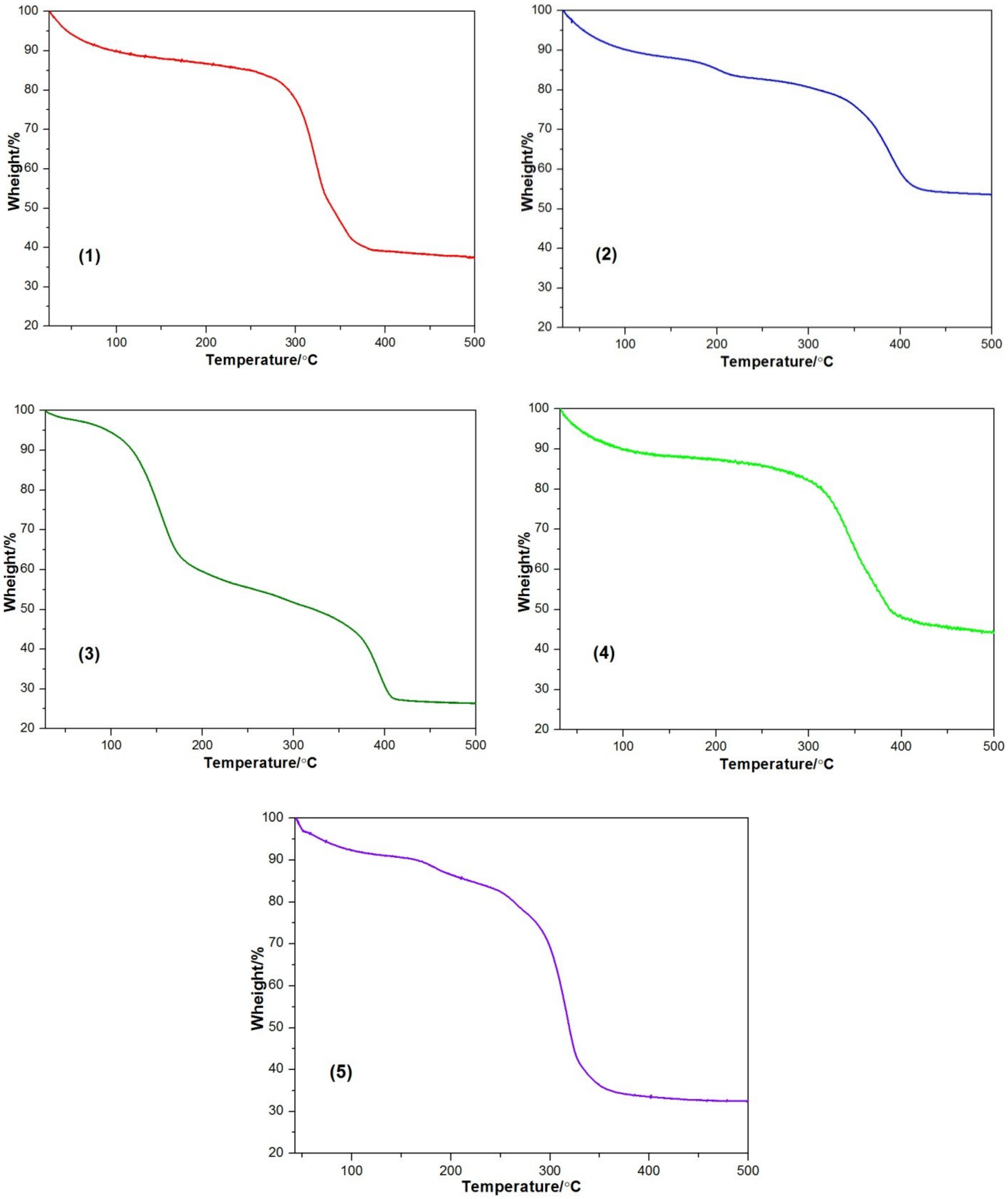

Figure S3: Thermogravimetric analysis of **1**, **2**, **3**, **4** and **5**.

