

## Electronic Supplementary Information:

### Following the Self Assembly of Supramolecular MOFs using X-ray Crystallography and Cryospray Mass Spectrometry

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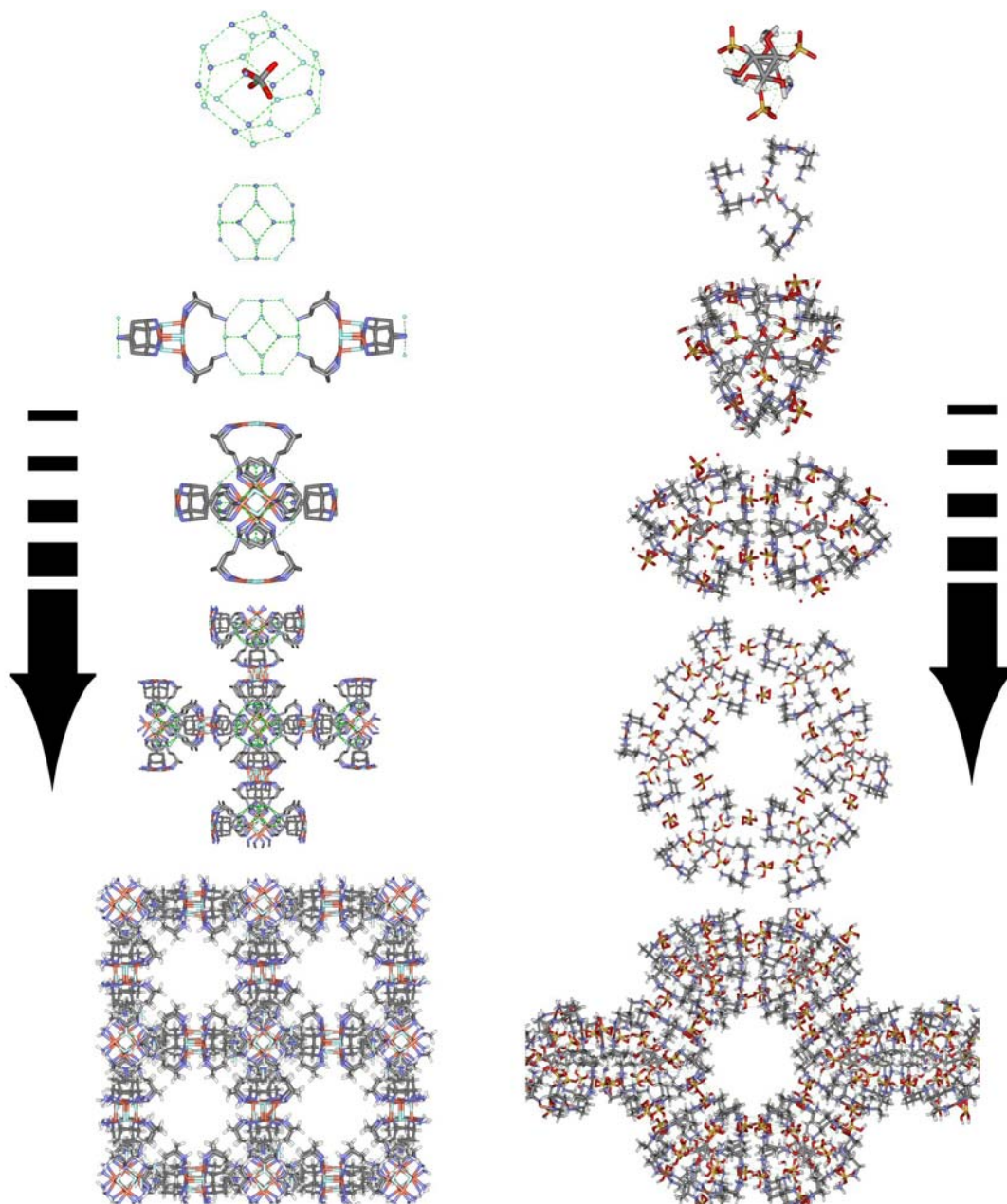
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#### Structural Analysis of 1 and 2

