

MIMICKING MINERAL NEOGENESIS FOR THE CLEAN SYNTHESIS OF METAL-ORGANIC MATERIALS FROM MINERAL FEEDSTOCKS: COORDINATION POLYMERS, MOFs AND METAL OXIDE SEPARATION

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1. EXPERIMENTAL DETAILS

Preparation of samples: in a typical reaction towards metal oxalate coordination polymer, a mixture of 0.163 g (2mmol) ZnO and 0.252 g (2mmol) H₂ox·2H₂O was gently ground manually (ca 30 seconds) using a mortar and pestle. In typical experiments towards 2-D or 3-D metal oxalate structures, a mixture of 0.379 g (2mmol) Znox·2H₂O and 0.164 g (1mmol) [pn][ox] or 0.208 g (1mmol) [pa]₂[ox] was gently ground manually using a mortar and pestle. Ground mixtures were then placed in open vials and aged at 45°C and 98%RH in a glass desiccator in which a constant humidity level was maintained by equilibrating the atmosphere with a saturated K₂SO₄ solution. The desiccator was placed in a large volume incubator set at 45 °C. The same procedure was repeated for reactions involving all other metal oxalates, typically using a 1:1 stoichiometric ratio of metal oxide to oxalic acid dehydrate for coordination polymer and a 2:1 stoichiometric ratio of metal oxalate dihydrate to organic ammonium oxalate salts for organic-ammonium templated 2-D or 3-D frameworks. In large scale reactions towards Znox·2H₂O and Niox·2H₂O, 4.88 g (60 mmol) ZnO or 4.48 g (60 mmol) NiO was mixed with 7.56 g (60 mmol) H₂ox·2H₂O and aged at 45°C 98%RH for 7 days.

In a typical milling activated reaction, 0.177 g (2.5mmol) MnO was ground at 30Hz for 5 minutes with a yield of 82% (2.05 mmol) due to the material loss in transfer. The ground oxide powder was then mixed with 0.258 g (2.05 mmol) H₂ox·2H₂O and the mixture aged at room temperature, 98%RH or at 45°C, 98%RH for up to 10 days.

For the solid state oxide separation experiment of ZnO and CuO, a mixture of 0.163 g (2mmol) ZnO, 0.159g (2 mmol) CuO and 0.252 g (2 mmol) H₂ox·2H₂O was gently ground manually using a mortar and pestle and then aged at 45°C 98%RH for 5 days.

Powder X-ray diffraction (PXRD): Room temperature PXRD patterns were collected in the 2θ range 3° to 60° on a Bruker D8 Discovery X-ray diffractometer using a Cu-K_α(λ=1.54 Å) source, equipped with a Vantech area detector and a nickel filter. The X-ray tube was operating at the power setting of 40 kV and 40 mA power. Data analysis was carried out using the Panalytical X'pert Highscore Plus program.

Fourier-transform infrared attenuated total reflection (FTIR-ATR) spectroscopy: Fourier transform infrared spectra were collected using a Perkin Elmer Fourier Transform-Infrared Attenuated Total Reflection spectrometer in the range 400 cm⁻¹ to 4000 cm⁻¹.

UV-Vis reflectance spectroscopy: UV-Vis reflection measurements were conducted on the Ocean Optics Jaz-Combo spectrometer using LS-1_Tungsten Halogen Light Source (360-2000nm), 0.4mm fiber

optic reflection R400-Angle-UV probe with RPH-1 reflection probe holder, and WS-1 PTFE diffuse reflection standard. The spectrums were collected in the range of 400-800nm using Spectrasuite software.

Thermogravimetric analysis (TGA): TGA measurements were conducted on a TA Instruments Q500 Thermogravimetric System with a Pt pan under dynamic atmosphere of N₂ or air with 40ml/min balance flow and 60ml/min purge flow. The upper temperature limit ranged from 500°C to 800°C depending on the sample, with a heating rate of 10°C/min.

Differential scanning calorimetry (DSC): DSC measurements were conducted on a TA Instruments Q2000 Differential Scanning Calorimeter with a standard aluminum pan of 40 µL. Nitrogen flow rate was set at 50ml/min and the upper temperature limit ranged from 105°C to 150°C depending on the sample, with a constant heating rate of 10°C/min.

Solid-state NMR spectroscopy: Solid-state NMR ¹³C studies of [pa]₂[Zn₂(ox)₃]·3H₂O were performed on a standard-bore Bruker Avance III spectrometer operating at 500.13 MHz using a Bruker 4 mm double-resonance probe under spinning at 5 kHz. Spectra were referenced using the chemical shift of the carbonyl carbon of glycine at 174.1 ppm with respect to TMS. Solid-state NMR ¹³C studies of [pn][Zn₂(ox)₃]·3H₂O were performed on a 400 MHz Varian VNMRS spectrometer operating at 100.52 MHz using a T3HX probe, 7.5mm zirconia rotor under spinning at 4.5 kHz. The spectrum was acquired in 1000 scans using cross-polarization for 1 ms and a recycle delay of 2 s.

Crystallographic data for [pa]₂[ox]: C₈H₂₀N₂O₄, M_r=208.26, Orthorhombic, a=11.0906(3) Å, b=14.6981(5) Å, c=7.6029(8) Å, α=90.00°, β=90.00°, γ=90.00°, V=1239.4(1) Å³, T=250(2) K, space group Pna2₁, Z=4, 6064 reflections measured, 1310 independent reflections (R_{int}=0.0352). The final R₁ value was 0.0807 (I > 2σ₁). The final wR₂ value was 0.2215 (I > 2σ₁). For all data, the final R₁ value was 0.11877 and final wR₂ was 0.2622.

2. SELECTED POWDER X-RAY DIFFRACTION PATTERNS

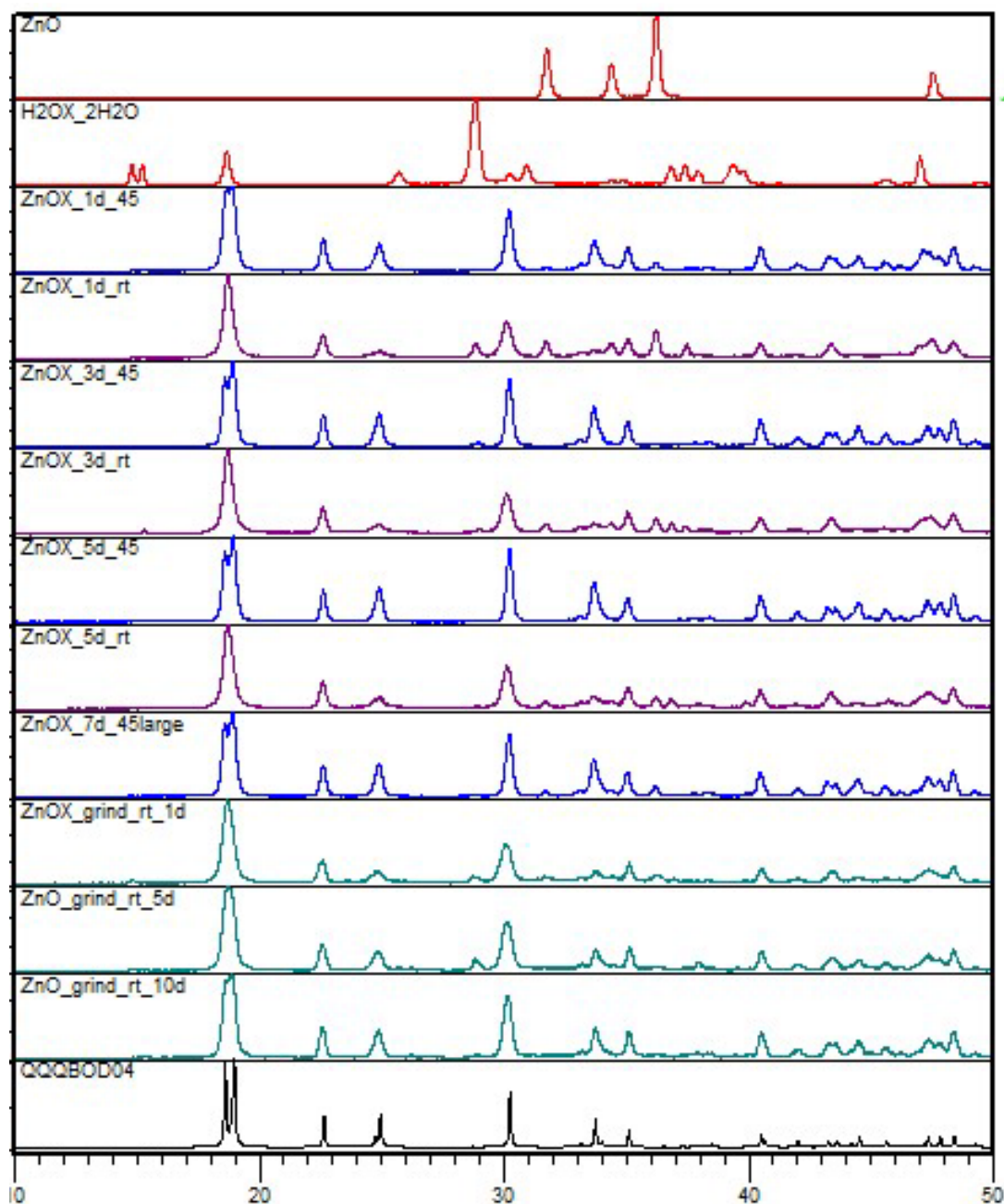


Figure S1. Comparison of PXRD patterns for the aging reactions of ZnO and oxalic acid dihydrate at 98% relative humidity and different conditions (top to bottom): commercial ZnO; oxalic acid dihydrate; manually prepared reaction mixture after 1 day at 45 °C; manually prepared reaction mixture after 1 day at room temperature; manually prepared reaction mixture after 3 days at 45 °C; manually prepared reaction mixture after 3 days at room temperature; manually prepared reaction mixture after 5 days at 45 °C; manually prepared reaction mixture after 5 days at room temperature; manually prepared reaction mixture after 7 days at 45 °C (10 gram scale) ;briefly milled reaction mixture after 1 day at room temperature; briefly milled reaction mixture after 5 days at room temperature and briefly milled reaction mixture after 1 day at room temperature. For comparison, the simulated pattern of $\text{ZnOx} \cdot 2\text{H}_2\text{O}$ (CCDC code QQQBOD04) is also given.

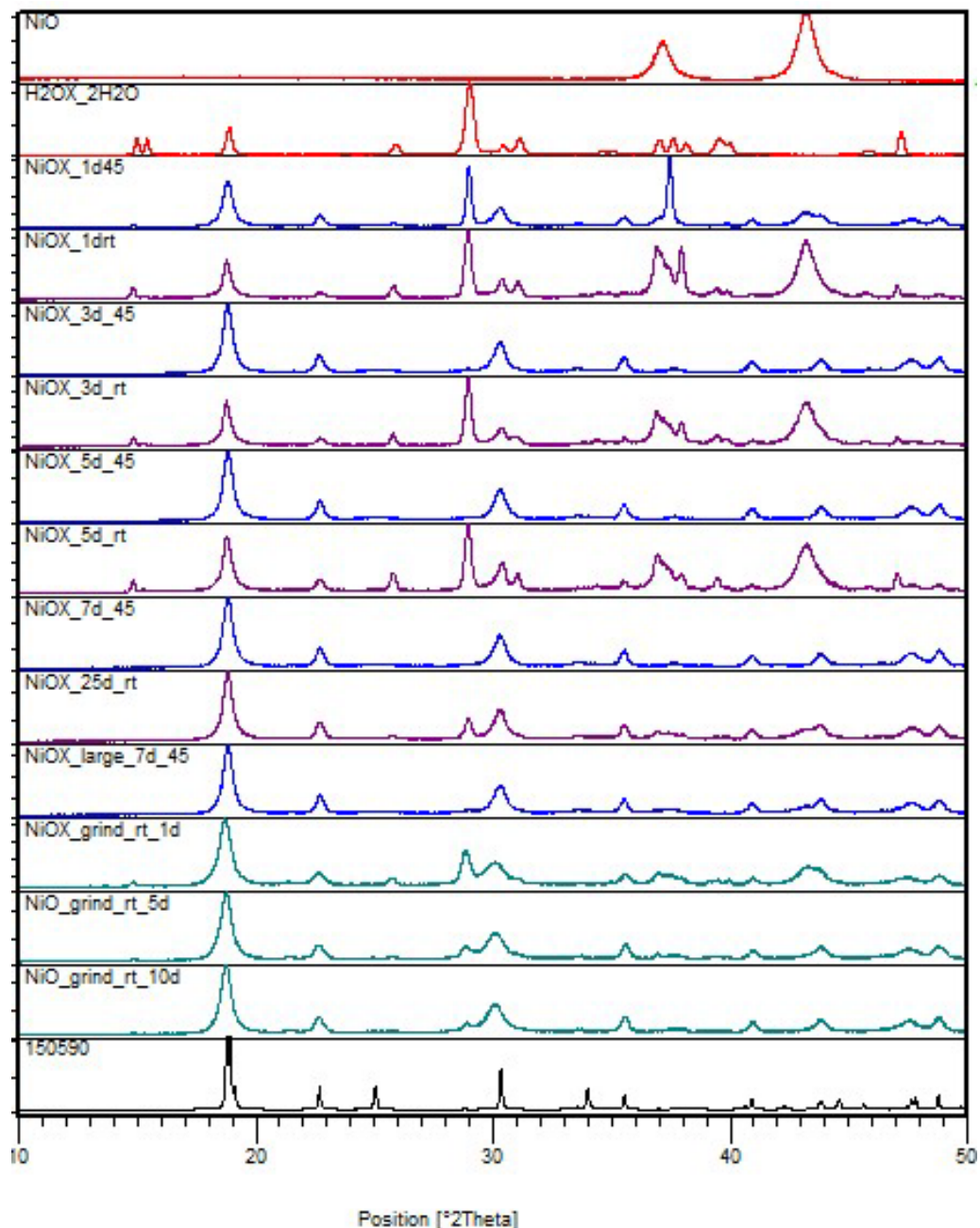


Figure S2. Comparison of PXRD patterns for the aging reactions of NiO and oxalic acid dihydrate at 98% relative humidity and different conditions (top to bottom): commercial NiO; oxalic acid dihydrate; manually prepared reaction mixture after 1 day at 45 °C; manually prepared reaction mixture after 1 day at room temperature; manually prepared reaction mixture after 3 days at 45 °C; manually prepared reaction mixture after 3 days at room temperature; manually prepared reaction mixture after 5 days at 45 °C; manually prepared reaction mixture after 5 days at room temperature; manually prepared reaction mixture after 7 days at 45 °C; manually prepared reaction mixture after 25 days at room temperature; manually prepared reaction mixture after 7 days at 45 °C (10 gram scale); briefly milled reaction mixture after 1 day at room temperature; briefly milled reaction mixture after 5 days at room temperature and briefly milled reaction mixture after 1 day at room temperature. For comparison, the simulated pattern of $\text{ZnOx} \cdot 2\text{H}_2\text{O}$ (ICSD code 150590) is also given.

