

# Electronic Supplementary Information 1

## Crystal engineering with copper and melamine

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# Experimental

## *Chemicals*

The ligand 1,3,5-Triazine-2,4,6-triamine (Melamine, C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>, 99%) and the metal salt, copper chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O, ≥99.0 %) were purchased from Sigma Aldrich.

As for the solvents employed, dimethyl sulfoxide (DMSO, (CH<sub>3</sub>)<sub>2</sub>SO, ≥99.7 %), N, N-Dimethylformamide anhydrous (DMF, (CH<sub>3</sub>)<sub>2</sub>-N-CHO, 99.8 %) and methanol (CH<sub>3</sub>OH, ≥99.9 %) were also purchased from Sigma Aldrich. Acetic acid (CH<sub>3</sub>COOH, 99.0 %) from Penta and ammonia solution (NH<sub>3</sub>, 4 mol/L, in methanol) from Sigma Aldrich were used. Deionized water (18.2 MΩ·cm) was used for all synthesis.

## *Optical microscope*

Optical micrographs of crystals were taken with an optical microscope (BX41M-LED, Olympus, Japan) equipped with a Infinity 1 camera, Lumenera (Canada), and QuickPHOTO CAMERA 3.1 software.

## *Raman spectroscopy*

Raman spectroscopy was performed using a Raman spectrometer (Model LabRAM HR, HORIBA, Japan) with a He-Ne integrated laser (wavelength 633 nm).

## *Single crystal X-Ray diffraction*

The X-ray intensity data were measured on Bruker D8 Venture diffractometer equipped with multilayer monochromator, Mo K/α INCOATEC micro focus sealed tube and Oxford cooling system.

## *Magnetization measurements*

The magnetisation data were recorded at temperatures between 2K and 300K at applied magnetic fields up to 7T using a Quantum design MPMSXL magnetometer. 33.7 mg of

Cu<sub>2</sub>Mn crystals encapsulated in a gelatin capsule were measured. We assume that most of planar crystals lying horizontally were stuck on one another and hence the magnetic field was applied normal to the crystal plane. 24.0 mg of a planar single crystal of Cu<sub>4</sub>Mn was measured with the magnetic field applied normal to the crystal plane.

## Synthesis

In this section, complementary information related to the optimization of the synthesis is represented. Three solutions of 0.05, 0.1 and 0.2 mol/L of melamine in DMSO are prepared. Solubility tests show DMSO, DMF, methanol and water can dissolve melamine, but only DMSO cannot fully dissolve if the concentration is above 0.2 mol/L at room temperature. As for the  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  solutions, common solvents were tested: water, methanol, DMF and DMSO. Five mother solutions of 0.8, 0.6, 0.4, 0.3, 0.2, 0.1, 0.05 and 0.025 mol/L were prepared for each solvent system. In each case, 2 mL of a  $\text{CuCl}_2$  solution was placed in a 5 mL glass vial, then 2 mL of a melamine solution was added to the  $\text{CuCl}_2$  solution. The mixture was homogenized using a Transsonic T 470/H ultrasonic bath. After that, the vial was tightly closed and put aside at room temperature in a fume hood gas extractor for 3 days. The same procedure was followed for the syntheses at 50 °C in an oven, Ecocell model of BMT Medical Technology (Czech Republic). The main objective of this synthesis at a higher temperature is to determine the influence of temperature on the crystallization kinetics.

Figure S1-1 displays the results of crystal synthesis at room temperature with different solvents and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  concentrations. The concentration of melamine is A) 0.1 mol/L and B) 0.2 mol/L.

Different molar ratios and concentrations of melamine in DMSO and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in four different media, DMSO, water + DMSO (1:1 volume ratio), DMF + DMSO (1:1 volume ratio) and Methanol + DMSO (1:1 volume ratio) were tested for crystal growth at room temperature.

As observed in Fig. S1-1, crystals are formed only in (1:1) methanol and DMSO media. This could be due to the hydroxyl group (-OH-) of methanol interacting with the metal ions to form a metal-organic structure Chen et al. [2006], or due to a low solubility of melamine in the solution necessary to form high quality crystals Robin et al. [2006]. In fact, as observed experimentally, methanol does not dissolve properly melamine. Alternatively, it can be attributed to high polarity of DMSO, DMF and water as compared to alcohols, which destabilizes the coordination bonds Kettle [2013].

