

SI

## Experimental procedures

### Synthesis of **1**

H<sub>4</sub>TC[4]A (0.225 g, 0.312 mmol) and CuCl<sub>2</sub>·2H<sub>2</sub>O (0.213 g, 1.248 mmol) were dissolved in a 1:1 dmf/MeOH mixture (24 mL) and stirred for 10 minutes. NEt<sub>3</sub> (0.2 mL, 1.43 mmol) was added and the resultant brown solution stirred for 2 hours. After filtration, the solution was allowed to evaporate slowly to afford crystals of **1** in 17.2% yield after 3 days. Elemental analysis (%) calculated for **1**: C, 46.33; H, 4.59; N, 1.23. Found: C, 46.32; H, 4.44, N, 0.92.

### Synthesis of **2**

H<sub>4</sub>TC[4]A (0.225 g, 0.312 mmol) and CuBr<sub>2</sub> (0.279 g, 1.248 mmol) were dissolved in a 1:1 dmf/MeOH mixture (20 mL) and stirred for 10 minutes. NEt<sub>3</sub> (0.2 mL, 1.43 mmol) was added and the resultant brown solution stirred for 2 hours. After filtration, the solution was allowed to evaporate slowly to afford crystals of **2** in 15% yield after 3 days. Elemental analysis (%) calculated for **2**: C, 40.69; H, 4.25; N, 1.58. Found: C, 40.43; H, 4.46, N, 2.04.

### Single crystal X-ray diffraction

A suitable crystal of **1** with dimensions 0.12 × 0.14 × 0.20 mm<sup>3</sup> was selected and mounted on a loop in Paratone oil on a Bruker D8 diffractometer. The crystal was kept at a steady  $T = 100(2)$  K during data collection. The structure was solved with the ShelXT 2018/2 solution program using dual methods and by using Olex2 1.5-beta as the graphical interface. The model was refined with ShelXL 2014/7 using full matrix least squares minimisation on  $F^2$ .<sup>1-3</sup> **Crystal Data for **1** (CCDC 2417304).** C<sub>325.5</sub>H<sub>448.5</sub>Cl<sub>6</sub>Cu<sub>24</sub>N<sub>27</sub>O<sub>77</sub>S<sub>24</sub>,  $M_r = 8478.69$ , triclinic,  $P-1$  (No. 2),  $a = 22.2855(4)$  Å,  $b = 22.2953(3)$  Å,  $c = 40.7937(7)$  Å,  $\alpha = 75.7320(1)^\circ$ ,  $\beta = 84.1880(1)^\circ$ ,  $\gamma = 89.7150(10)^\circ$ ,  $V = 19538.46(6)$  Å<sup>3</sup>,  $T = 100(2)$  K,  $Z = 2$ ,  $\mu(\text{Cu } K_\alpha) = 4.984$ , 46220 reflections measured, 46220 unique (twin refinement) which were used in all calculations. The final  $wR_2$  was 0.3137 (all data) and  $R_1$  was 0.1003 ( $I \geq 2 \sigma(I)$ ). The structure of **1** showed significant disorder that was handled using partial occupancies and a range of restraints. Disorder was present in upper-rim *p*-tert-butyl groups of the some TC[4]A ligands, bridging carbonates / hydroxides, encapsulated hydroxides, and dmf of crystallisation. The latter were handled with the use of a solvent mask as it was not possible to model all of the disorder, noting that the structure was already challenging with a large number of non-H atoms (~300) in the ASU. The data were collected several times but showed twinning in all cases. This was handled using TWINABS (2012/1) and resulted in the assignment of all major peaks to a sensible model, affording a reasonable agreement index irrespective of these collective challenges.