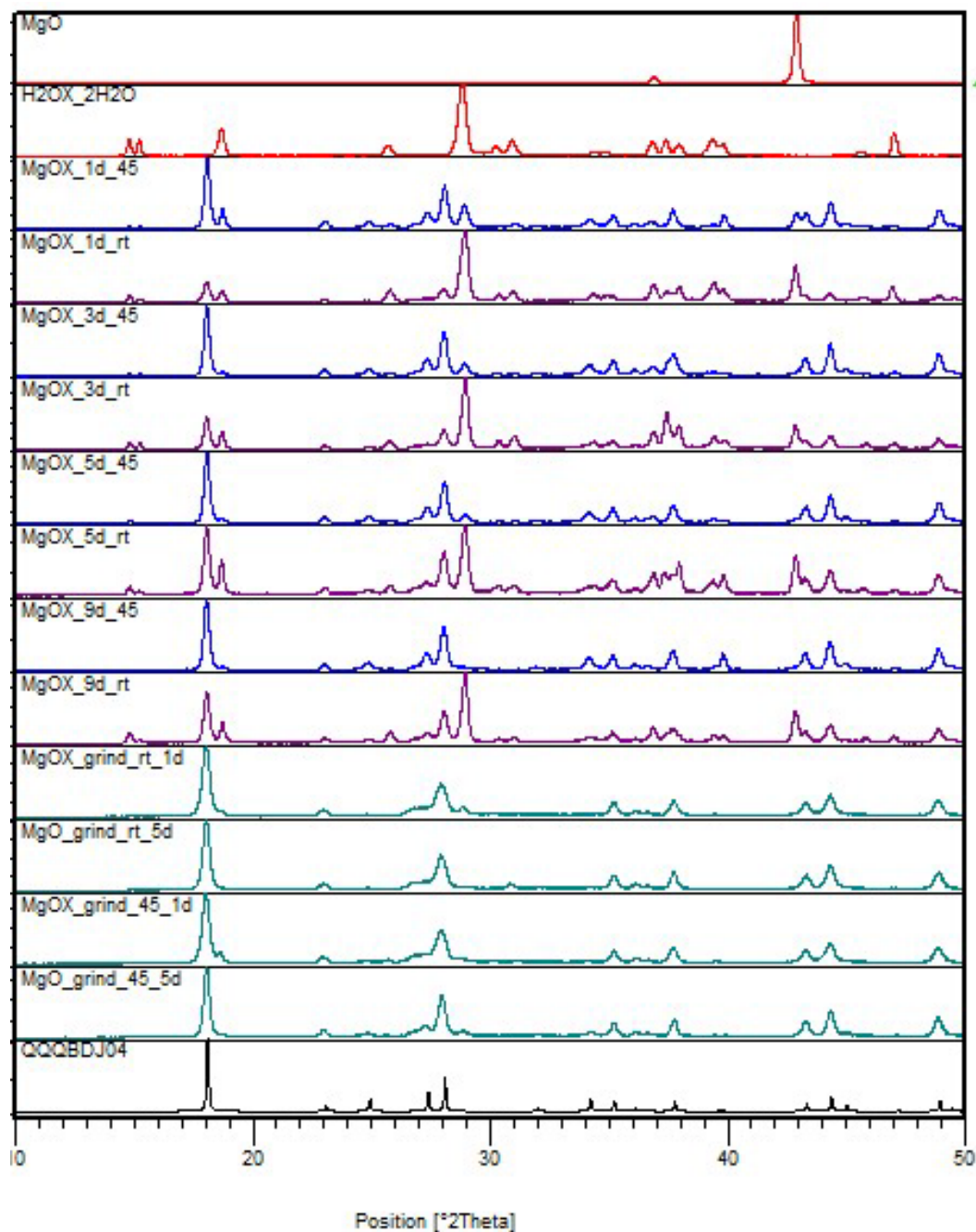


Figure S3. Comparison of PXRD patterns for the aging reactions of MgO and oxalic acid dihydrate at 98% relative humidity and different conditions (top to bottom): commercial MgO after calcination; oxalic acid dihydrate; manually prepared reaction mixture after 1 day at 45 °C; manually prepared reaction mixture after 1 day at room temperature; manually prepared reaction mixture after 3 days at 45 °C; manually prepared reaction mixture after 3 days at room temperature; manually prepared reaction mixture after 5 days at 45 °C; manually prepared reaction mixture after 5 days at room temperature; ; manually prepared reaction mixture after 9 days at 45 °C; manually prepared reaction mixture after 9 days at room temperature; briefly milled reaction mixture after 1 day at room temperature; briefly milled reaction mixture after 5 days at room temperature; briefly milled reaction mixture after 1 day at 45°C; briefly milled reaction mixture after 5 days at 45°C. For comparison, the simulated pattern of $\text{MgOx} \cdot 2\text{H}_2\text{O}$ (CCDC code QQQBDJ04) is also given.

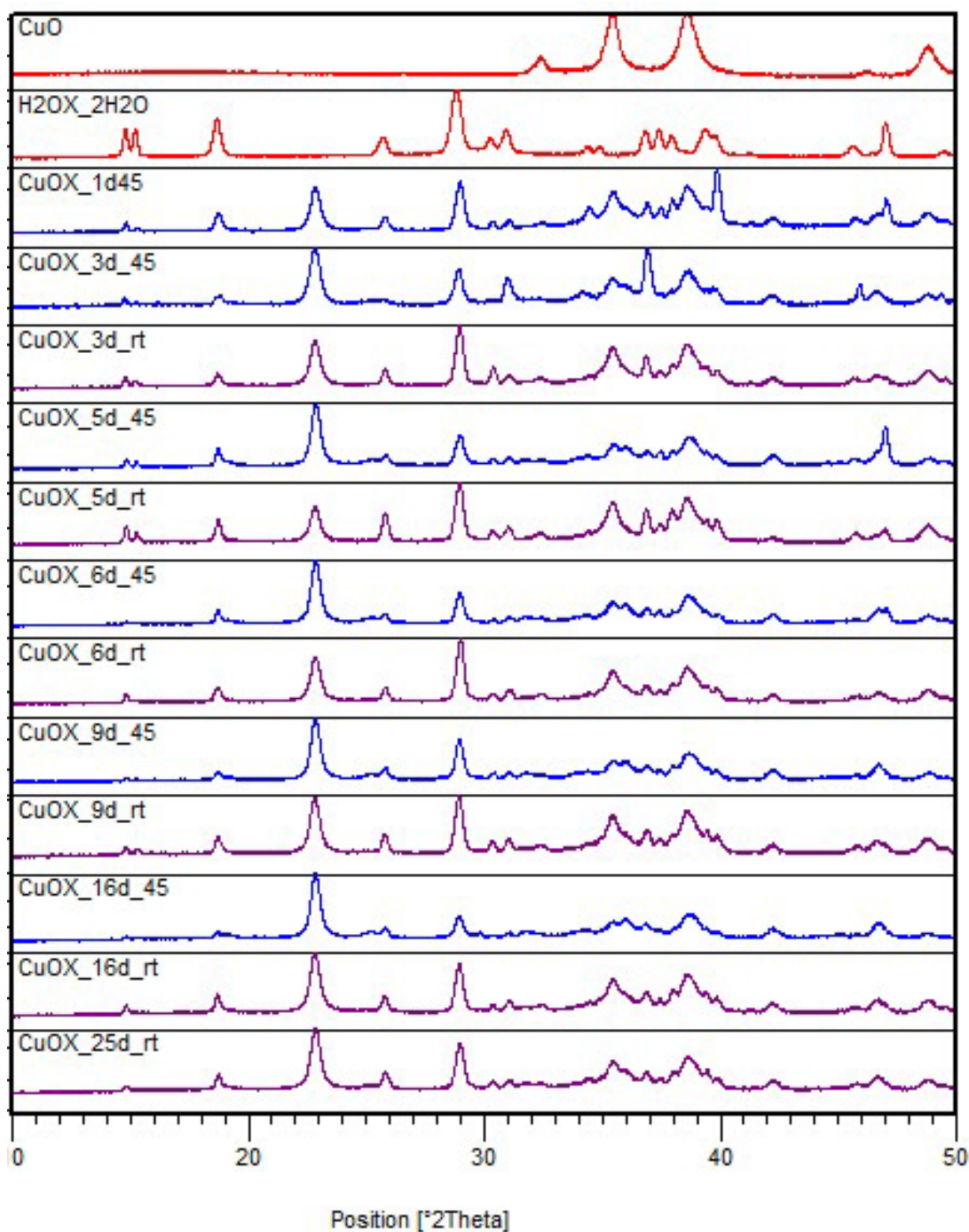


Figure S4. Comparison of PXRD patterns for the aging reaction of a manually prepared mixture of CuO and oxalic acid dihydrate at 98% relative humidity and different temperature conditions (top to bottom): commercial CuO; oxalic acid dihydrate; reaction mixture after 1 day at 45 °C; 3 days at 45 °C; 3 days at room temperature; ; 5 days at 45 °C; 5 days at room temperature; ; 6 days at 45 °C; 6 days at room temperature; ; 9 days at 45 °C; 9 days at room temperature; ; 16 days at 45 °C; 16 days at room temperature and 25 days at room temperature.

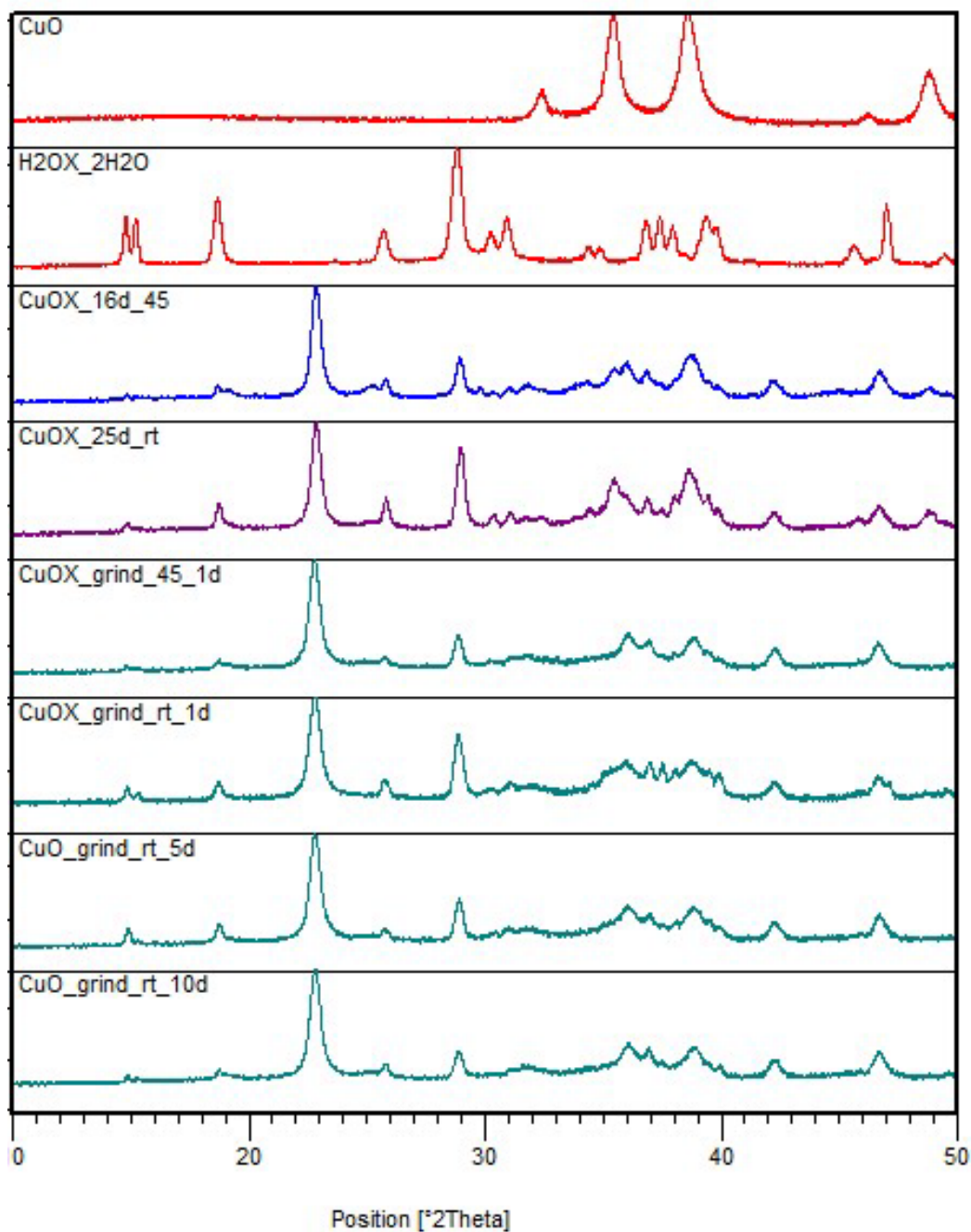


Figure S5. Comparison of PXRD patterns for the aging reaction of a briefly milled mixture of CuO and oxalic acid dihydrate at 98% relative humidity (top to bottom): commercial CuO; oxalic acid dihydrate; manually prepared mixture after 16 days at 45 °C; manually prepared mixture after 25 days at room temperature; milled mixture after 1 day at 45°C; milled mixture after 1 day at room temperature; milled mixture after 5 days at room temperature and milled mixture after 10 days at room temperature.