Figure S1-2 shows that there are not significant differences in the crystal morphology and

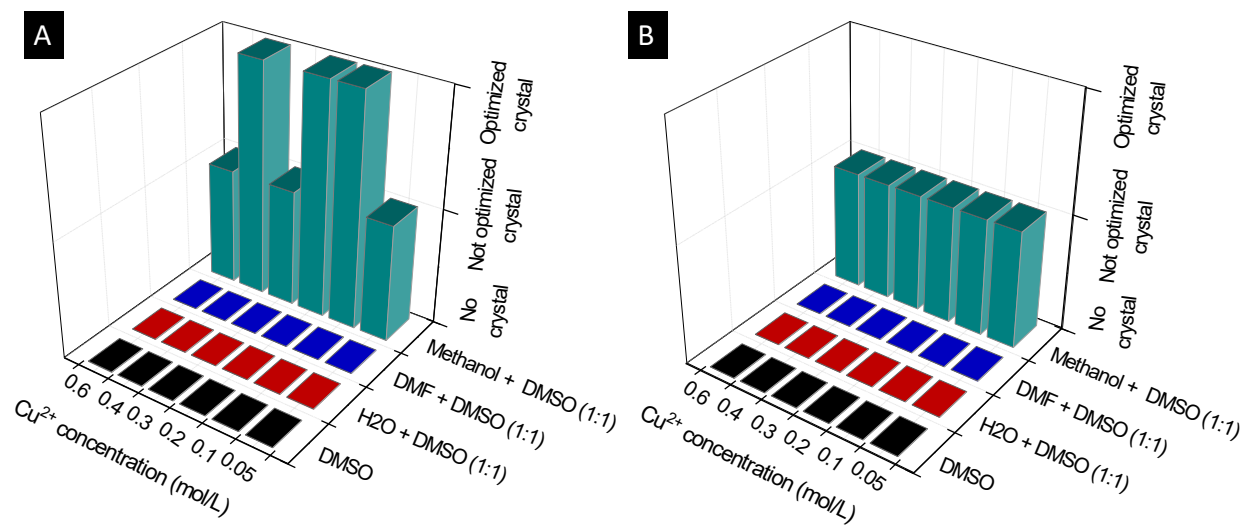


Figure S1-1: Crystal growth at room temperature with different solvents and  $\text{CuCl}_2$  concentrations. The concentration of melamine is A) 0.1 mol/L and B) 0.2 mol/L.

size between the samples synthesized at room temperature and 50°C. No crystals are formed at 70°C.

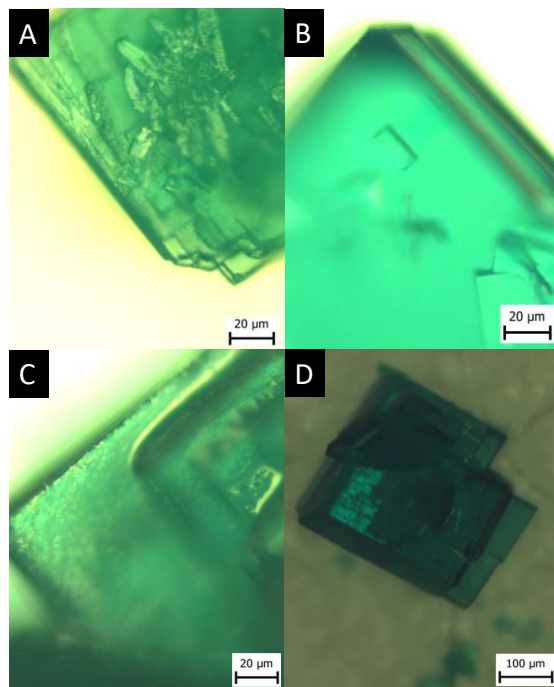


Figure S1-2: Optical micrographs of A) Cu1M1 at 50°C, B) Cu2M1 at 50°C, C) Cu1M1 at room temperature and D) Cu2M1 at room temperature. Cu1M1 stands for 0.1 mol/L of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol and 0.1 mol/L of melamine in DMSO mixed in 1:1 volume ratio. Cu2M1 stands for 0.2 mol/L  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in methanol and 0.1 mol/L of melamine in DMSO mixed in 1:1 volume ratio.