A common building up principle can be hypothesised, at least structurally, that centres around disordered methanol solvent. In compound **1** a disordered methanol (on a four fold axis) is included in a truncated octahedron that is defined by the hydrogen bonding between the pendent amine of the tach ligand and the fluoride anions, see Figure S1. This is built up in 3D to give an octahedral branched building block of cubanes and hydrogen bonded truncated octahedra. In compound **2**, a methanol disordered (on a three fold axis) is hydrogen bonded with the pendent amines of the tach ligand and the sulphates, although involved in many extensive hydrogen bonded interactions, are much less well defined.



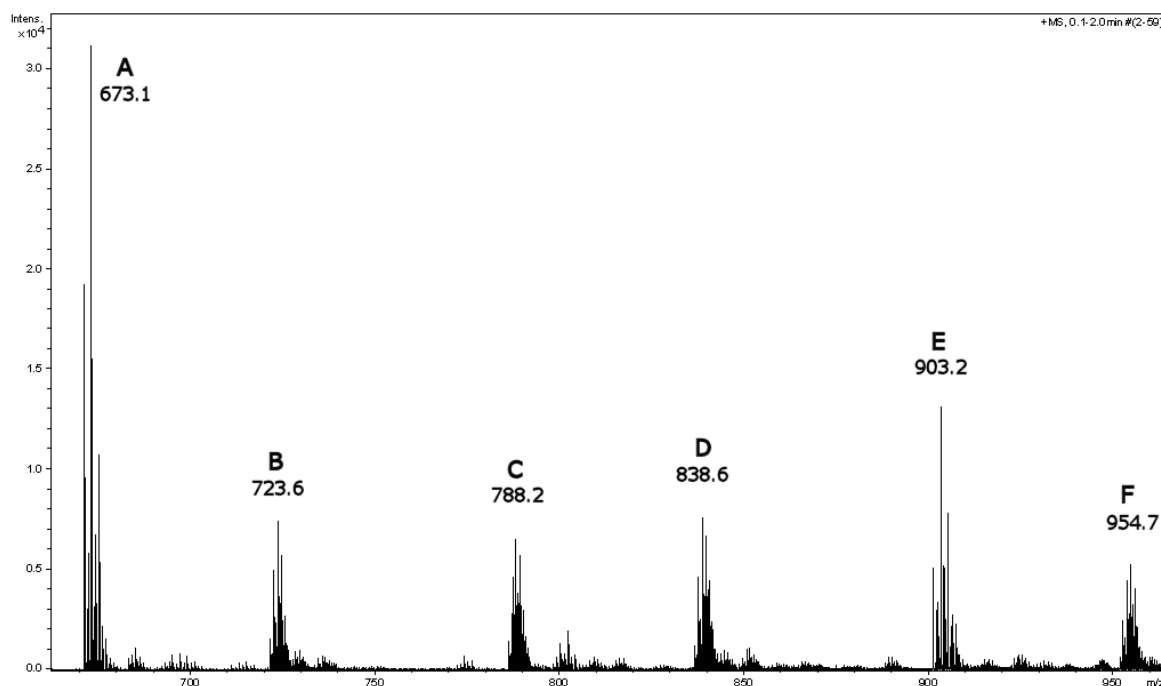
**Figure S1:** Aufbau principle for structures **1**(left) and **2**(right) starting from the building blocks top to the complete packed structures at the bottom. Despite being formed under similar conditions, the anions define the topology of the structures. Colour scheme: Carbon, grey; oxygen, red; nitrogen, blue; sulphur, yellow; copper, orange; fluoride, cyan.