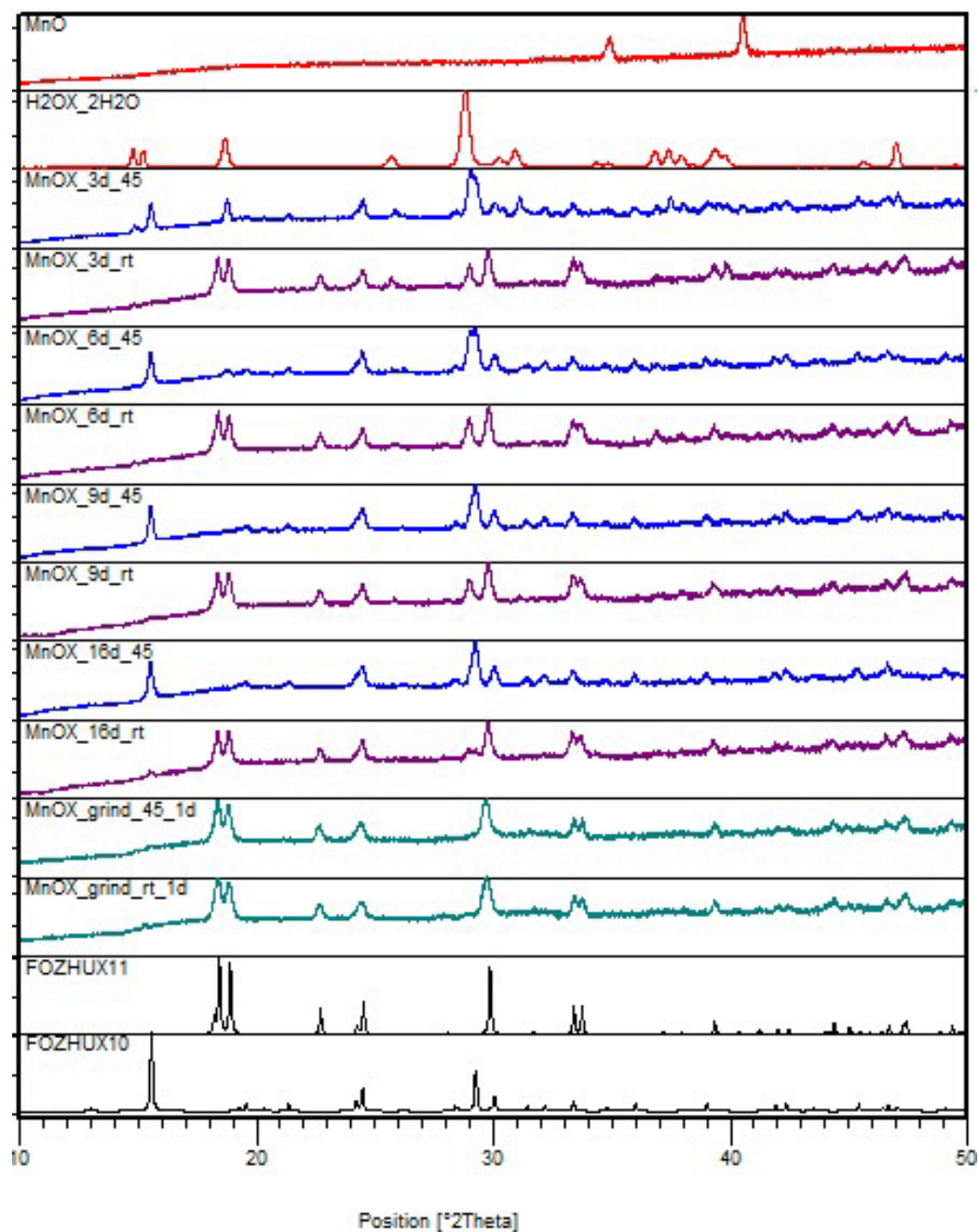


Figure S6. Comparison of PXRD patterns for the aging reactions of MnO and oxalic acid dihydrate at 98% relative humidity and different conditions (top to bottom): commercial MnO; oxalic acid dihydrate; manually prepared reaction mixture after 3 days at 45 °C; manually prepared reaction mixture after 3 days at room temperature; manually prepared reaction mixture after 6 days at 45 °C; manually prepared reaction mixture after 6 days at room temperature; manually prepared reaction mixture after 9 days at 45 °C; manually prepared reaction mixture after 9 days at room temperature; manually prepared reaction mixture after 16 days at 45 °C; manually prepared reaction mixture after 16 days at room temperature; reaction mixture involving pre-milled MnO after 1 day at 45 °C; reaction mixture involving pre-milled MnO after 1 day at room temperature. For comparison, the simulated patterns of metastable α -polymorph of $\text{MnOx} \cdot 2\text{H}_2\text{O}$ (CCDC code FOZHUX11) and the stable γ -form of $\text{MnOx} \cdot 2\text{H}_2\text{O}$ (CCDC code FOZHUX10) are also given.

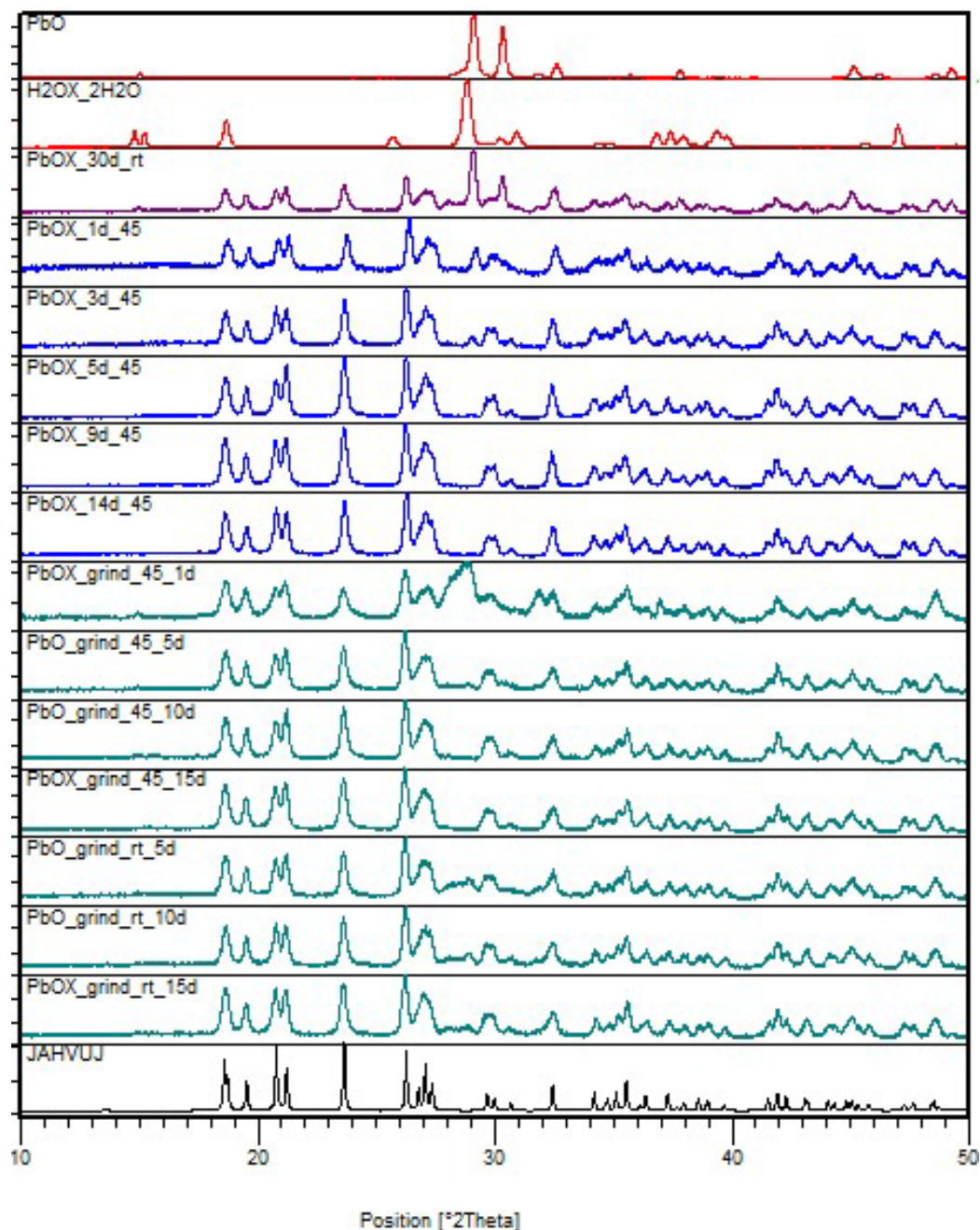


Figure S7. Comparison of PXRD patterns for the aging reactions of PbO and oxalic acid dihydrate at 98% relative humidity and different conditions (top to bottom): commercial PbO; oxalic acid dihydrate; manually prepared reaction mixture after 30 days at room temperature; manually prepared reaction mixture after 1 day at 45 °C; manually prepared reaction mixture after 3 days at 45 °C; manually prepared reaction mixture after 5 days at 45 °C; manually prepared reaction mixture after 9 days at 45 °C; manually prepared reaction mixture after 14 days at 45 °C; briefly milled reaction mixture after 1 day at 45 °C; briefly milled reaction mixture after 5 days at 45 °C; briefly milled reaction mixture after 10 days at 45 °C; briefly milled reaction mixture after 15 days at 45 °C; briefly milled reaction mixture after 5 days at room temperature; briefly milled reaction mixture after 10 days at room temperature; briefly milled reaction mixture after 15 days at room temperature; For comparison, the simulated pattern of PbOx (CCDC code JAHVUJ) is also given.

3. SELECTED FTIR-ATR SPECTRA

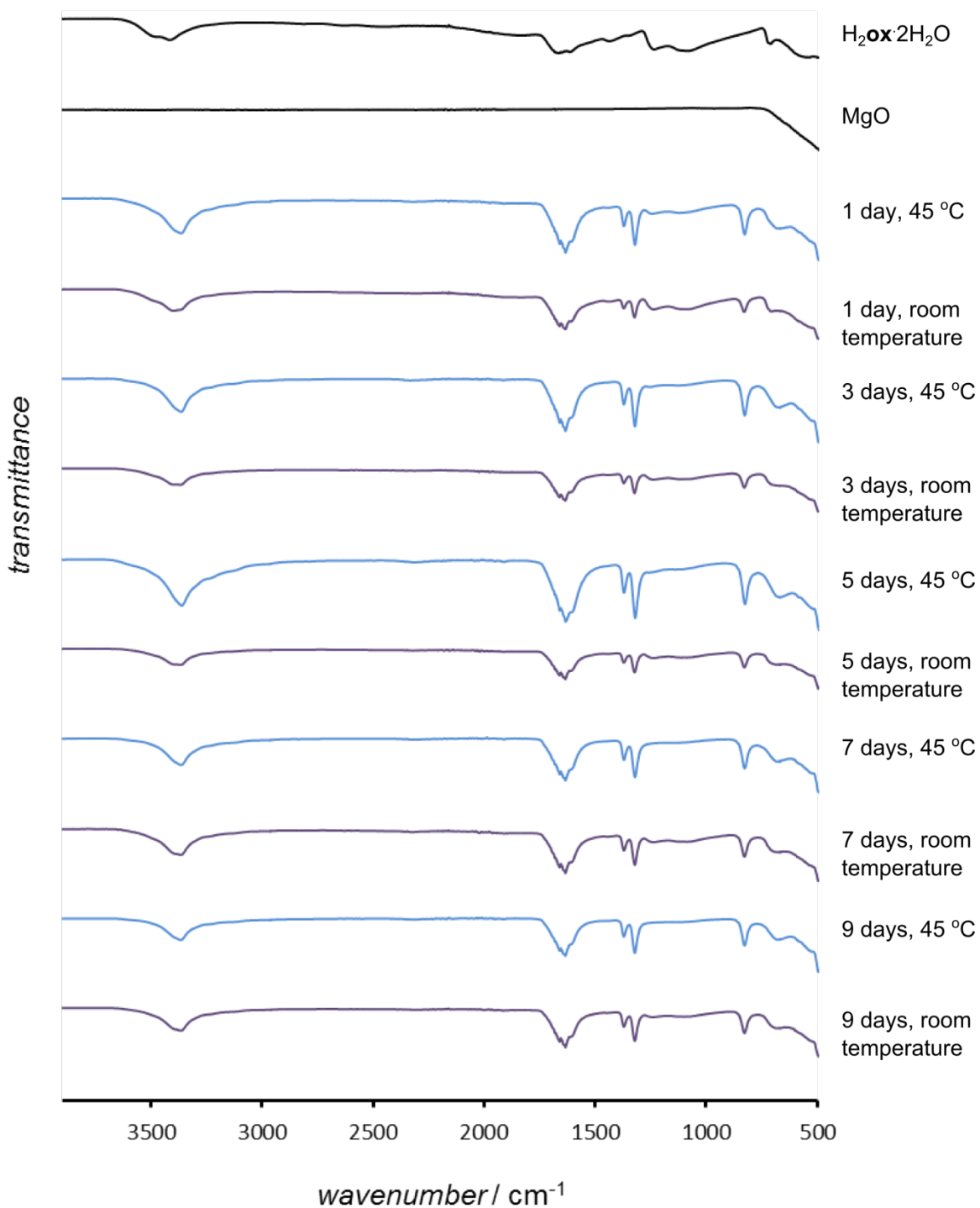


Figure S8. Overlay of FTIR-ATR spectra for the reaction mixtures involving calcinated MgO and oxalic acid dihydrate.