## Stability

The stability of the copper-melamine complex and the copper coordination polymer in air and various solvents are showed in Fig. S1-3. The solvents tested are DMSO, DMF, methanol, deionized water, air, acidic media (crystal media but pH 4, reached by adding acetic acid) and basic media (crystal media but al pH 9, reached adding ammonia solution ( $\text{NH}_3$ , 4 mol/L, in methanol).

### *Chemical stability*

To test its chemical resistance to different solvents, the crystal filtered out and rinsed with DMSO was subjected to a 3 mL pure solvent solution in a closed glass vial of 5 mL volume. After a day, the crystal was observed by an optical microscope and compared with a similar one which was left in its forming solution.

### *pH stability*

To test the stability in acid and basic media, acetic acid anhydrous and a solution of ammonium hydroxide in methanol were added to the original solution where the crystals were formed. pH 9 and 4 were reached for basic and acidic cases, respectively. The pH was measured using a pH tester HI98100 Checker Plus of Hanna Instruments.

### *Air stability*

As for their stability in air, the crystals were separated from the supernatant by vacuum filtration. They are washed with the respective suitable solvent and also, they are left on a glass slide for one day. Then, they were observed by an optical microscope and compared with freshly synthesized crystals.

### *Copper-melamine complex Cu<sub>2</sub>M1*

The copper-melamine complex stands the longest time in DMSO, relatively longer in methanol and air, much shorter in DMF and the shortest in water. The instability in water is common

Crystal	Cu-melamine complex Cu2M1	Cu coordination polymer Cu4M1
Air	Yellow	Blue
DMSO	Green	Orange
DMF	Orange	Yellow
Methanol	Yellow	Yellow
Water (pH 6.5±0.04)	Red	Red
Acid solution (pH 4±0.02)	Orange	Blue
Basic solution (pH 9±0.05)	Red	Orange

**Red:** decomposed in less than ten minutes; **Orange:** decomposed after an hour; **Yellow:** decomposed after two hours; **Green:** decomposed after a day; **Blue:** did not decompose.

Figure S1-3: The stability of the copper-melamine complex and the copper coordination polymer in air and various solvents.

in coordination complexes, due to the labile nature of coordination bonds which destroy the structure by hydrolysis of the network (Cychosz and Matzger, 2010). The coordination of Cu (II) to N of the triazine ring is weak and susceptible to be attacked by polar solvents. Also, organic solvents do not involve a stable media for these crystals either. This behavior is characteristic of coordination materials, since polar solvents break the weak bonds that form their crystalline structures (Kettle, 2013). It is unstable in basic systems as the decomposition is caused by the replacement of linkers by OH<sup>-</sup> that competitively binds to the metal ions. In acid solutions, their poor stability is related to a higher concentration of H<sup>+</sup>, which exchange with Cu (II) ions in the crystalline structure (Yuan et al., 2018). These properties are associated with ligands, being coordination complexes.



### *Copper coordination polymer Cu<sub>4</sub>M1*

As shown in Fig. S1-3, the copper coordination polymer is generally more stable than the copper-melamine complex, owing to the strong Cu-Cl. It shows the highest stability in air and acidic conditions.

## Crystallization control

Control of the crystallisation of both Cu<sub>2</sub>M1 and Cu<sub>4</sub>M1 in the same media was demonstrated as follows. Cu<sub>4</sub>M was formed without melamine by mixing 2 mL of Cu (II) 0.4 mol/L in methanol with a 2mL mixture of DMSO and acetic acid with a pH of  $9.64 \pm 0.02$ . Then, 2 mL of a DMSO solution of melamine 0.1 mol/L was added in the solution to reach a copper-to-melamine concentration ratio of 2:1. As observed in Fig.S1-4, the dark green Cu<sub>2</sub>M1 crystals grow on the surface of the light-green Cu<sub>4</sub>M crystals as long as 6 hours. The Cu<sub>2</sub>M1 crystals grow as long as 6 hours reaching a maximum size around 800  $\mu\text{m}$ , which is more than twice as large as 350  $\mu\text{m}$  for Cu<sub>2</sub>M1 crystals grown with melamine. Also, the Cu<sub>2</sub>M1 crystals on the surface of Cu<sub>4</sub>M1 is thicker and less edgy as compared with those grown alone (See Fig. 2 in the manuscript). This phenomenon can be related with the crystallization mechanism. According to Ostwald ripening Ostwald [1900], the crystallization is governed by four steps: dissolution, ripening, regrowth and relaxation. A higher presence of copper ions on the surface of Cu<sub>4</sub>M1 boosts the regrowth and ripening steps, enlarging the size of the Cu<sub>2</sub>M1 crystals.