Electron Microscopy

Photomicrographs of the single crystals surface were obtained by scanning electron microscopy (**SEM**) on a Hitachi SU-70 with a thermal field emission source and operating voltage of 20 kV in samples covered with a gold layer (Sputter coater: 20 mA, Emitech K550). The chemical composition was performed using an X-ray detector (model XMax, Oxford instruments) for energy-dispersive X-ray spectroscopy (**EDX**).

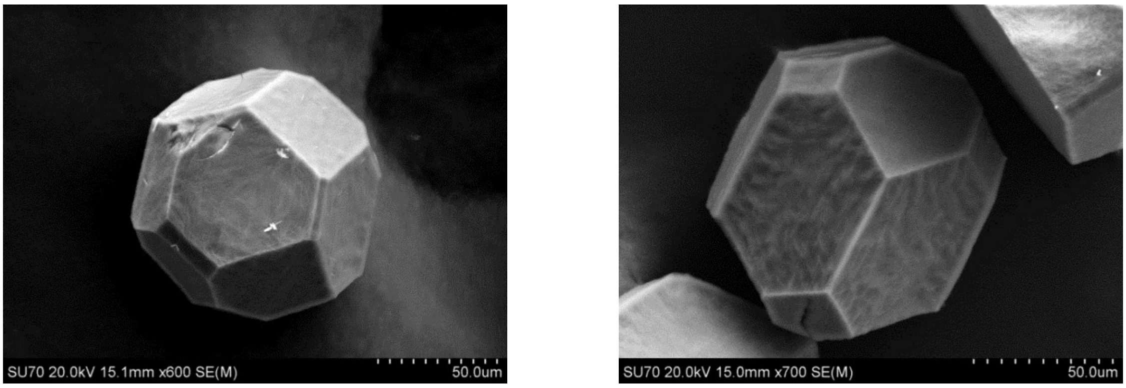

Figure S4: SEM images of [Cu_6(Tripp)$_8$(SiF_6)$_3$]X (**5**) single crystals.

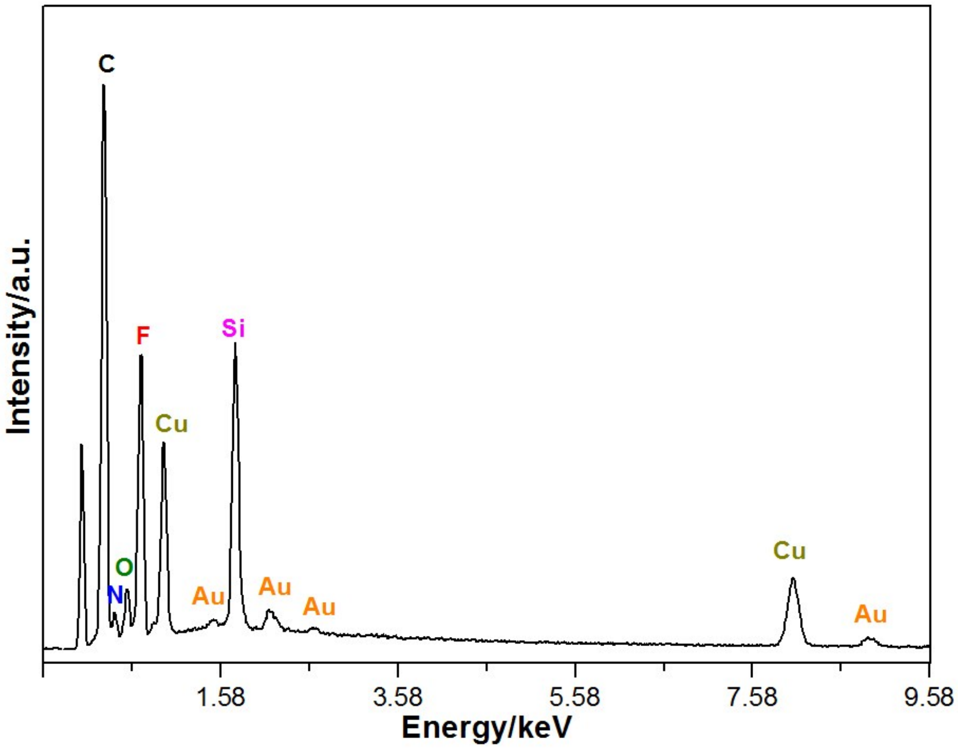

Figure S5: EDX spectroscopy of [Cu_6(Tripp)$_8$(SiF_6)$_3$]X single crystals.