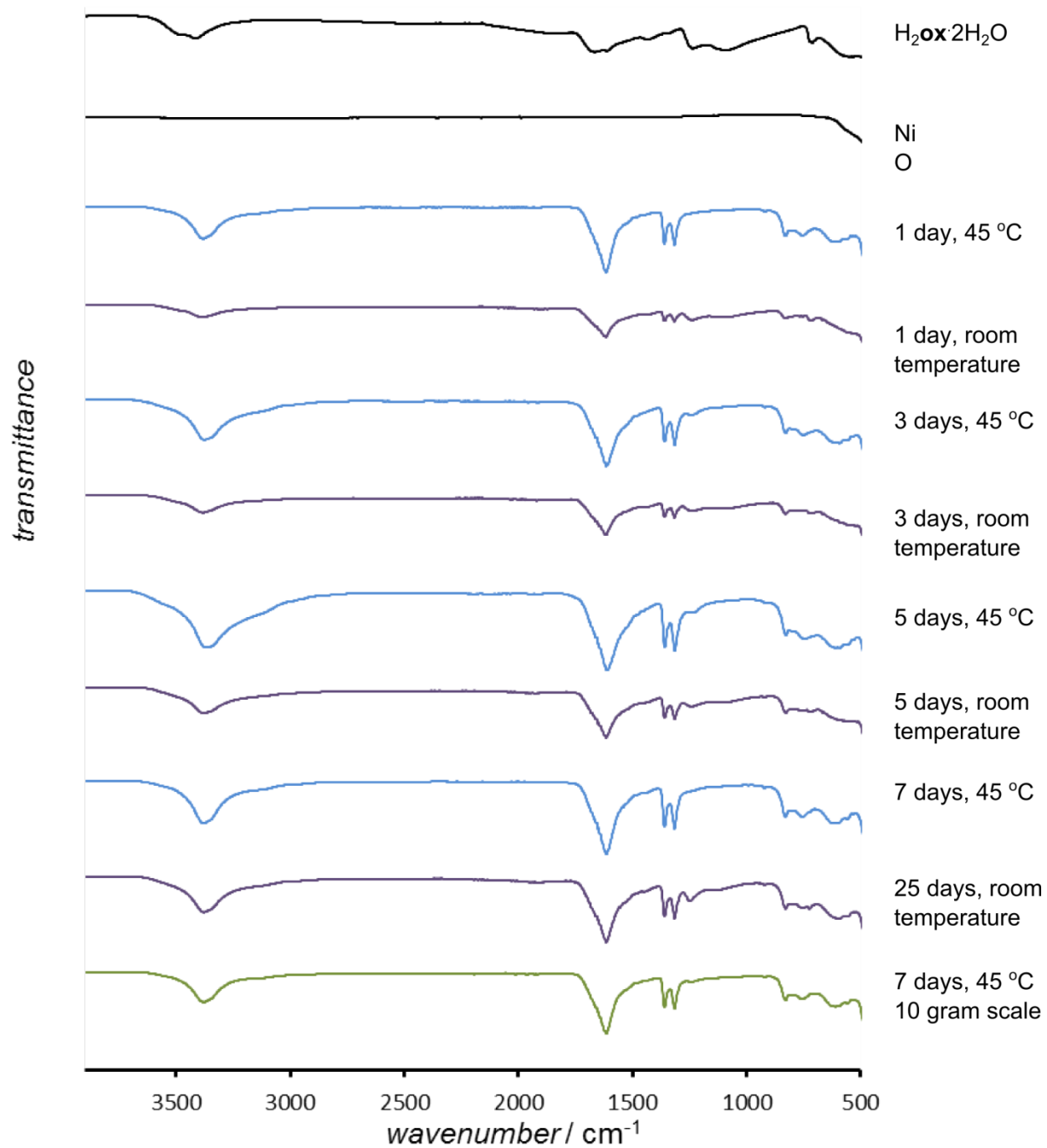


Figure S9. Overlay of FTIR-ATR spectra for the reaction mixtures involving NiO and oxalic acid dihydrate.

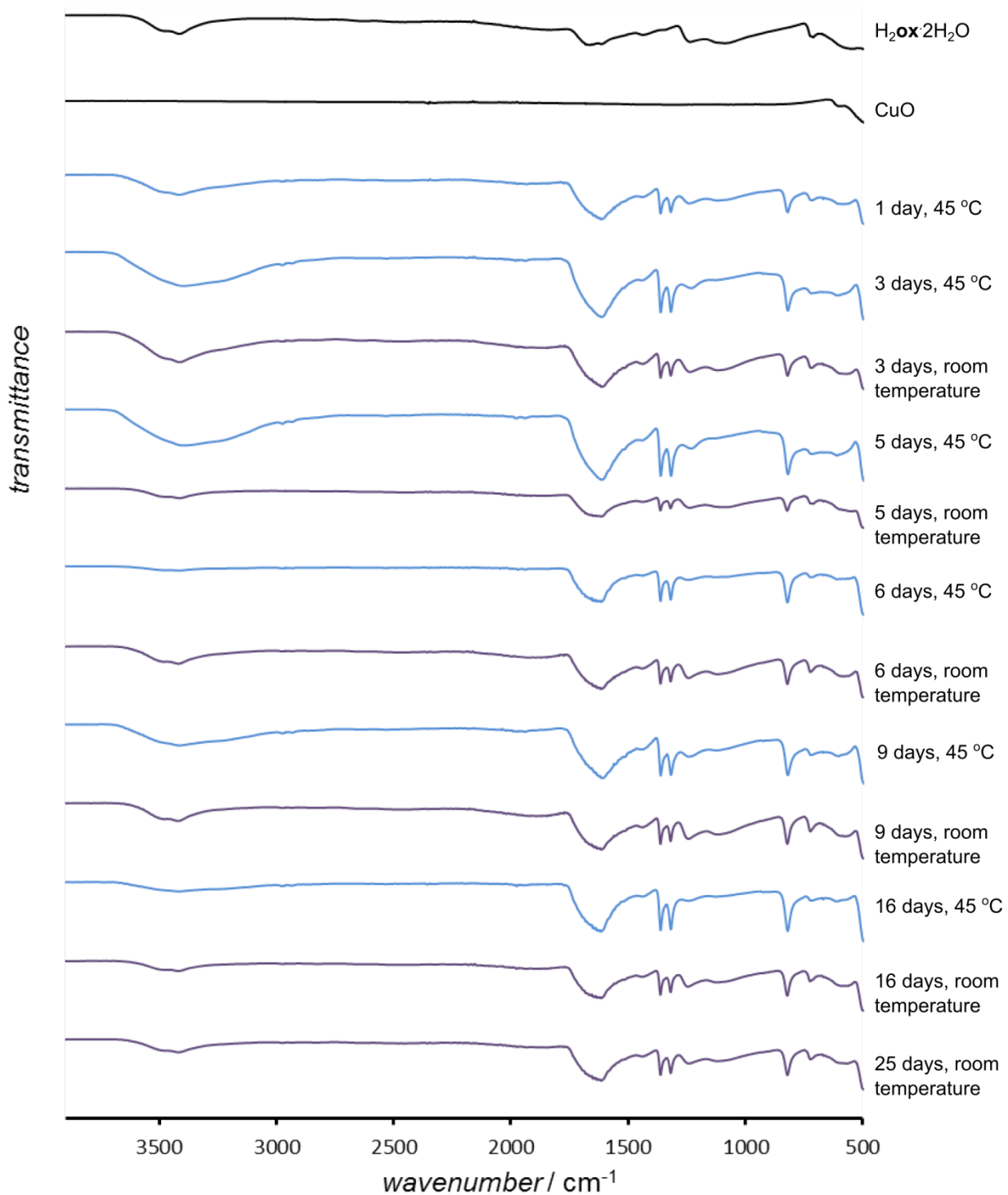


Figure S10. Overlay of FTIR-ATR spectra for the reaction mixtures involving CuO and oxalic acid dihydrate.

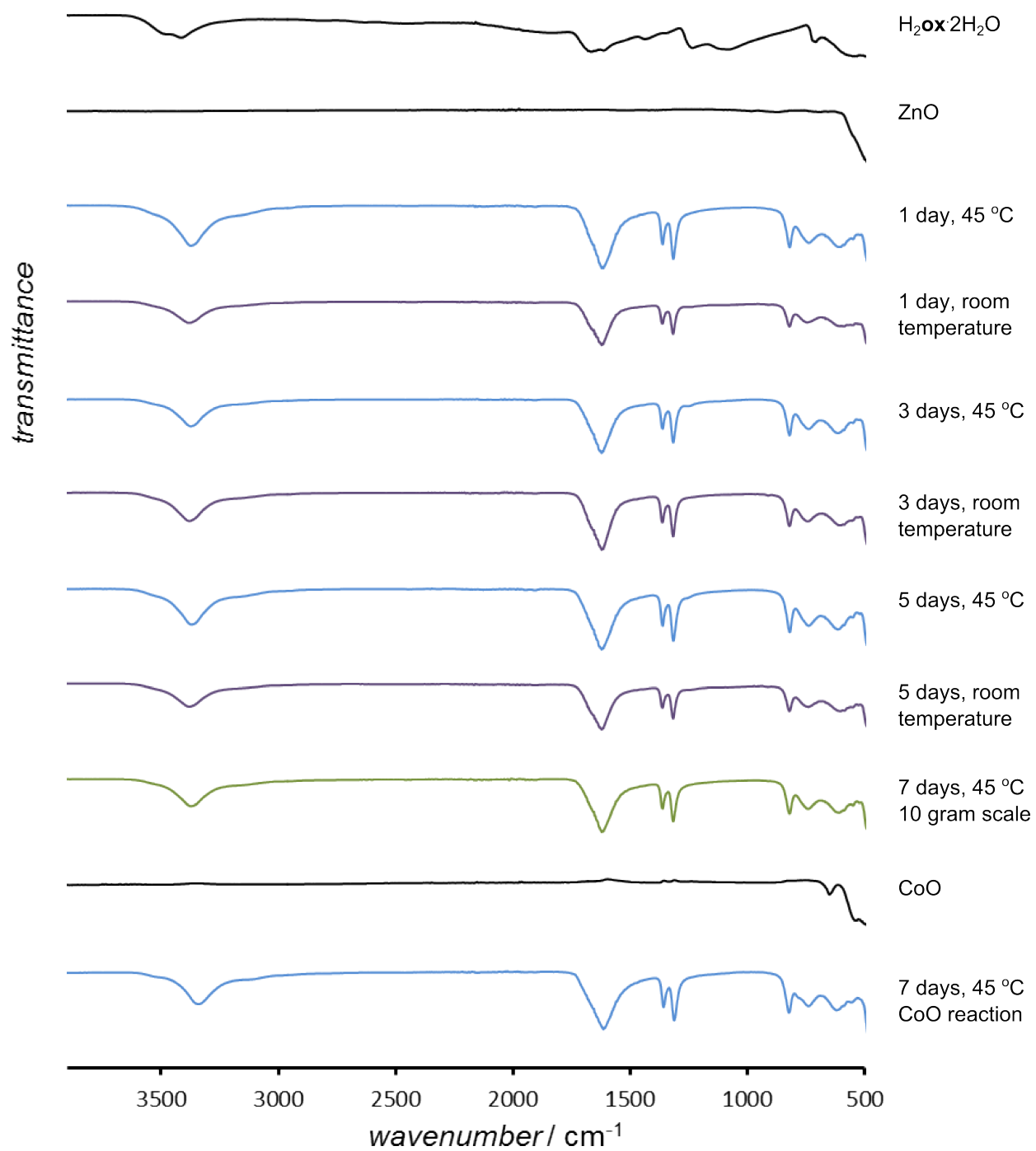


Figure S11. Overlay of selected FTIR-ATR spectra for the reaction mixtures involving ZnO and oxalic acid dihydrate, as well as CoO and oxalic acid dihydrate.

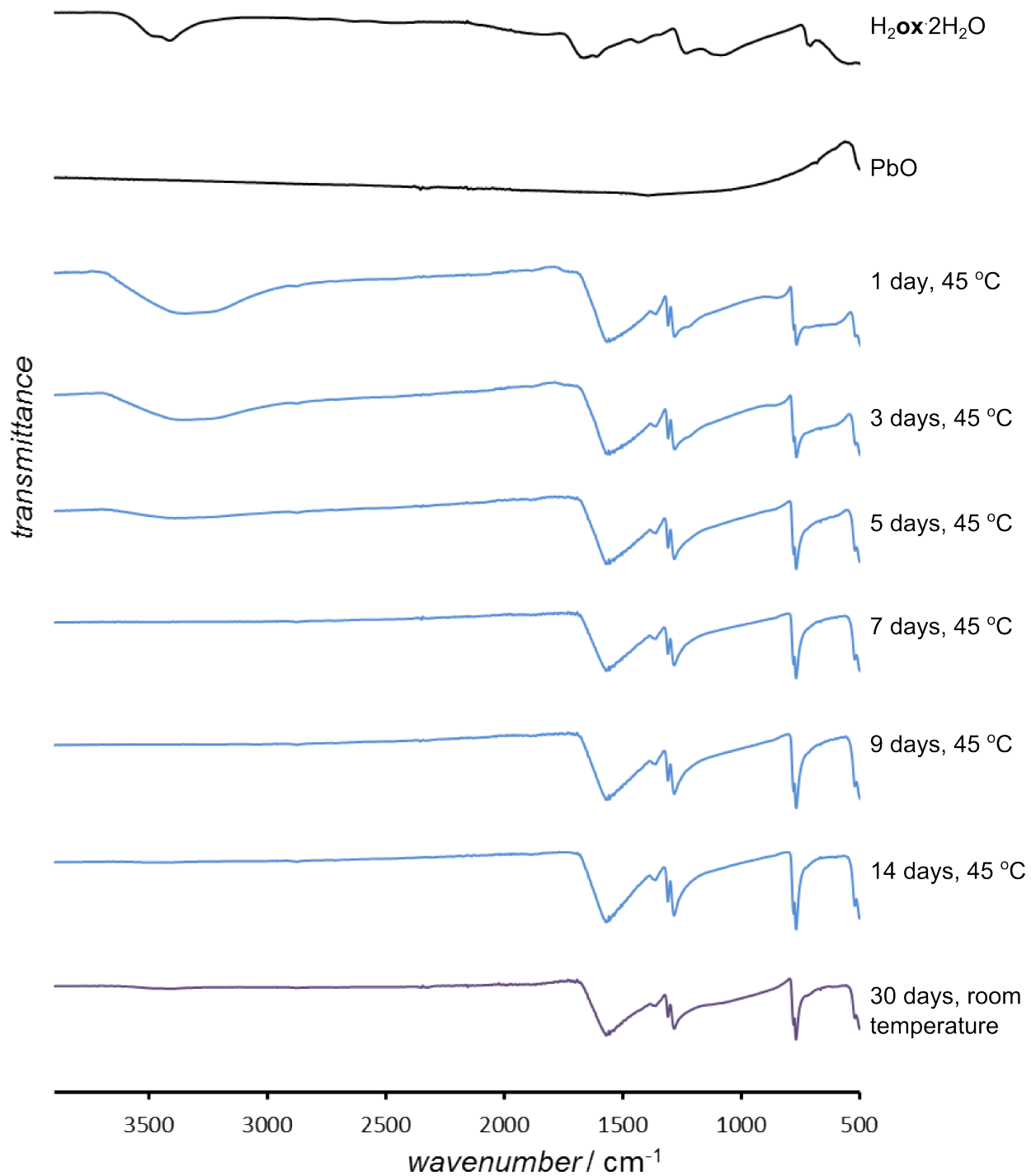


Figure S12. Overlay of selected FTIR-ATR spectra for the reaction mixtures involving PbO and oxalic acid dihydrate.

