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Supporting information

Reversible and Vapochromic Chemisorption of Ammonia by a Copper(II) Coordination Polymer

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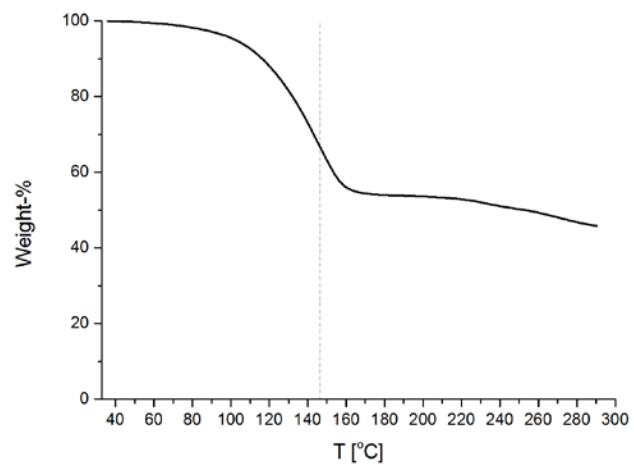


Figure S1. TGA measurement on *catena-[[Cu(tpt)(o-phthalate)]·3¹₃(C₂H₂Cl₄)]_n*. The dotted line indicates the boiling point of the solvent 1,1,2,2-tetrachloroethane (147 °C).

Quantification of copper content by EPR

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is mixed and mortared to a fine powder with K_2SO_4 in 4 different concentrations to make reference samples with concentrations 0.506, 0.932, 2.475 and 4.054 weight% Cu, respectively.

5 – 10 mg of the reference samples and the $[\text{Cu}(\text{tpt})(\text{o-phthalate})]$ samples were measured individually with X-band EPR in suprasil 4 mm quartz tubes with identical settings during two different experimental sessions. Instrument parameters: Average of 3 sweeps, 2000 points, frequency 9.599 GHz (+/- 0.1 GHz), field interval 220-400 mT, power 6.568 mW, modulation frequency 100 kHz, modulation amplitude 0.8 mT, conversion time 30 ms, time constant 20.48 ms. A background measurement was performed on an empty tube with the same settings. All data treatment was performed using MatLab.

The EPR spectra were corrected individually by subtracting the background spectrum and were subsequently integrated twice. The value of the double integral in the last point was plotted as a function of the concentration of copper for the reference samples. A linear regression was used to calculate the copper concentration of the $[\text{Cu}(\text{tpt})(\text{o-phthalate})]$ samples.

The results are shown in Figure S2.

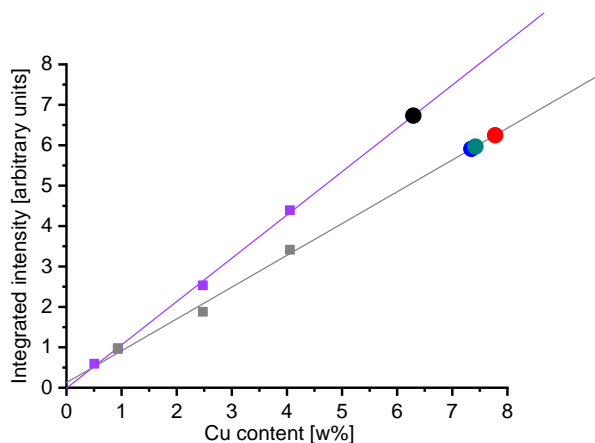


Figure S2: Quantification of copper content in different samples during two different experimental sessions (grey and purple) using the same reference samples. The determined Cu concentrations are 6.3 w% for ‘Solvated powder’ (black dot), 7.8 w% for ‘Crushed single crystal’ (red dot), 7.3 w% for ‘Spontaneously desolvated’ (blue dot) and 7.4 w% for ‘Desolvated w. acetone 1’ (teal dot).

The concentration of the samples is too high for confident determination of the spin concentration and also too high compared to the most concentrated reference sample, so the determination is tentative. The result for the solvated powder (black trace in Figure S3 and black dot in Figure S2) is close to the calculated Cu value for $\{[\text{Cu}(\text{tpt})(\text{o-phthalate})]3^{1/3}(\text{C}_2\text{H}_2\text{Cl}_4)_3\}_n$ of 5.8 %. The value of the crushed single crystals is higher, although the EPR spectra in Figure S1 indicate the same dominant species present. The value for the desolvated samples is too low since the copper content should increase significantly to reach 11.8 w% for $[\text{Cu}(\text{tpt})(\text{o-phthalate})]$ after complete desolvation. This fits well with the shape of the EPR spectra in Figure S3, since the spectra are clearly not approaching the shape of an efficiently desolvated sample as given as the green trace in Figure 10 of the main text.