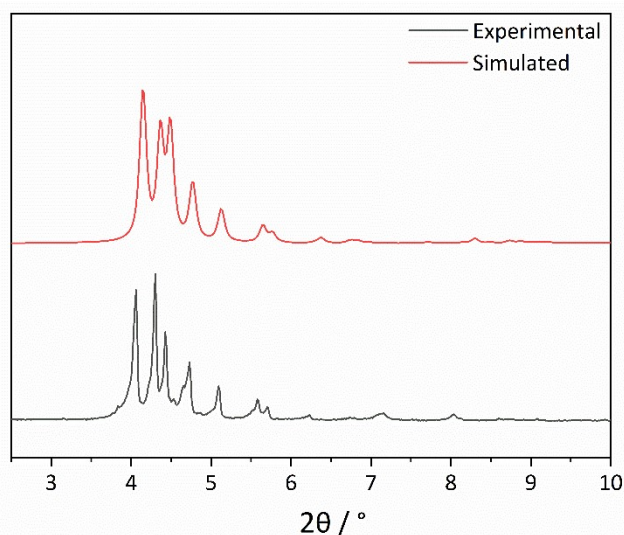
A suitable crystal of **2** with dimensions  $0.14 \times 0.09 \times 0.03 \text{ mm}^3$  was selected and mounted on a MITIGEN holder in Paratone oil on a Rigaku Oxford Diffraction SuperNova diffractometer. The crystal was kept at a steady  $T = 200.01(10) \text{ K}$  during data collection. The structure was solved with the ShelXT 2018/2 solution program using dual methods and by using Olex2 1.5-beta as the graphical interface. The model was refined with ShelXL 2018/3 using full matrix least squares minimisation on  $F^2$ .<sup>1-3</sup> **Crystal Data for 2 (CCDC 2417305)**.  $\text{C}_{96}\text{H}_{126}\text{Br}_5\text{Cu}_8\text{N}_5\text{O}_{18}\text{S}_8$ ,  $M_r = 2802.36$ , orthorhombic, *Pbca* (No. 61),  $a = 23.4990(4) \text{ \AA}$ ,  $b = 25.0057(5) \text{ \AA}$ ,  $c = 43.0467(8) \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 25294.6(8) \text{ \AA}^3$ ,  $T = 200.01(10) \text{ K}$ ,  $Z = 8$ ,  $Z' = 1$ ,  $\mu(\text{Cu K}\alpha) = 4.984$ , 177307 reflections measured, 13238 unique ( $R_{\text{int}} = 0.1074$ ) which were used in all calculations. The final  $wR_2$  was 0.2607 (all data) and  $R_1$  was 0.0906 ( $I \geq 2 \sigma(I)$ ).

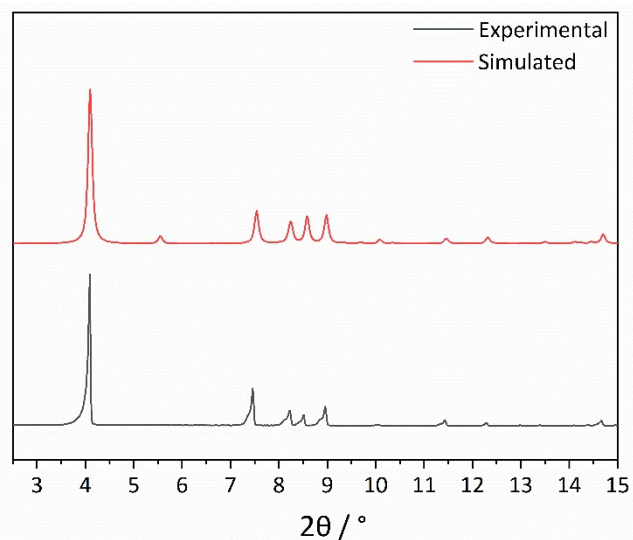
### Powder X-ray diffraction

Diffraction data for compounds **1-2** were collected on polycrystalline powders using a Bruker D8 ADVANCE with Cu radiation at 40 kV, 40 mA and a Johansson monochromator, 2 mm divergence slit and 2.5 degree Soller slits on the incident beam side, LynxEye detector and Bruker DIFFRAC software. Diffraction data were measured from  $2\theta = 2.5^\circ - 30^\circ$ ; step size,  $0.0101^\circ$ . Freshly prepared crystalline powders were loaded into borosilicate capillaries with a 0.7 mm inside diameter and measured while spinning.