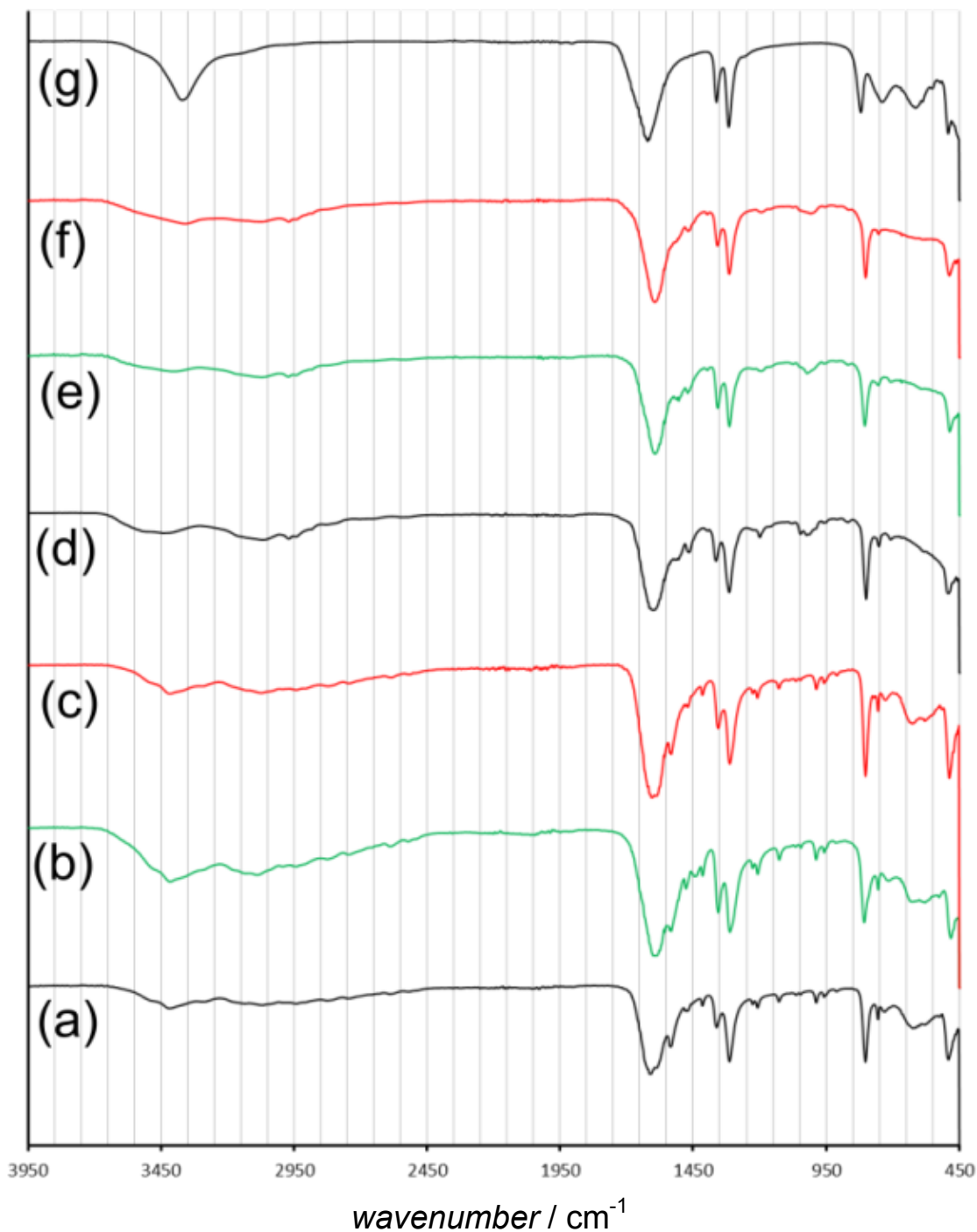


Figure S13. FTIR-ATR spectra for the products of templated aging reactions of $(\text{pn})(\text{ox})$ with $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}$ and: (a) ZnO; (b) NiO; (c) CoO and of $(\text{pa})_2(\text{ox})$ with $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}$ and: (d) ZnO; (e) NiO; (f) CoO. Reference FTIR-ATR spectrum of $\text{ZnOx}\cdot 2\text{H}_2\text{O}$ is given under (g). The difference between $\text{ZnOx}\cdot 2\text{H}_2\text{O}$, $[\text{pn}][\text{Zn}_2(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ and $[\text{pa}]_2[\text{Zn}_2(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ is evident from the appearance of new features in the spectra of the 2- and 3-D MOFs, by the broadening of the O-H stretching band at 3350 cm^{-1} , and by the fine shift of 1604 cm^{-1} and 816 cm^{-1} bands of $\text{ZnOx}\cdot 2\text{H}_2\text{O}$ to ca. 1580 cm^{-1} and 816 cm^{-1} in the 2-D and 3-D MOFs, respectively.

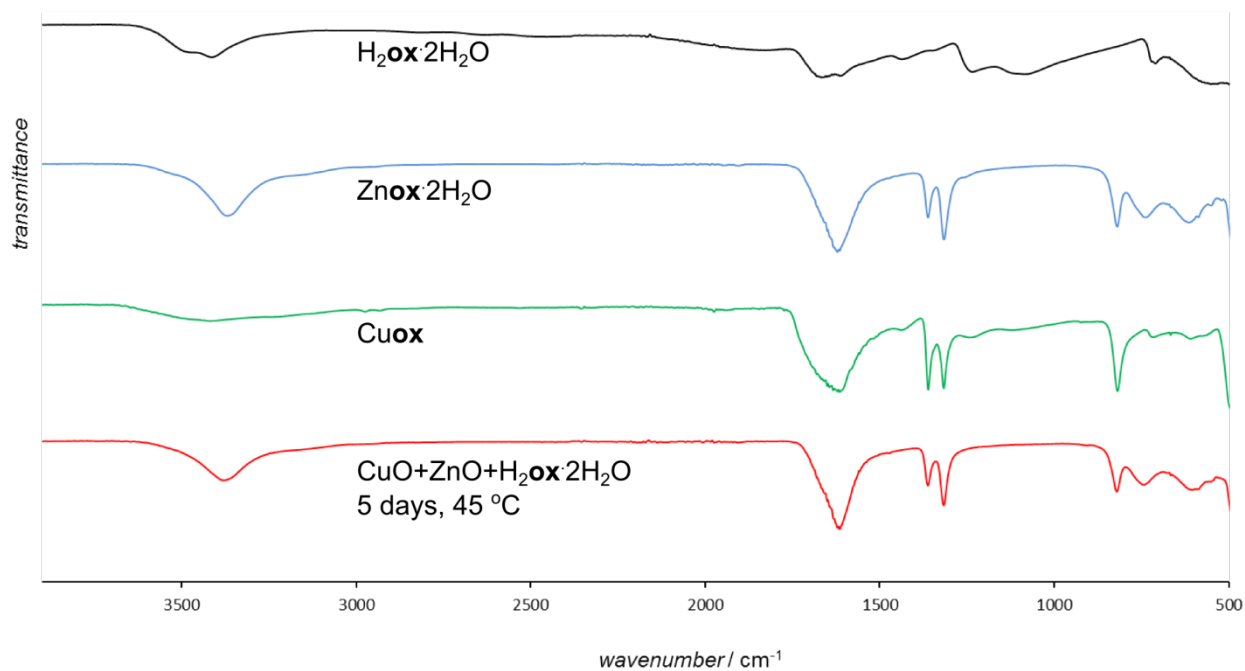


Figure S14. Overlay of selected FTIR-ATR spectra for (top to bottom): H₂Ox·2H₂O (black); ZnOx·2H₂O (blue); copper(II) oxalate (green) and the 1:1:1 mixture of CuO, ZnO and H₂Ox·2H₂O after aging for 5 days at 45 °C and 98% RH (red).

4. RESULTS OF THERMOGRAVIMETRIC ANALYSIS

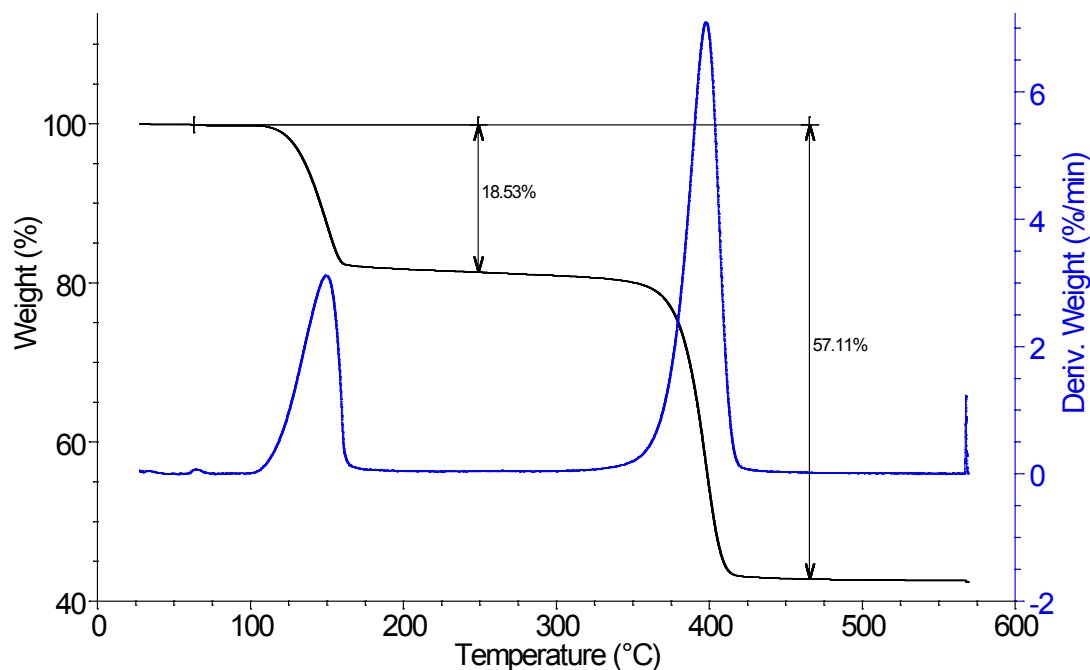


Figure S15. Thermogram of ZnOx·2H₂O obtained by aging of ZnO and H₂ox·2H₂O at 45 °C and 98% RH. Calculated ZnO residue: 43.0% ; calculated water loss: 19.0%.

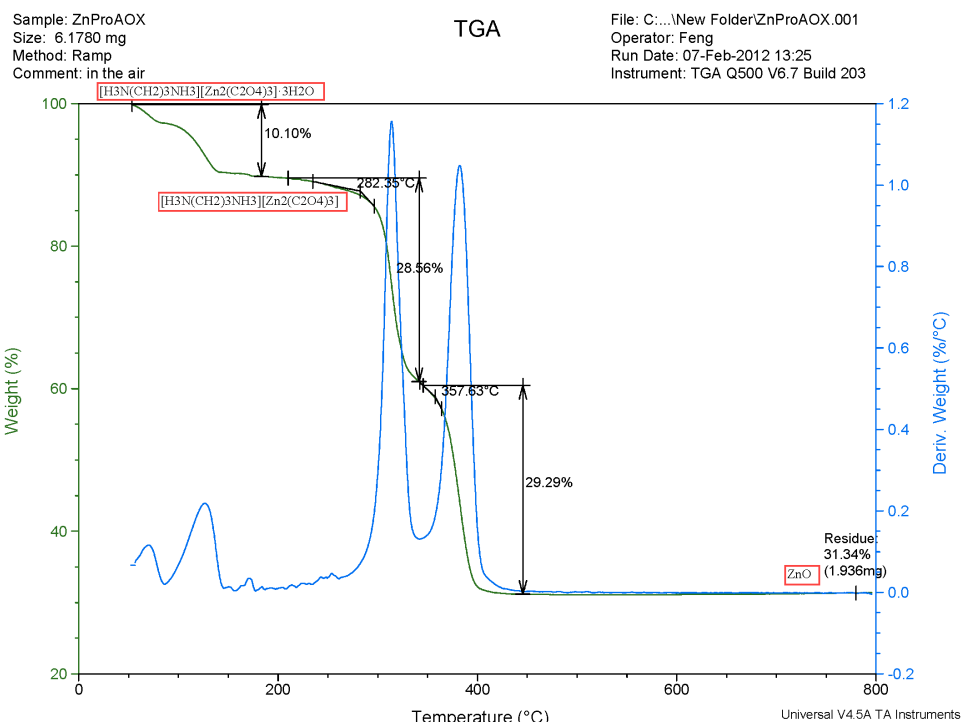


Figure S16. Thermogram of [pn][Zn₂(ox)₃]·3H₂O obtained by aging of ZnO and H₂ox·2H₂O at 45 °C and 98% RH. Calculated ZnO residue: 31.0% ; calculated water loss: 10.3%.

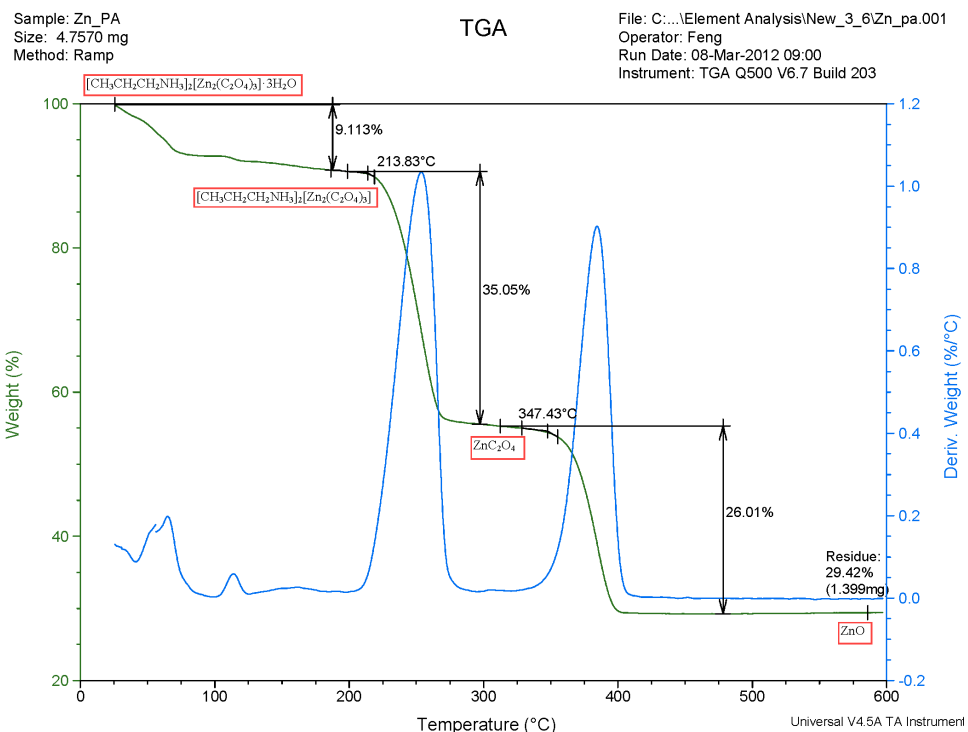


Figure S17. Thermogram of $[\text{pa}]_2[\text{Zn}_2(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ obtained by aging of ZnO and $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}$ at 45 °C and 98% RH. Calculated ZnO residue: 28.6% ; calculated water loss: 9.5%.