Table 2: EDX analysis for **5**.

	C	N	O	F	Si	Cu
point a*	46.85	11.86	5.09	23.40	3.94	7.84
point b*	44.90	9.33	6.02	24.62	4.80	8.97
point c*	43.30	10.91	8.11	23.16	4.34	8.75
point d*	44.64	10.88	6.46	25.95	4.20	6.82
avg	44.92	10.75	6.42	24.28	4.32	8.10
std	1.27	0.91	1.09	1.11	0.31	0.85
weight (g/mol)	*12.01*	*14.01*	*15.99*	*19.00*	*28.08*	*63.55*
ratio observed	**176.21**	**36.13**	**18.91**	**60.21**	**7.25**	**6.00**
std	4.97	3.05	3.22	2.75	0.52	0.63
ratio calculated	**160.00**	**32.00**	**0.00**	**18.00**	**3.00**	**6.00**

** Weight percentage was calculated from the sum of the reported elements plus gold (≈1%).*

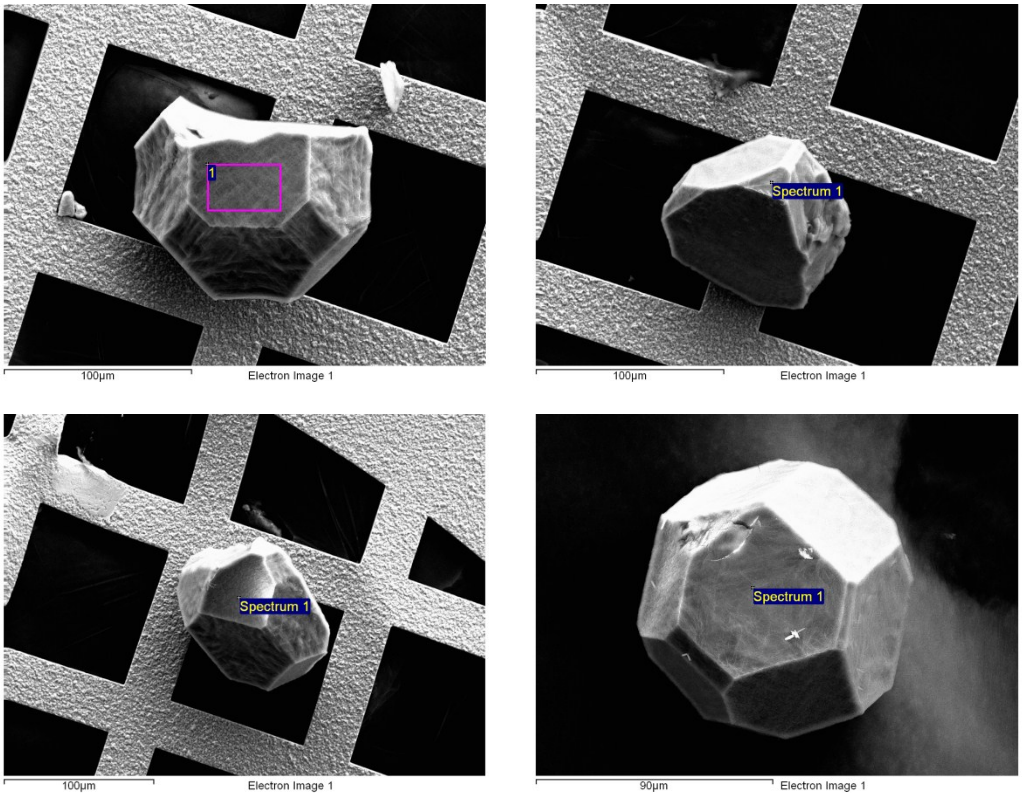

Figure S6: SEM images of the EDX targets. From the top left, clockwise point a, b, c and d respectively.