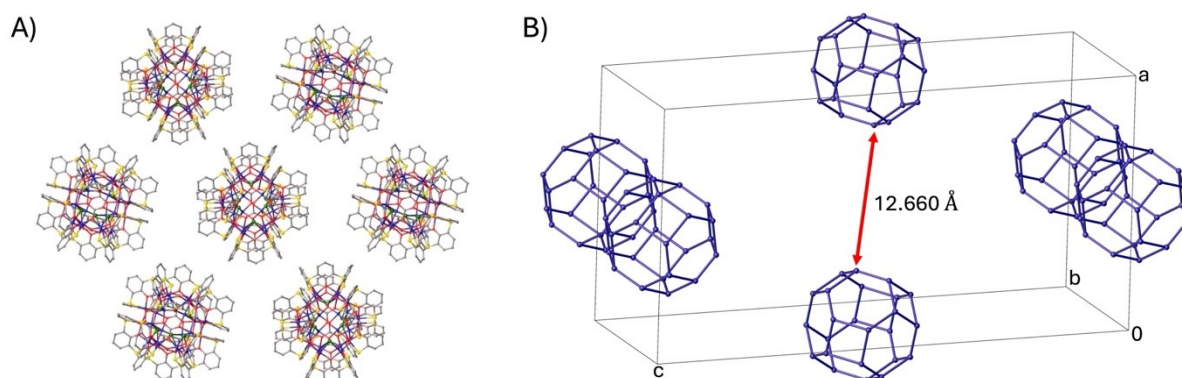
### Magnetometry

Magnetic susceptibility and magnetisation data were collected on freshly prepared polycrystalline powders of **1-2** on a Quantum Design Dynacool PPMS equipped with a 9 T magnet in the temperature and field ranges,  $T = 300 - 2.0 \text{ K}$ ,  $B = 0.1 \text{ T}$  and  $T = 2-10 \text{ K}$ ,  $B = 0.5 - 9.0 \text{ T}$ , respectively. Samples were placed into a Quantum Design VSM Powder Sample Holder (P125E) with eicosane present and then transferred to a PPMS brass half-tube sample holder. Diamagnetic corrections from the holders and eicosane were applied. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

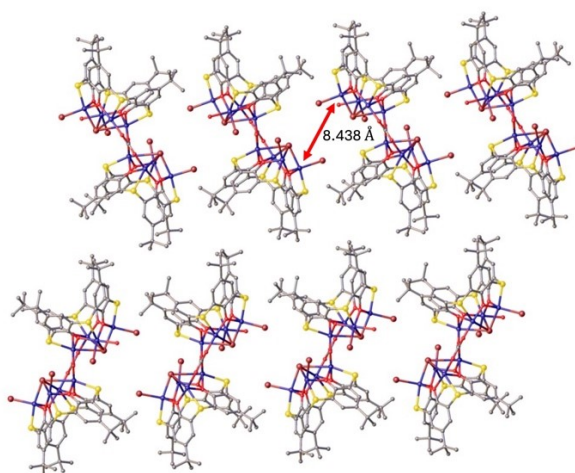




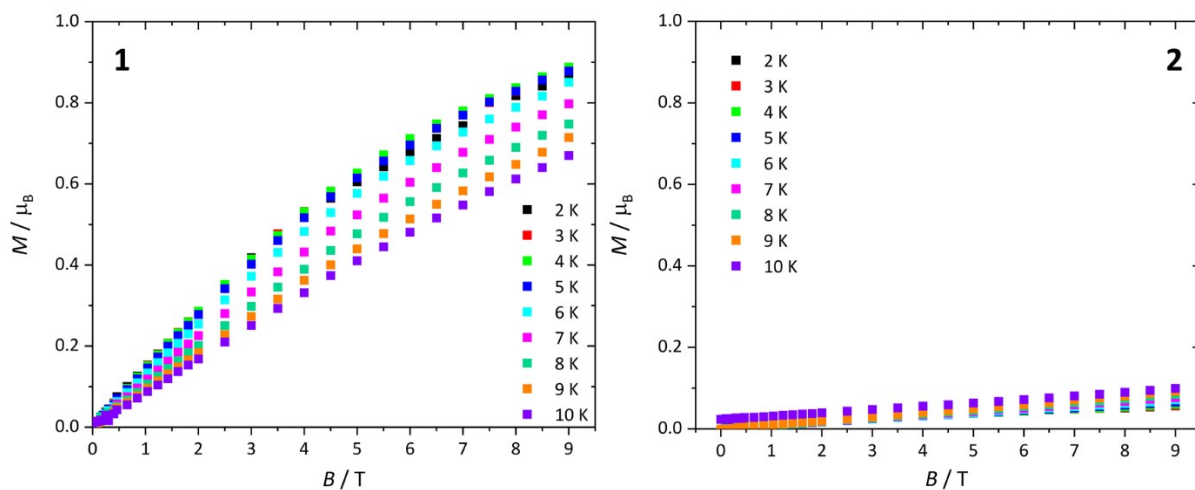
**Figure S1.** Powder X-ray diffraction of **1** (top) and **2** (bottom) showing the experimental (black) and simulated (red) data.