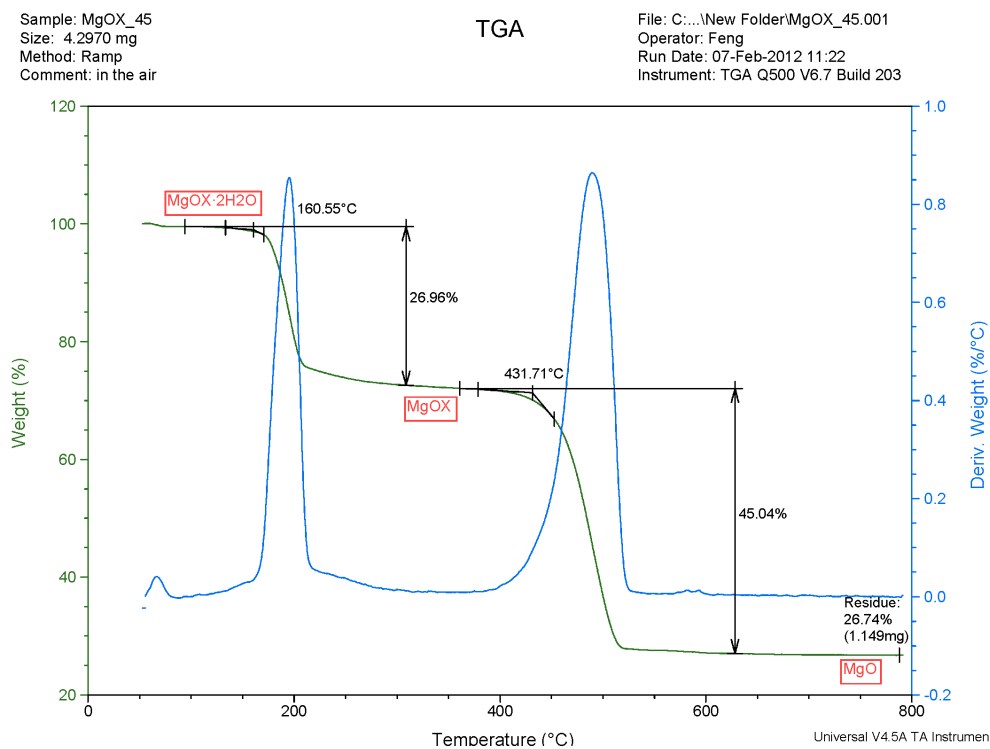


Figure S18. Thermogram of $\text{Mgox}\cdot 2\text{H}_2\text{O}$ obtained by aging of MgO and $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}$ at 45 °C and 98% RH. Calculated MgO residue: 27.1% ; calculated water loss: 24.3%.

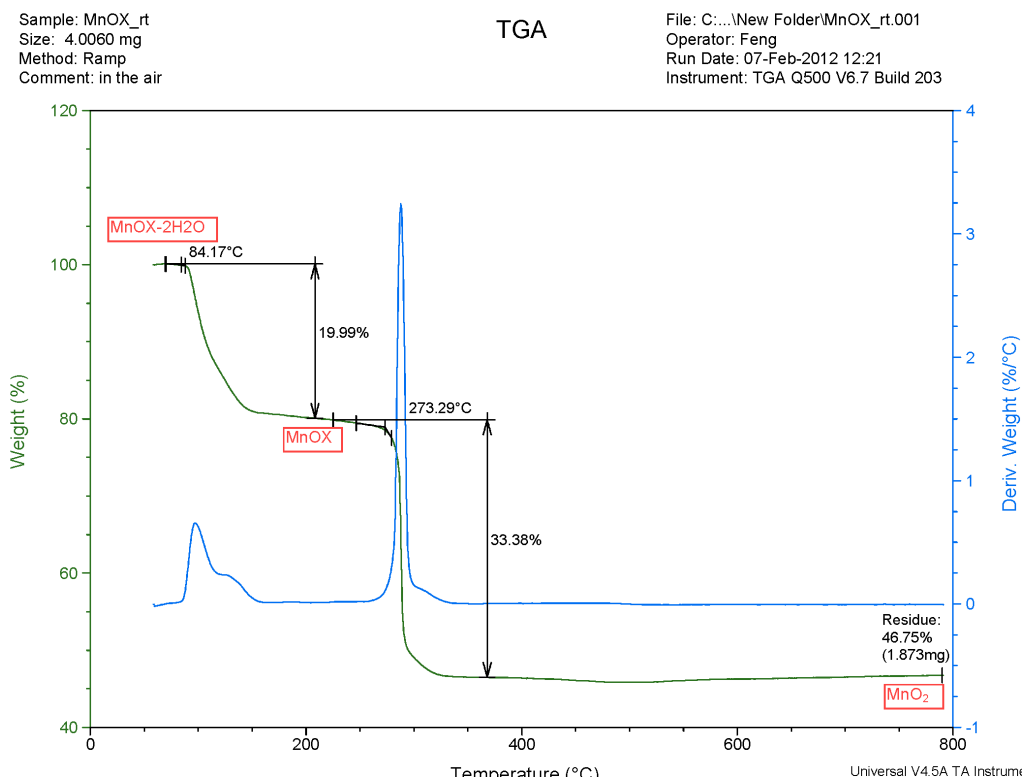


Figure S19. Thermogram of Mn_{ox}-2H₂O obtained by aging of MnO and H₂O_x-2H₂O at room temperature and 98% RH. Calculated MnO₂ residue: 48.6% ; calculated water loss: 20.1%.

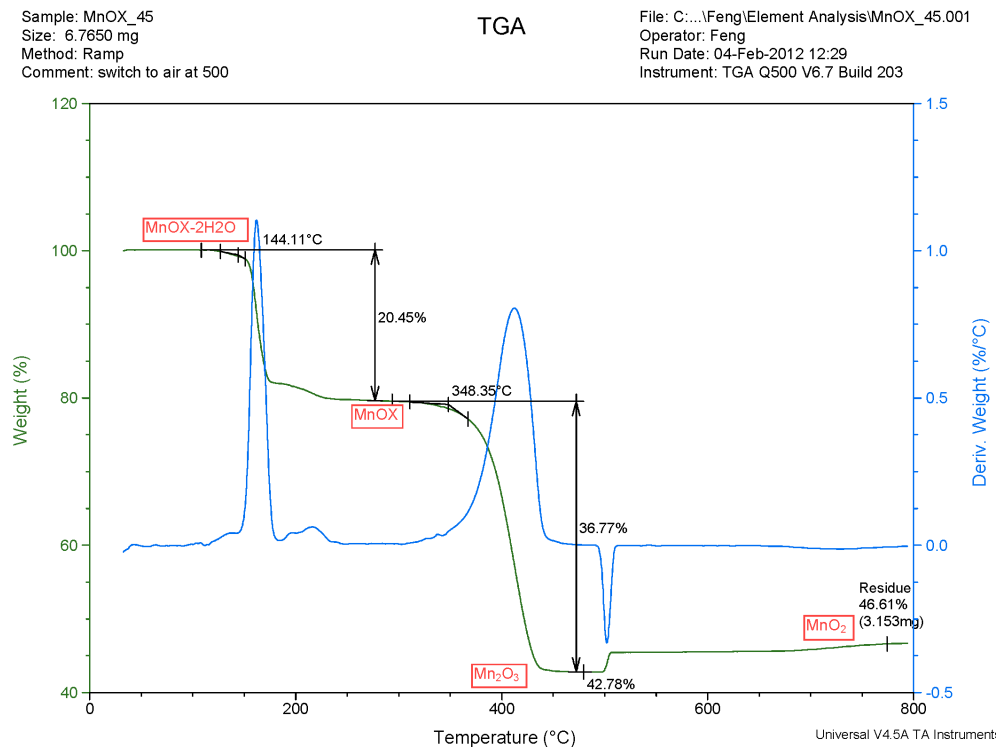


Figure S20. Thermogram of Mn_{ox}-2H₂O obtained by aging of MnO and H₂O_x-2H₂O at 45°C and 98% RH. Calculated MnO₂ residue: 48.6% ; calculated water loss: 20.1%.

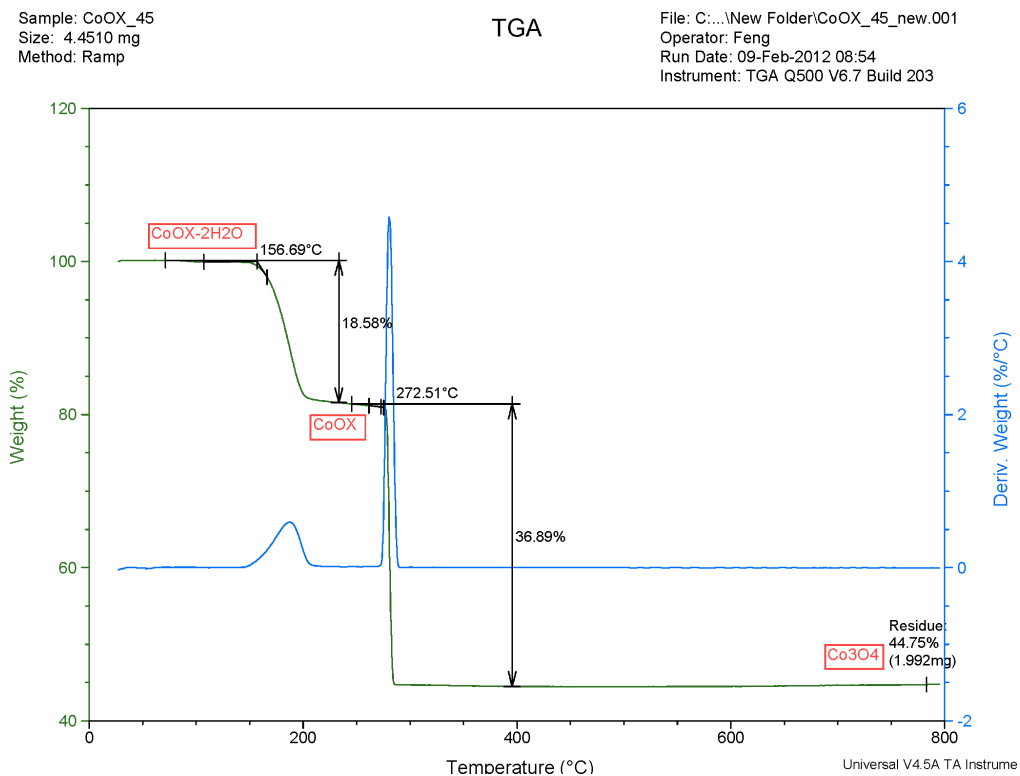


Figure S21. Thermogram of Coox·2H₂O obtained by aging of CoO and H₂ox·2H₂O at 45°C and 98% RH. Calculated Co₃O₄ residue: 43.9% ; calculated water loss: 19.7%.

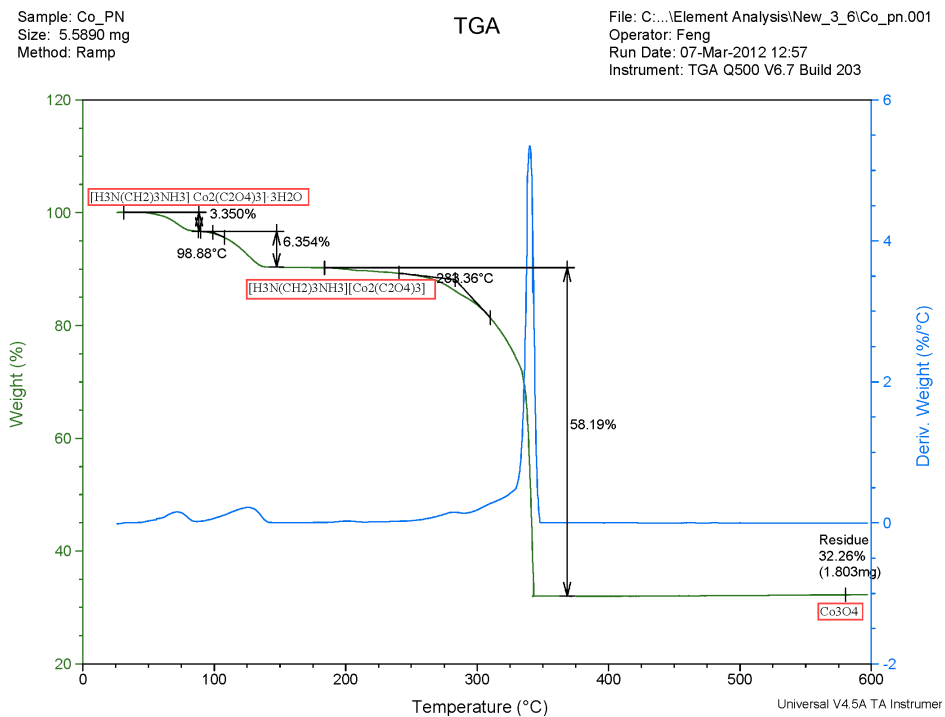


Figure S22. Thermogram of [pn][Co₂(ox)₃]·3H₂O obtained by aging of CoO and H₂ox·2H₂O at 45 °C and 98% RH. Calculated Co₃O₄ residue: 31.4% ; calculated water loss: 10.5%.