### **Electrospray mass spectrometric measurements of 1 and 2**

All MS data was collected using a Q-trap, time-of-flight MS (MicroTOF-Q MS) instrument supplied by Bruker Daltonics Ltd. A cryospray source, also supplied by

Bruker Ltd, was used to collect data under the conditions specified below. The detector was a time-of-flight, micro-channel plate detector and all data was processed using the Bruker Daltonics Data Analysis 3.4 software, whilst simulated isotope patterns were investigated using Bruker Isotope Pattern software and Molecular Weight Calculator 6.45. Electrospray Mass Spectrometry measurements were conducted using the cryospray attachment at  $-40^{\circ}\text{C}$ . The sample was injected into the device at  $180\ \mu\text{L/h}$ . The mass spectrometer used for the measurements was a Bruker microTOFQ and the data was collected in positive ion mode. The spectrometer was previously calibrated with the standard tune mix to give a precision of ca. 1.5 ppm in the region of 500-5000 m/z. The end plate voltage was set to -500 V and the capillary to -4500 V. The collision cell was set to a collision energy of  $-9.0\ \text{eV/z}$  with a gas flow rate at 25% of maximum and the cell RF was set at 1600 Vpp.

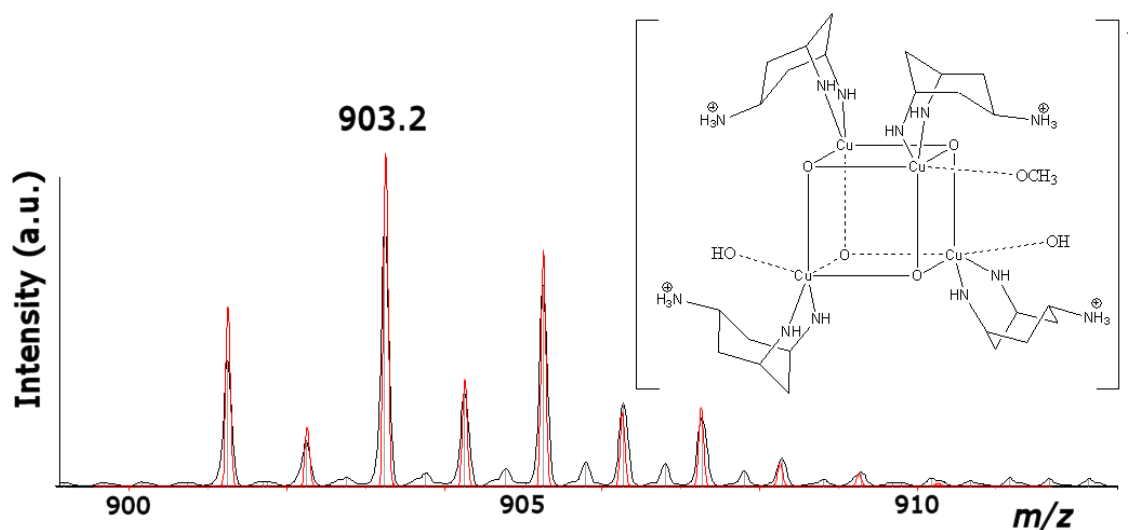
The cryospray mass spectra and assignments for compounds **1** are shown below (Figure S2 and S3, Table S1) and **2** (Figure S4 and S5, Table S2).