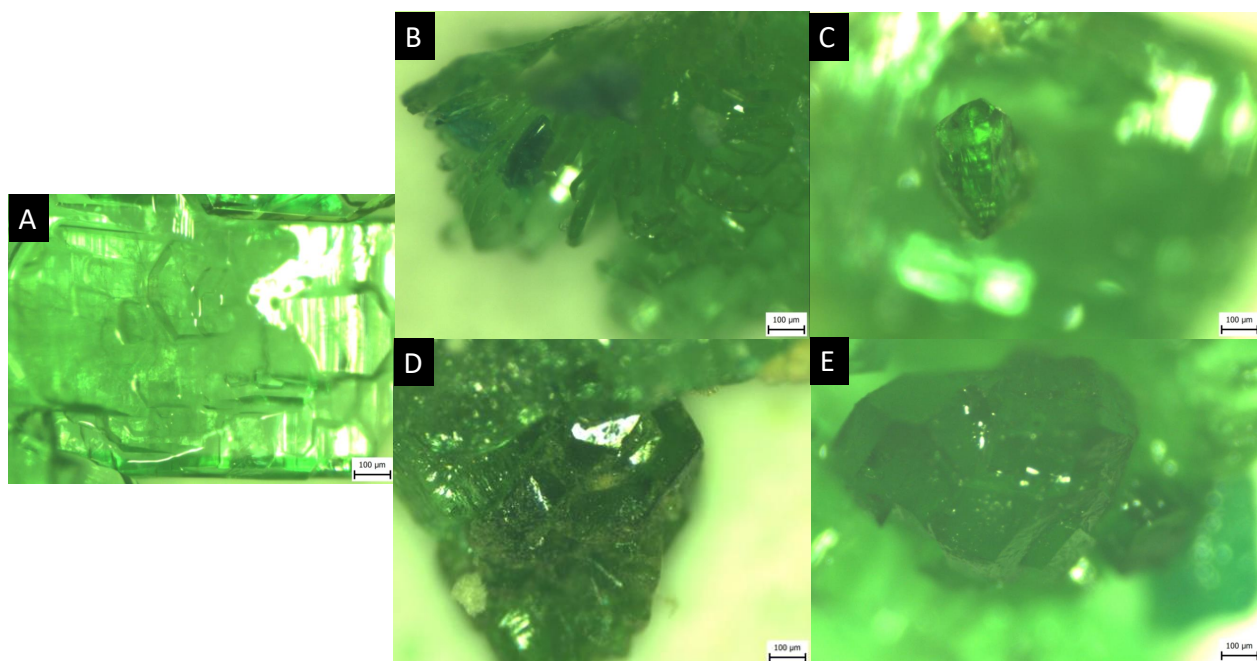


Figure S1-4: Micrographs demonstrating crystallisation of  $\text{Cu}_2\text{M1}$  on the surface of  $\text{Cu}_4\text{M1}$  over time. A) Before adding melamine, B) 1 hour after adding melamine, C) 3 hours after adding melamine, D) 6 hours after adding melamine and E) 24 hours after adding melamine.

# Magnetism

## *Magnetic susceptibility*

The temperature dependent magnetizatic susceptibility of the Cu4M1 can be fitted by the following equation derived for a S=1/2 Ising chain Fisher [1964]:

$$\chi_{Cu} = \frac{g_S^2 \mu_B^2}{12k_B T} \frac{1 + u(K)}{1 - u(K)} (1 - \zeta) + \frac{g_S^2 \mu_B^2}{4k_B T} \zeta, \quad (1)$$

where  $u(K) = \tanh(K)$  and  $K = J/2k_B T$ , and  $\zeta$  corresponds to a concentration of 1/2 paramagnetic impurities or the inverse-temperature term that arises from staggered spins Feyerherm et al. [2000]. As shown in Fig. S1-5, the fitted curve reproduces the peak, but not as good as Eq. 1 in the manuscript for a S=1/2 Heisenberg chain. The least square fit leads to  $g = 2.201 \pm 0.005$ ,  $J = -0.997 \pm 0.007$  meV,  $\zeta = 0.067 \pm 0.001$ .