Comparison of EPR spectra of solvated and acetone desolvated samples

EPR spectra of different of $\{[\text{Cu}(\text{tpt})(\text{o-phthalate})]3^{\ddagger}/_3(\text{C}_2\text{H}_2\text{Cl}_4)_3\}_n$ before and after spontaneous desorption of TCE and after treatment with acetone (2 different batches) were compared. The results are shown in Figure S3.

The EPR spectra are very sensitive to the local coordination sphere around Cu, revealing that the investigated samples have different distributions. The most pristine samples with high content of TCE ('Solvated powder' and 'Crushed single crystals' in Figure S1) have a dominant contribution from a species giving a prominent positive feature at $g = 2.18$ and a prominent negative feature at $g = 2.05$. As the desorption proceeds the feature at $g = 2.05$ disappears and the negative feature at $g = 2.09$ takes over. At the same time the positive feature at $g = 2.18$ decreases and a new feature at $g = 2.25$ grows in.

The new features are coinciding with the well-determined peaks in the EPR spectra of the heat-desorbed $[\text{Cu}(\text{tpt})(\text{o-phthalate})]$ shown as a green trace in Figure 10 of the main text.

The average g -value is difficult to determine for composite samples, but an indication of the g -value can be read as the zero-crossing point of the spectra. This value lies between 2.13 and 2.14 for all samples.

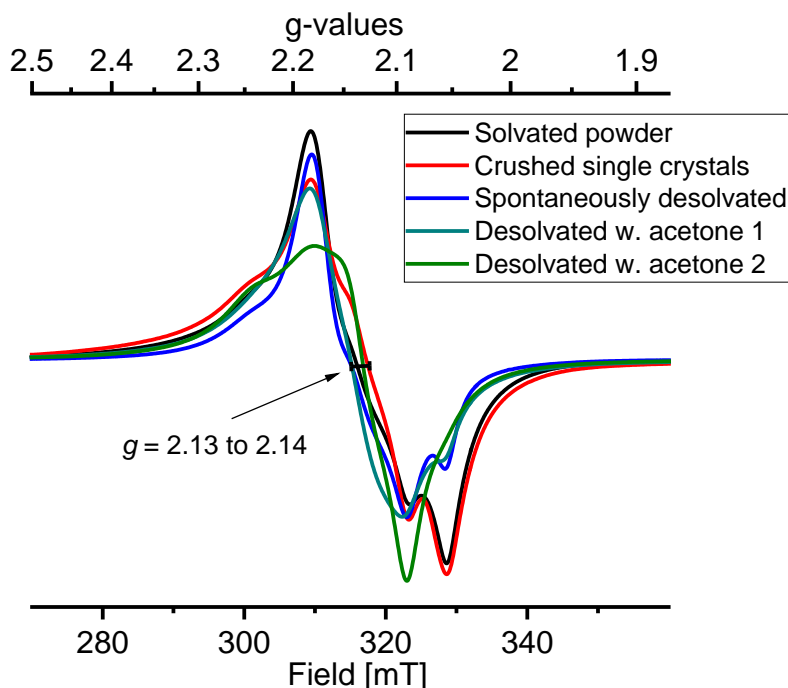


Figure S3 Comparison of EPR spectra of $\{[\text{Cu}(\text{tpt})(\text{o-phthalate})]3^{\ddagger}/_3(\text{C}_2\text{H}_2\text{Cl}_4)_3\}_n$ before and after desorption at room temperature. 'Solvated powder' is the as-prepared $\{[\text{Cu}(\text{tpt})(\text{o-phthalate})]3^{\ddagger}/_3(\text{C}_2\text{H}_2\text{Cl}_4)_3\}_n$, 'Crushed single crystals' is a batch prepared for crystallisation as described in the main text, and then carefully crushed. 'Spontaneously desolvated' is a batch of the as-prepared material that has been left in open air for weeks before measurement. 'Desolvated with acetone 1 and 2 have been treated with acetone as described in the main text in order to wash out the TCE.

Relative signal intensity during absorption and desorption of ammonia

The EPR spectra given in Figure 10 of the main text show EPR spectra after absorption of ammonia and subsequent desorption. The signal intensity was determined using the same protocol as described above and referenced relative to the start spectrum of the experimental session. The results are given in Figure S4.

The integral of the start spectrum is given as a black column with height 1.00 and corresponds to the spectrum 'Desolvated w. acetone 2' in Figure S3. The next columns correspond to the spectrum after absorption of ammonia (purple), after desorption at 150 degrees for 30 minutes (teal), two intermediate spectra (grey), after complete desorption at 175 degrees (green) and after reabsorption of ammonia (red-violet).