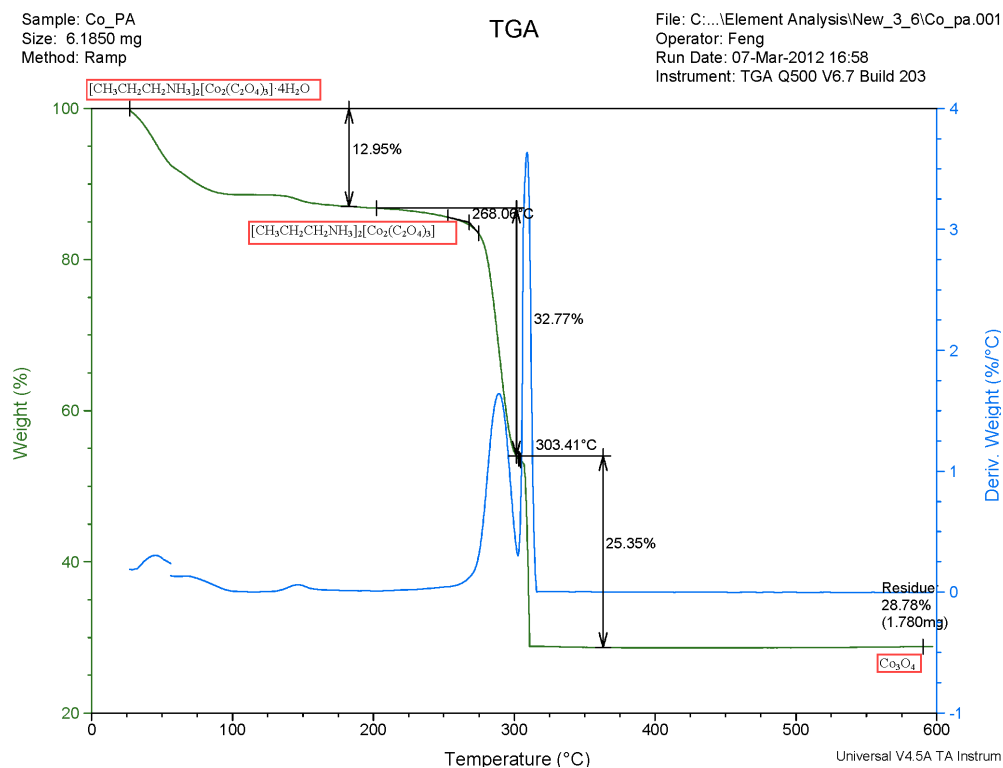


Figure S23. Thermogram of $[\text{pa}]_2[\text{Co}_2(\text{ox})_3] \cdot 4\text{H}_2\text{O}$ obtained by aging of CoO and $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ at 45 °C and 98% RH. Calculated Co_3O_4 residue: 28.0% ; calculated water loss: 12.5%.

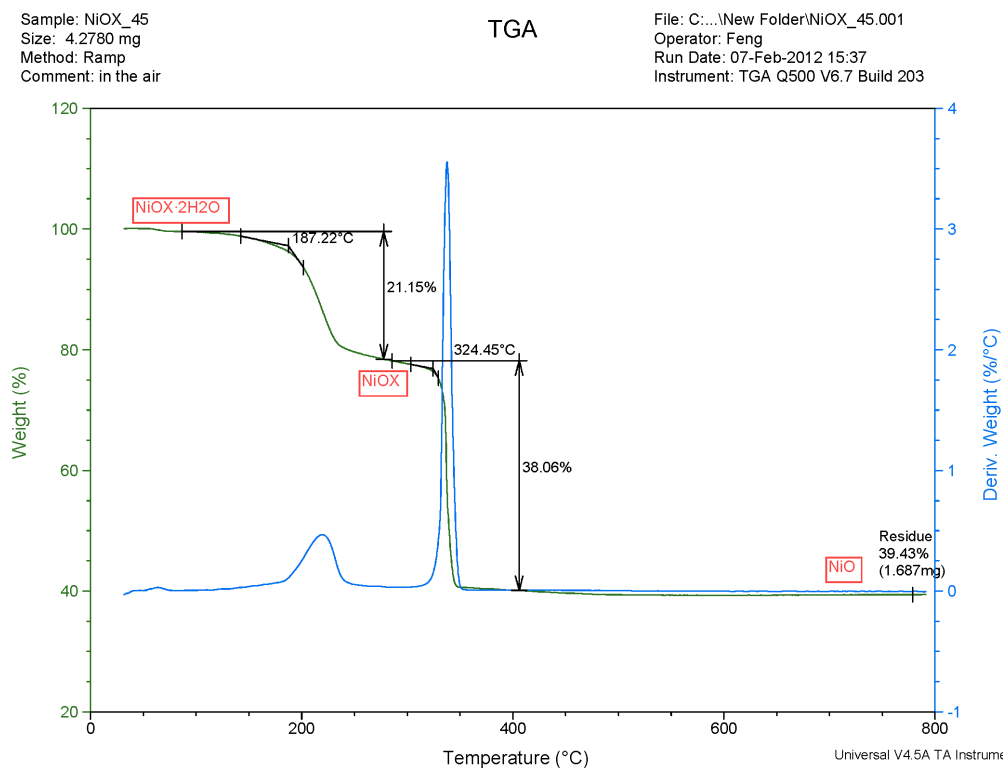


Figure S24. Thermogram of $\text{NiOX} \cdot 2\text{H}_2\text{O}$ obtained by aging of NiO and $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ at 45 °C and 98% RH. Calculated NiO residue: 40.9% ; calculated water loss: 19.8%.

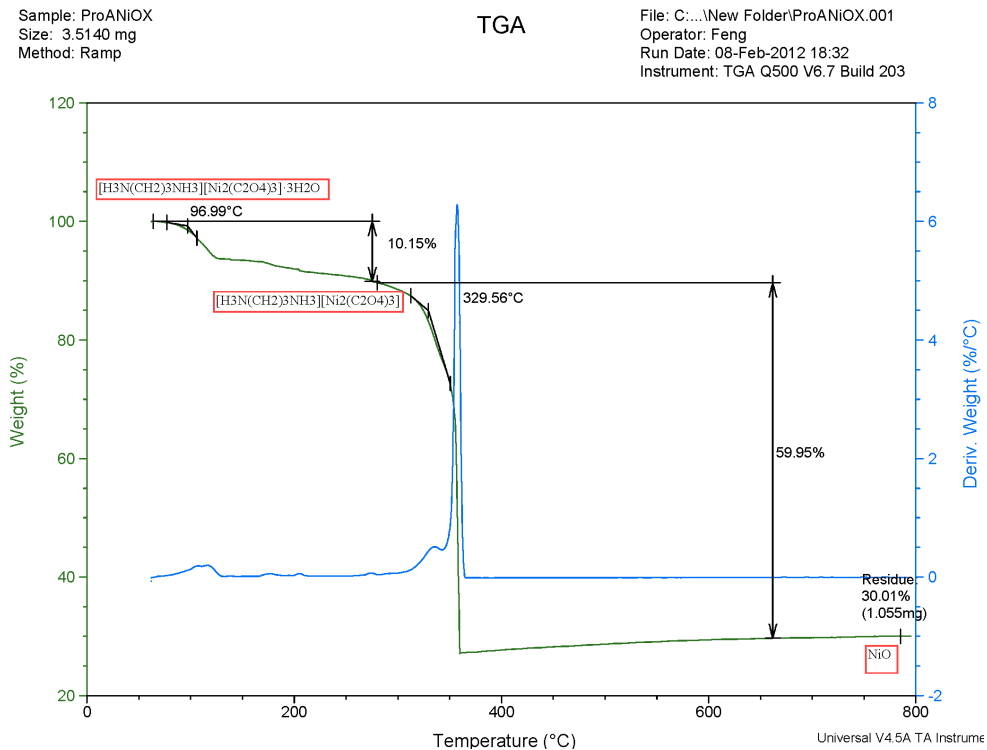


Figure S25. Thermogram of $[\text{pn}][\text{Ni}_2(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ obtained by aging of NiO and $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ at 45 °C and 98% RH. Calculated NiO residue: 29.2% ; calculated water loss: 10.6%.

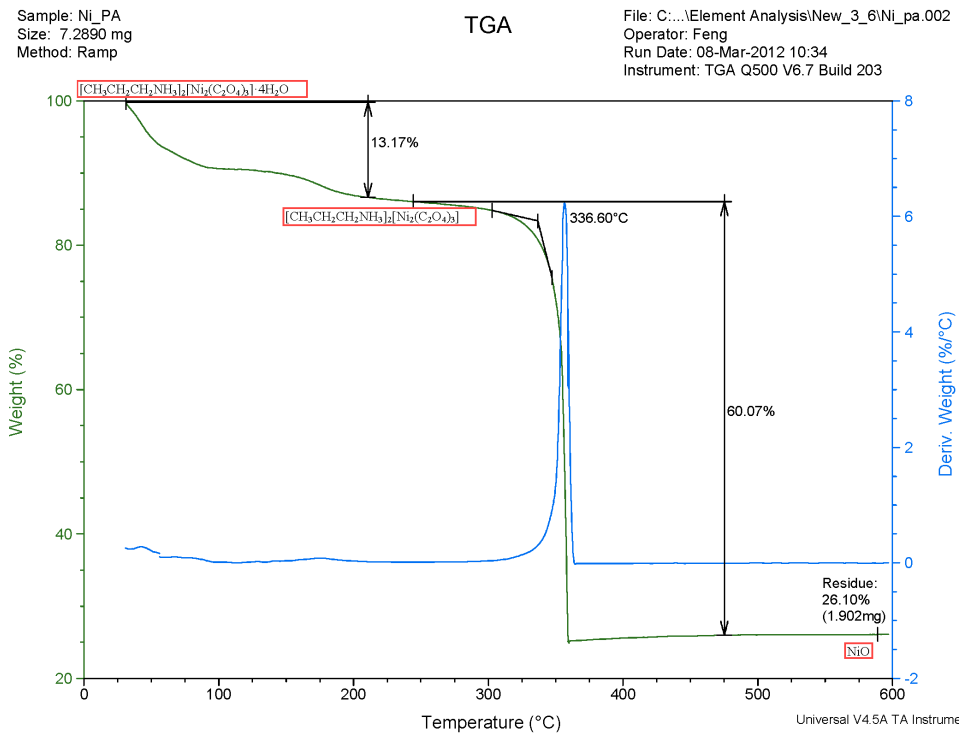


Figure S26. Thermogram of $[\text{pa}]_2[\text{Ni}_2(\text{ox})_3] \cdot 4\text{H}_2\text{O}$ obtained by aging of NiO and $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ at 45 °C and 98% RH. Calculated NiO residue: 26.0% ; calculated water loss: 12.6%.

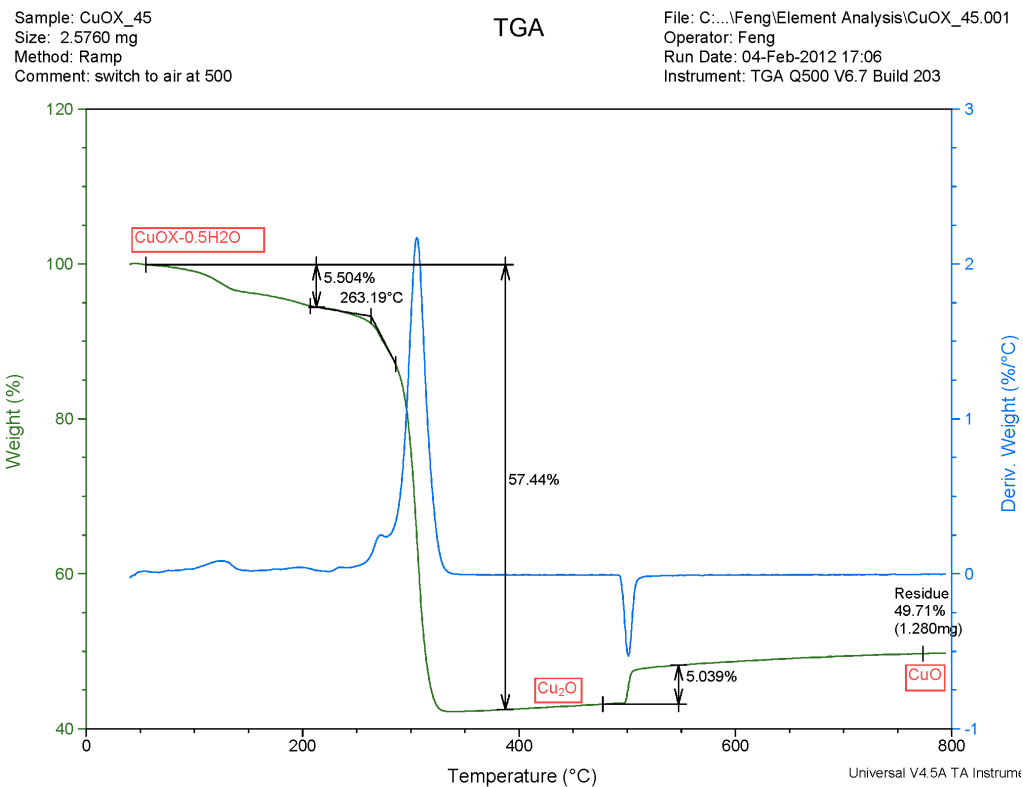


Figure S27. Thermogram of copper(II) oxalate obtained by aging of CuO and H₂ox·2H₂O at 45 °C and 98% RH. Calculated CuO residue: 50.2% ; calculated water loss: 5.6%.