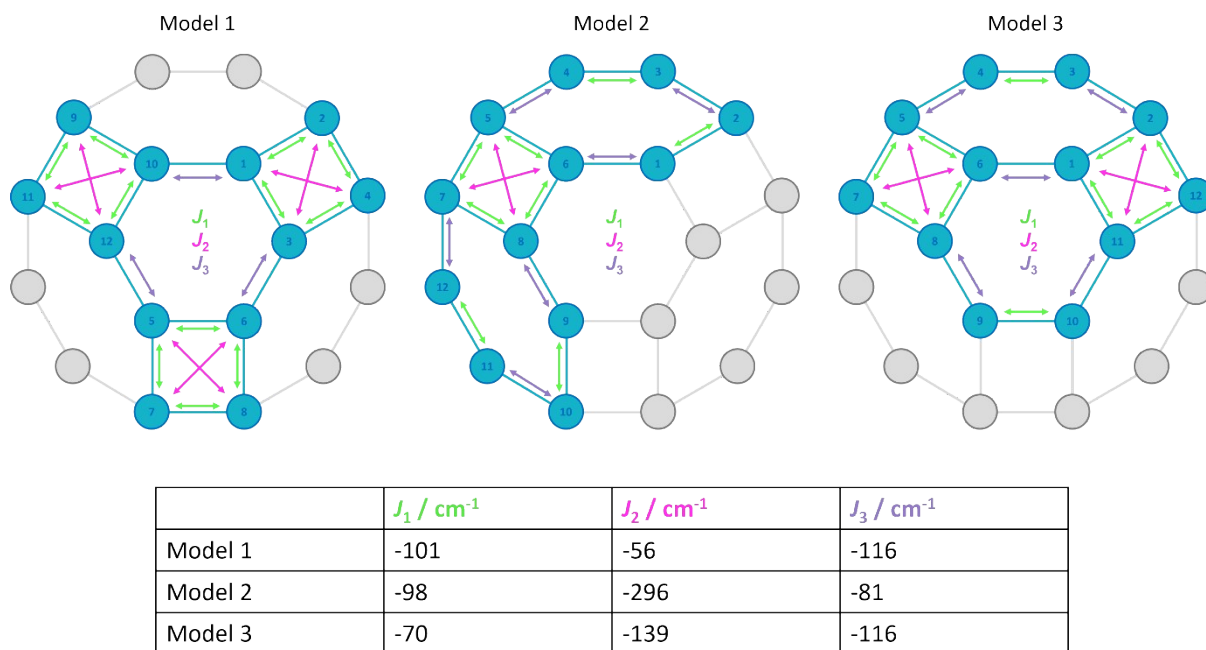
**Figure S2.** Extended structure of **1** showing (A) packing of clusters in a plane with TC[4]A ligands present, and (B) symmetry equivalent cages in the unit cell with an indication of closest Cu...Cu contact as a red double-headed arrow. H atoms, tBu groups and dmf are omitted for clarity in A.



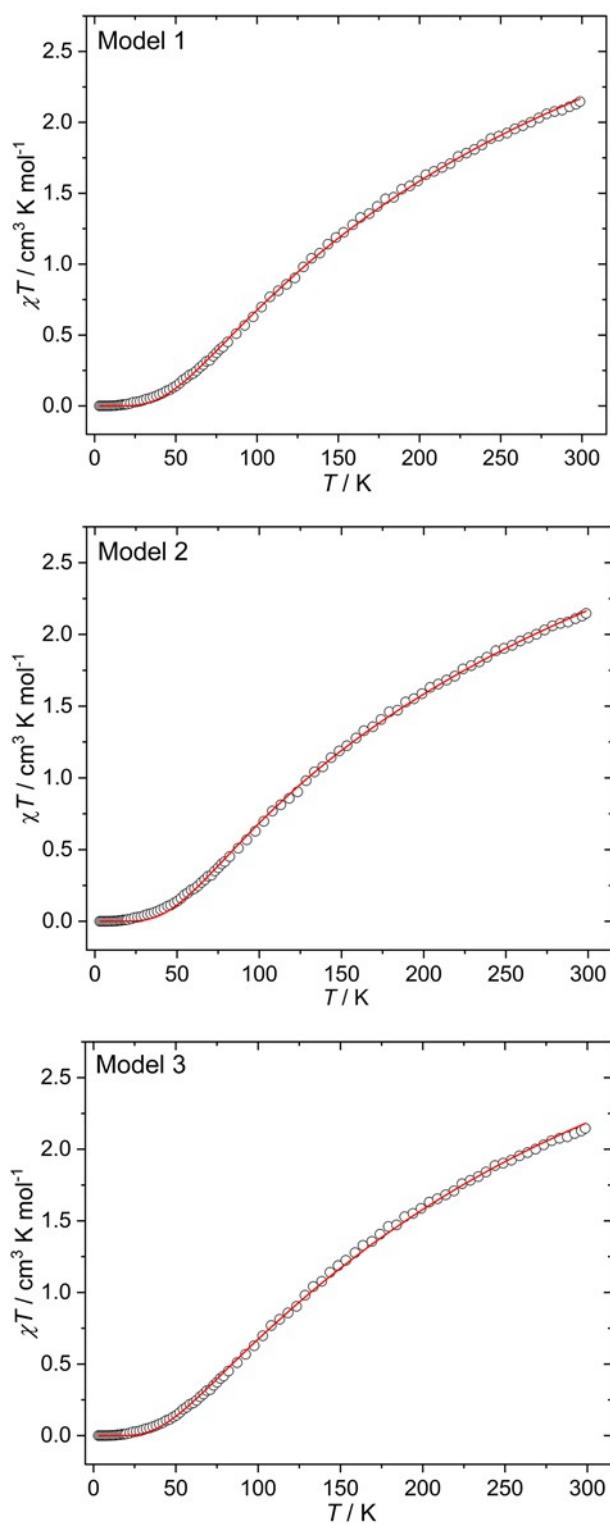
**Figure S3.** A *bc* cross-section of the extended structure of **2** showing a bi-layer type assembly and closest Cu...Cu contact between neighbouring clusters as a red double-headed arrow. H atoms, ligated dmf and dmf of crystallisation are omitted for clarity.