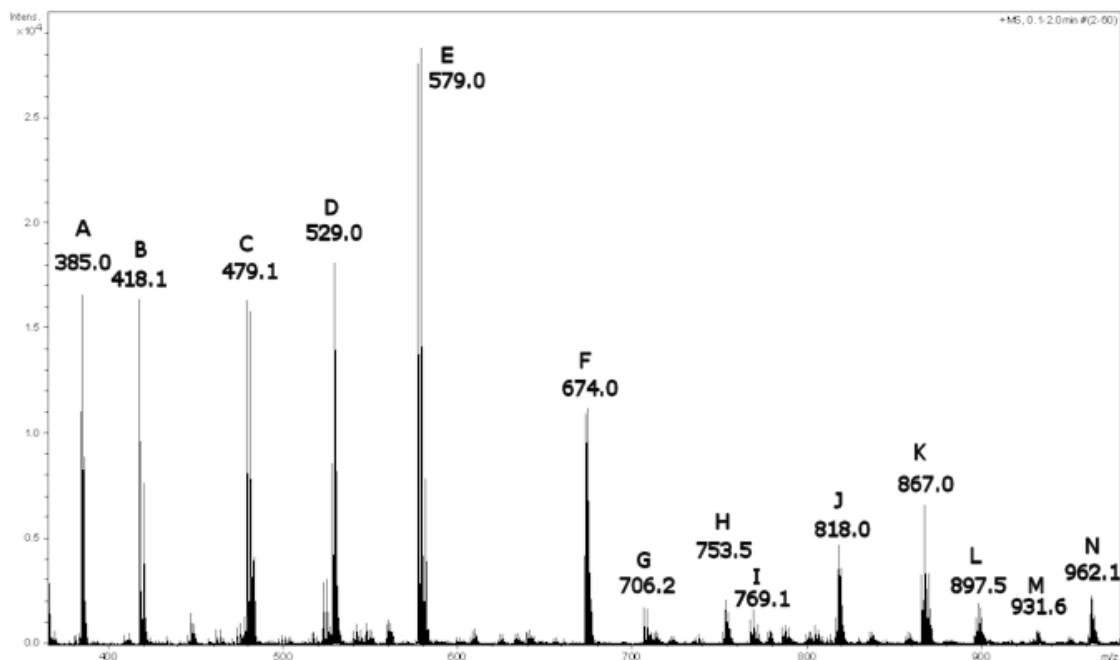
**Figure S2:** CSI-MS spectrum of dilute mother liquor of **1**.

**Table S1:** Assignment and fitting of CSI-MS spectrum of **1**.

Peak	$m/z$ ( $z$ )	Assignment	$m/z$ (calc'd)
A	<b>673.1</b> ( $1+$ )	$[(\text{Cu}_3(\text{OH})\text{F}_5(\text{trans-tachH})_1) \cdot 3\text{CH}_3\text{OH} \cdot 8\text{H}_2\text{O}]^+$	<b>673.1</b>
B	<b>723.6</b> ( $2+$ )	$[(\text{Cu}_8\text{O}_8\text{F}_3(\text{trans-tachH})_5) \cdot \text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}]^{2+}$	<b>723.6</b>
C	<b>788.2</b> ( $2+$ )	$[(\text{Cu}_8\text{O}_8(\text{OH})\text{F}_3(\text{trans-tachH})_6) \cdot \text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}]^{2+}$	<b>788.1</b>
D	<b>838.6</b> ( $2+$ )	$[(\text{Cu}_8\text{O}_8\text{F}_5(\text{trans-tachH})_7) \cdot 2\text{H}_2\text{O}]^{2+}$	<b>838.7</b>
E	<b>903.2</b> ( $1+$ )	$[(\text{Cu}_4\text{O}_4(\text{OH})_2(\text{CH}_3\text{O})(\text{trans-tachH})_4)]^+$	<b>903.3</b>
F	<b>954.7</b> ( $2+$ )	$[(\text{Cu}_9\text{O}_8(\text{OH})\text{F}_7(\text{trans-tachH})_8) \cdot \text{H}_2\text{O}]^{2+}$	<b>954.7</b>



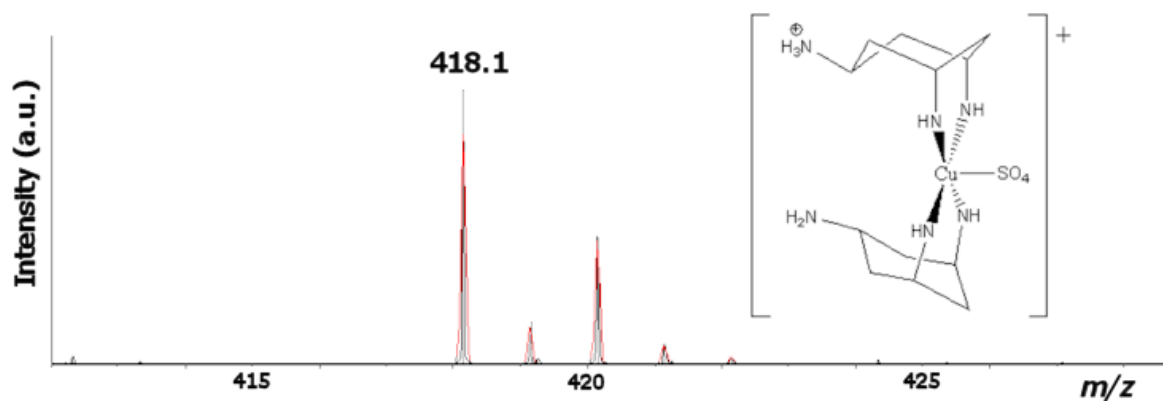
**Figure S3:** (Main) comparison of peak E experimental (black line) and calculated assignment as  $[(\text{Cu}_4\text{O}_4(\text{OH})_2(\text{CH}_3\text{O})(\text{trans-tachH})_4)]^+$  (red line); and (Inset) proposed species, based on assignment.