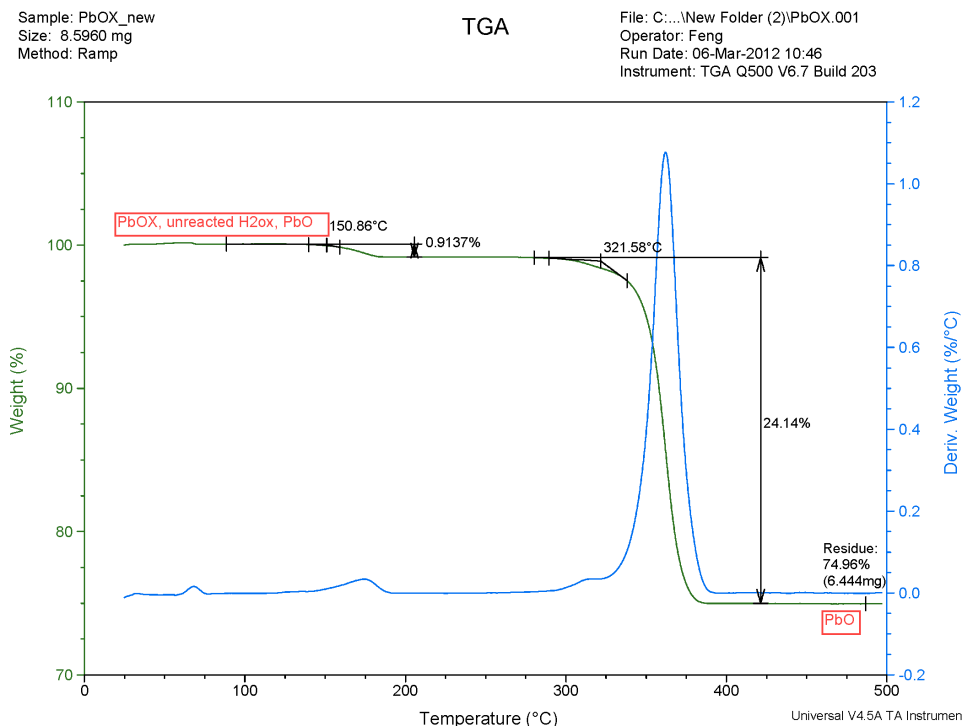


Figure S28. Thermogram of lead(II) oxalate obtained by aging of PbO and H₂ox·2H₂O at 45 °C and 98% RH. Calculated PbO residue: 75.6% ; calculated water loss: 0%.

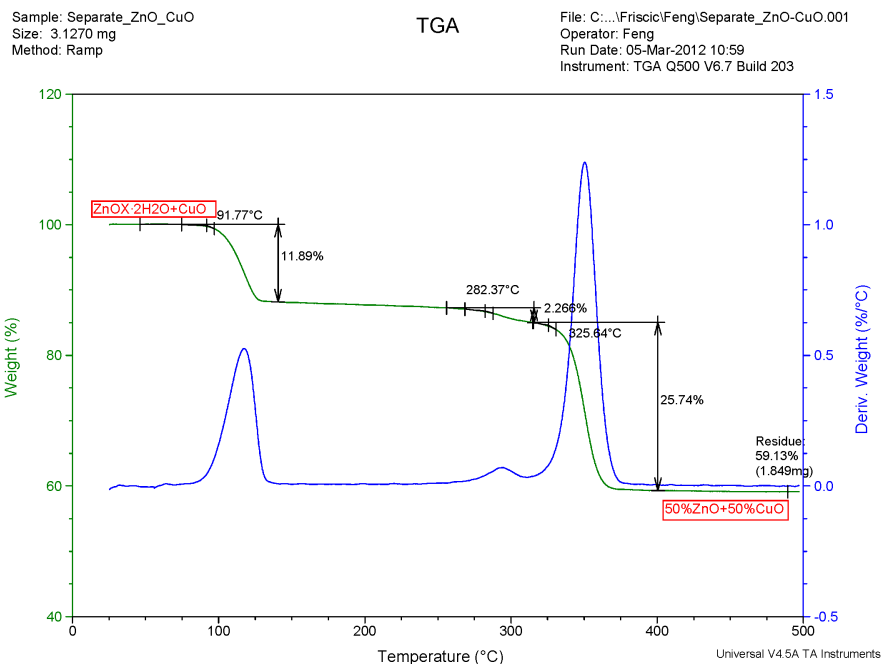


Figure S29. Thermogram of a 1:1:1 mixture of CuO, ZnO and $\text{H}_2\text{Ox}\cdot 2\text{H}_2\text{O}$ after aging for 5 days at 45 °C and 98% RH. The analysis of residue weight and weight loss steps indicates selective conversion of ZnO into $\text{ZnOx}\cdot 2\text{H}_2\text{O}$. Theoretical residue weight for the selective conversion of ZnO is 59.9%, and increases with increasing fraction of reacted CuO. A more conservative assessment of selectivity is provided by the less reliably measured water loss step (measured step: 11.9%, theoretical for pure $\text{ZnOx}\cdot 2\text{H}_2\text{O}$: 13.3%), which suggests the conversion of ZnO and CuO in the relative ratio 9:1. However, a further indication of the absence of any significant amounts of copper(II) oxalate is the absence of the characteristic copper(I) oxide re-oxidation step above 400 °C.

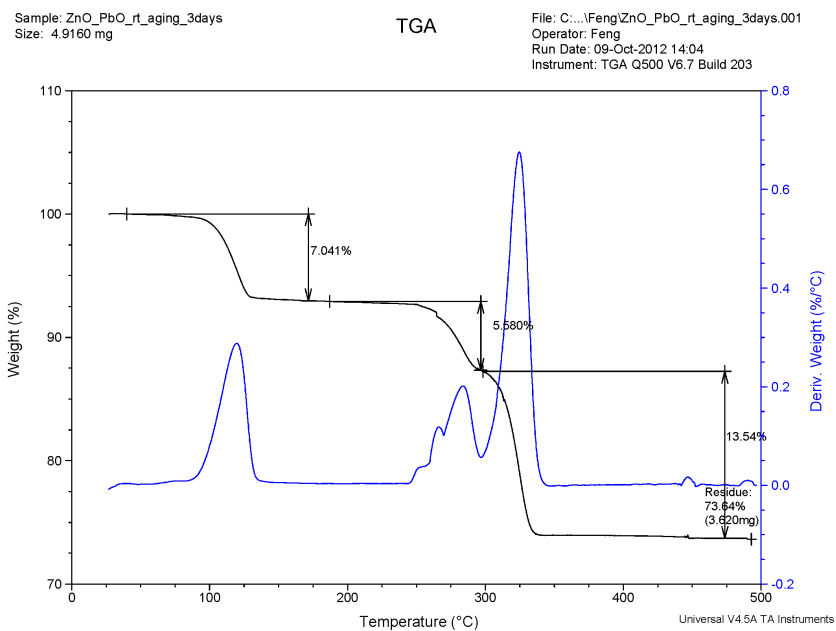


Figure S30. Thermogram of a 1:1:1 mixture of PbO, ZnO and $\text{H}_2\text{Ox}\cdot 2\text{H}_2\text{O}$ after aging for 3 days at room temperature and 98% RH. Residue weight indicates the selective conversion of ZnO with respect to PbO (calculated residue weight for a mixture of $\text{ZnOx}\cdot 2\text{H}_2\text{O}$ and PbO=73.8%). Almost identical selectivity is observed by conducting the separation at 45 °C and 98% RH

5. SELECTED ^{13}C SOLID-STATE NMR SPECTRA

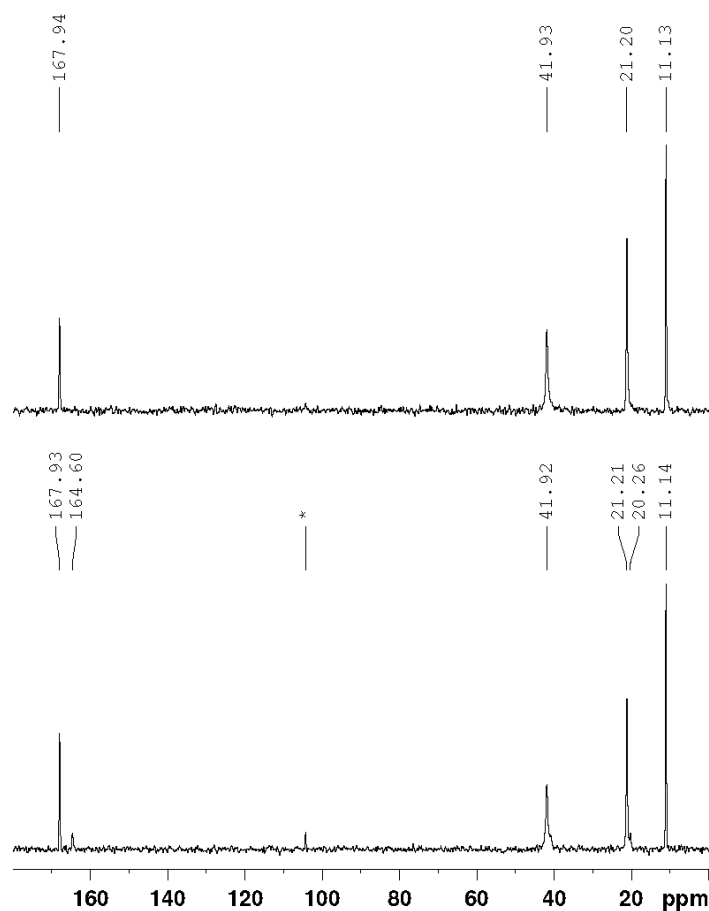


Figure S31. ^{13}C SSNMR spectrum of the 3-D framework material $[\text{pa}]_2[\text{Zn}_2(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ obtained by aging of ZnO and $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}$ at 45 °C and 98% RH: (top) cross-polarization spectrum (2 ms cross-polarization delay) and (bottom) direct polarization spectrum. Spinning sidebands are indicated by '*'.

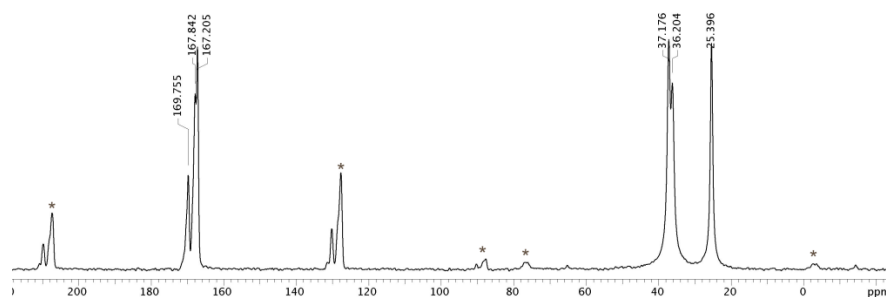


Figure S32. ^{13}C SSNMR cross-polarization spectrum of the 2-D framework material $[\text{pn}][\text{Zn}_2(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ obtained by aging of ZnO and $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}$ at 45 °C. The multiplicity of signals for the oxalate group (166 ppm-172 ppm) and for the propylene chain (20 ppm-40 ppm) are consistent with the published structure (CSD SEYQAO) which indicates four crystallographically independent oxalate carbon atoms and three crystallographically independent methylene groups in the asymmetric unit. Spinning sidebands are indicated by '*'

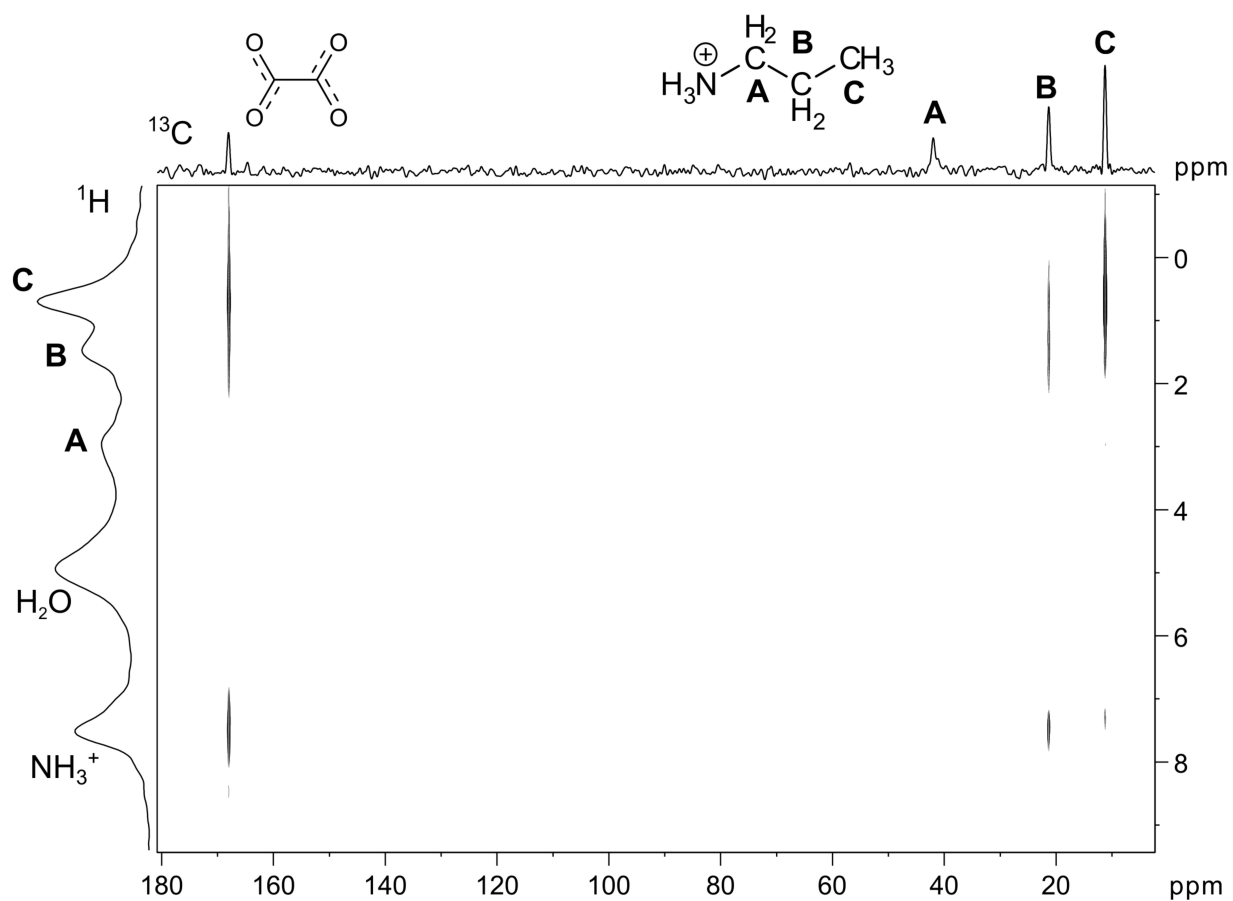


Figure S33. ^1H - ^{13}C HETCOR SSNMR of $[\text{pa}]_2[\text{Zn}_2(\text{ox})_3]\cdot 3\text{H}_2\text{O}$ (5 ms contact time) and tentative assignment. Absence of correlations to water is explained by disorder. For the nitrogen-bound CH_2 moiety the lack of correlations at this long correlation time and increased peak width are rationalized by the nearby ^{14}N quadrupole. The ^{13}C CP spectrum on top was acquired with a 2 ms contact time.