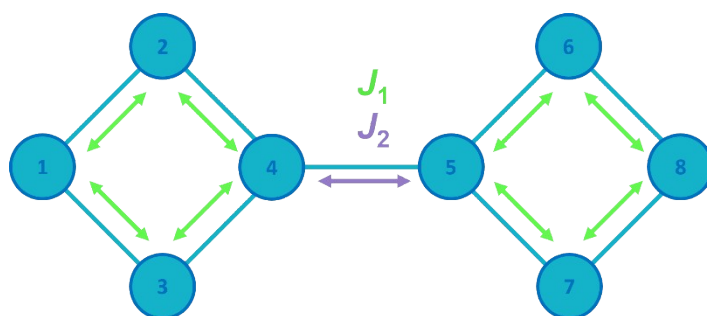
**Figure S4.** Magnetisation data for **1** (left) and **2** (right) collected in the  $T = 2.0$ - $10$  K,  $B = 0.5$ - $9.0$  T temperature and field ranges. The data is indicative of diamagnetic ground states in both cases.



**Figure S5.** The three  $[\text{Cu}_{12}]$  model compounds (Models 1-3) used to fit the magnetic susceptibility data of **1**. Each assign three distinct magnetic exchange interactions. These are  $J_1 = \text{Cu-O/Cl-Cu}$  along the sides of the square faces ( $\text{Cu-O-Cu} = \sim 109\text{-}112^\circ$ ,  $\text{Cu-Cl-Cu} = \sim 75^\circ$ );  $J_2 = \text{Cu-Cl-Cu}$  across the diagonal of the square faces ( $\text{Cu-Cl-Cu} = \sim 118^\circ$ ); and  $J_3 = \text{Cu-O-Cu}$  in the hexagonal faces ( $\text{Cu-O}_{\text{hydroxide}}\text{-Cu} = \sim 94^\circ$ ,  $\text{Cu-O}_{\text{carbonate}}\text{-Cu} = \sim 120^\circ$ ). We ignore any diagonal interactions across the hexagon through the three atom  $\text{Cu-O-C-O-Cu}$  carbonate bridges. The table shows the best fit parameters obtained with the  $g$ -value fixed at  $g = 2.00$ .



**Figure S6.** The best fit (solid red lines) using Models 1-3 for the experimental magnetic susceptibility data (empty circles) for **1** measured in the  $T = 300 - 2.0$  K temperature range in an applied field,  $B = 0.1$  T. The experimental data for **1** is divided by two and modelled using the  $[\text{Cu}_{12}]$  models shown in Fig. S4 and spin-Hamiltonian (1).



**Figure S7.** The model used to fit the magnetic susceptibility data of **2**. The model assigns two distinct magnetic exchange interactions - those within each  $[\text{Cu}_4]$  square ( $J_1$ ) and between the two squares ( $J_2$ ). We ignore any diagonal interactions across the Cu-Br-Cu bridge due to the considerable asymmetry of the Cu-Br bond lengths.

## References

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. G. M. Sheldrick, Crystal structure refinement with ShelXL, *Acta Cryst.* **2015**, *C71*, 3-8.
3. G. M. Sheldrick, ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.* **2015**, *A71*, 3-8.