**Figure S4:** CSI-MS spectrum of dilute mother liquor of **2**.

**Table S2:** Assignment and fitting of CSI-MS spectrum of  $\text{Cu}(\text{SO}_4)$  *trans*-tach.

Peak	$m/z$ ( $z$ )	Assignment	$m/z$ (calc'd)
A	385.0 (2+)	$[\text{Cu}_3(\text{trans-tach})_3(\text{SO}_4)_2]^{2+}$	385.0
B	418.1 (1+)	$[\text{Cu}(\text{trans-tach})_2(\text{SO}_4)\text{H}]^+$	418.1
C	479.1 (1+)	$[\text{Cu}_2(\text{trans-tach})(\text{C}_6\text{H}_{14}\text{N}_3)(\text{SO}_4)]^+$	479.1
D	529.0 (2+)	$[\text{Cu}_4(\text{trans-tach})_4(\text{SO}_4)_3]^{2+}$	529.0
E	579.0 (1+)	$[\text{Cu}_2(\text{trans-tach})_2(\text{SO}_4)_2\text{H}]^+$	579.0
F	674.0 (2+)	$[\text{Cu}_5(\text{trans-tach})_5(\text{SO}_4)_4]^{2+}$	674.0
G	706.2 (1+)	$[\text{Cu}_2(\text{trans-tach})_3(\text{SO}_4)_2\text{H}]^+$	706.2
H	753.5 (2+)	$[\text{Cu}_6(\text{trans-tach})_5(\text{SO}_4)_5]^{2+}$	753.5
I	769.1 (1+)	$[\text{Cu}_3(\text{trans-tach})(\text{C}_6\text{H}_{14}\text{N}_3)(\text{SO}_4)_2]^+$	769.1
J	818.0 (2+)	$[\text{Cu}_6(\text{trans-tach})_6(\text{SO}_4)_5]^{2+}$	818.0
K	867.0 (1+)	$[\text{Cu}_3(\text{trans-tach})_3(\text{SO}_4)_3\text{H}]^+$	867.0
L	897.5 (2+)	$[\text{Cu}_7(\text{trans-tach})_6(\text{SO}_4)_6]^{2+}$	897.5
M	931.6 (2+)	$[\text{Cu}_6(\text{trans-tach})_7(\text{SO}_4)_6\text{H}_2]^{2+}$	931.6
N	962.1 (2+)	$[\text{Cu}_7(\text{trans-tach})_7(\text{SO}_4)_6]^{2+}$	962.0



**Figure S5:** Comparison of the experimental spectrum (black line) and calculated assignment as  $[(\text{Cu}(\text{trans-tach})_2(\text{SO}_4)\text{H})]^+$  (red line); and (Inset) proposed species, based on assignment.

**Notes on the assignments:**

The formula assignments here should be viewed as tentative since, although we are confident that our fits are consistent with the data recorded, it is possible statistically that the more species (for the more complex species) could be fitted using more than one formula assignment. We are currently developing a methodology to quantify this issue and we will seek to, in later work, implement this along with more extensive fragmentation / mass isolation studies to allow us to fit even more complicate and high mass data sets.