Brunauer–Emmett–Teller (BET) Surface area

77K N2 sorption isotherm was measured using Micromeritics Tristar II 3030 surface characterization analyzer. Before the measurement, the chloroform-exchanged sample was desolvated under high vacuum at room temperature for 16 h to remove the chloroform molecules in the pores.

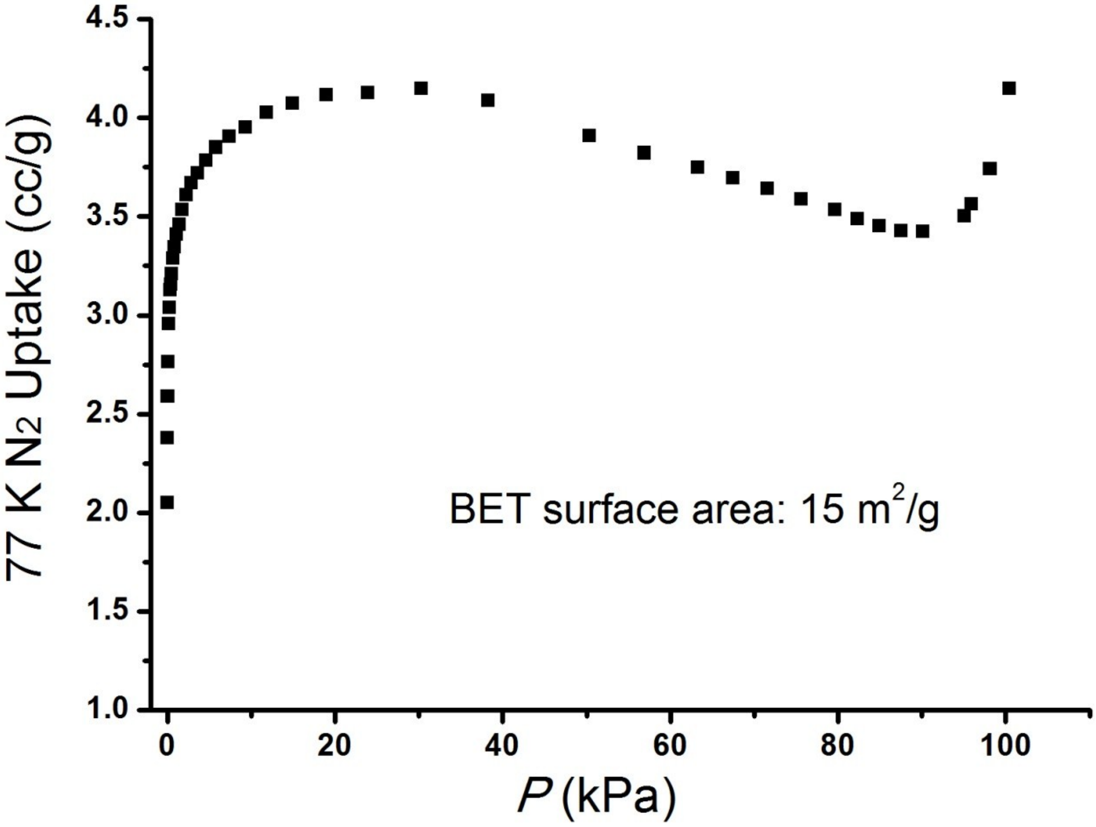

Figure S7: BET measurement of **4**.

Additional References

1. E. C. Constable, G. Zhang, C. E. Housecroft and J. A. Zampese, *CrystEngComm*, 2011, **13**, 6864-6870.
2. G. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.*, 2008, **64**, 112-122.
3. L. J. Barbour, *Journal of Supramolecular Chemistry*, 2001, **1**, 189-191.