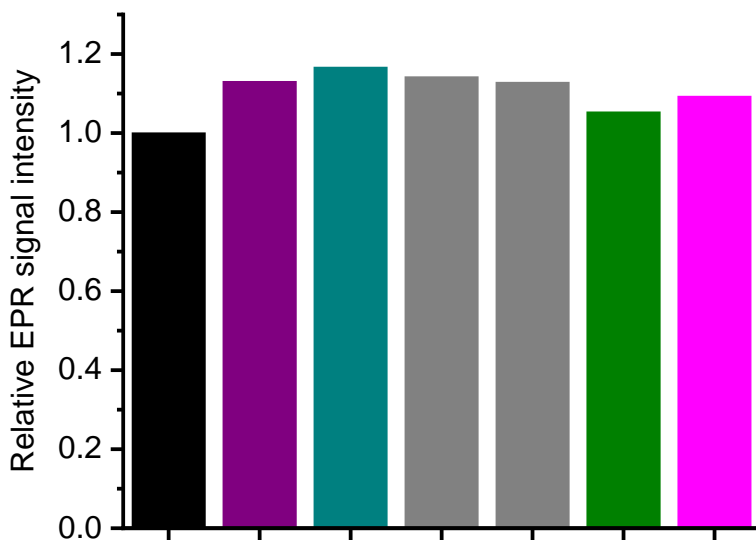


Figure S4: Relative EPR signal intensity obtained by double integration of the spectra shown in Figure 10 of the main text referenced to the spectrum of the start sample ('Desolvated w. acetone 2' shown in Figure S3). Colours are the same as in Figure 8 of the main text.

PXRD of solvated, desolvated and NH₃ sorbed samples

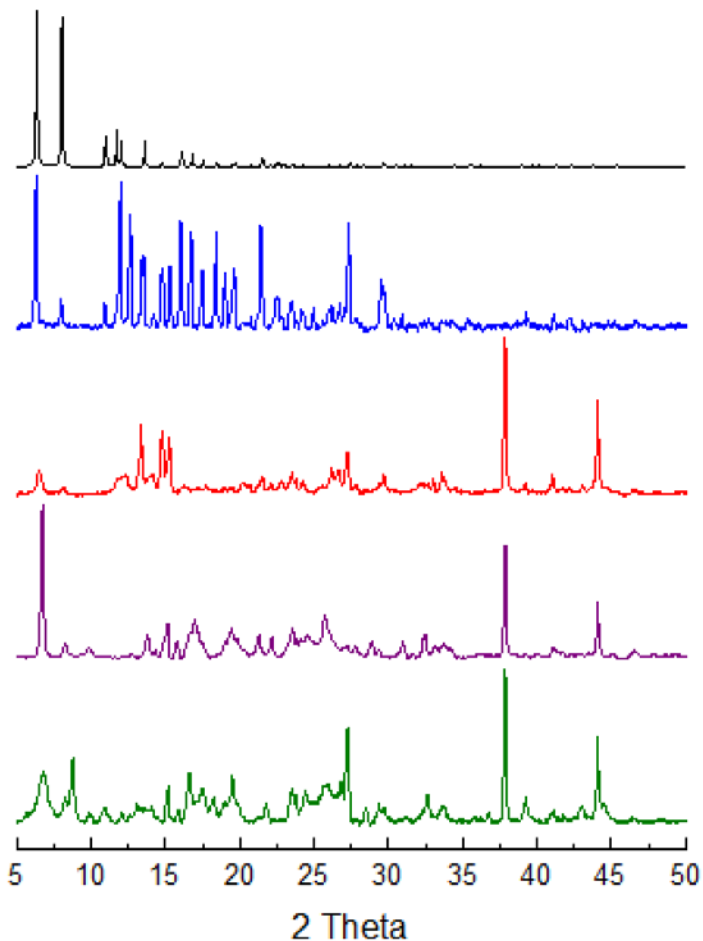


Figure S5. PXRD diffractograms of $\{[Cu(tpt)(o-phthalate)] \cdot 3/3(C_2H_2Cl_4)_3\}_n$ (calculated^{2y}, black; experimental, blue) $[Cu(tpt)(o-phthalate)]_n$ (red), $[Cu(tpt)(o-phthalate)]_n$ - ammonia adduct (purple) and the $[Cu(tpt)(o-phthalate)]_n$ (green) recovered after removal of ammonia. The reflections at $2\theta = 38$ and 44 originate from the sample holder.

- (1) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. *Mercury: Visualization and Analysis of Crystal Structures. J Appl Crystallogr* **2006**, *39* (3), 453–457.