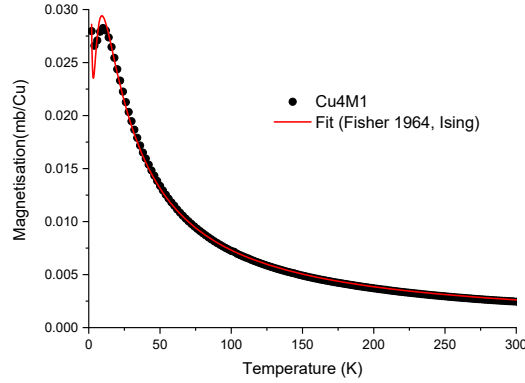


Figure S1-5: Magnetism versus field for dinuclear Cu-melamine complex and Cu coordination polymer

As shown in Fig. S1-6, the best fit can be obtained with the well-known rational equation Estes et al. [1978]:

$$\chi_{Cu} = \frac{g_S^2 \mu_B^2}{k_B T} \frac{0.25 + 0.14995x + 0.30094x^2}{1 + 1.9862x + 0.68854x^2 + 6.0626x^3} (1 - \zeta) + \frac{g_S^2 \mu_B^2}{4k_B T} \zeta. \quad (2)$$

The least square fit leads to  $g = 2.189 \pm 0.002$ ,  $J = -0.745 \pm 0.002$  meV,  $\zeta = 0.0197 \pm 0.0003$ .

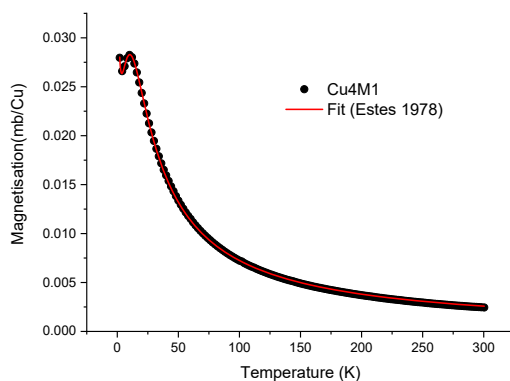


Figure S1-6: Magnetism versus field for dinuclear Cu-melamine complex and Cu coordination polymer

### *Magnetization isotherms*

Figure S1-7 shows the magnetization isotherms for dinuclear Cu-melamine complex Cu2M1 and Cu coordination polymer Cu4M1.

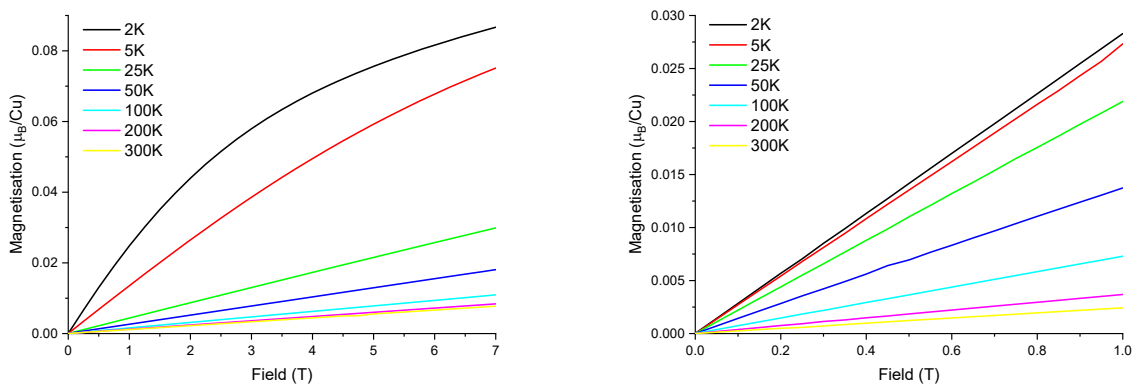


Figure S1-7: Magnetism versus field for dinuclear Cu-melamine complex Cu2M1 (left) and Cu coordination polymer Cu4M1 (right)

The magnetisation of Cu2M1 per Cu saturates well below  $\mu_B = g_S \sqrt{S(S+1)} \mu_B \simeq 1.73 \mu_B$ , the effective magnetic moment for a paramagnetic  $S=1/2$  spin. This is due to the impurity (15% of Cu) dominating the net magnetization in the measured temperature range 2–300 K. For both samples, the magnetization isotherm is linear up to 1T so that the Curie or

Curie-Weiss term used in the equations of the magnetic susceptibility is justified.

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