Electronic Supplementary Material (ESI) for Chemical Science

Supplementary Material

Accelerated aging: a low energy, solvent-free alternative to solvothermal and mechanochemical synthesis of metal-organic materials

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Experimental details

Preparation of samples: in a typical reaction, a mixture of 0.163 g (2mmol) ZnO and 0.306 g (4.5mmol) **Him** was gently ground manually using a mortar and pestle. For accelerated aging experiments, 10 mg (3.8 mol%) of $(NH_4)_2SO_4$ were added to the reaction mixture. The ground mixtures were placed in an open vial 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 K_2SO_4 solution. The desiccator was placed in a large volume incubator set at 45 ^oC. The same procedure was repeated for reactions involving all other imidazole ligands, typically using a 1:2 stoichiometric ratio of zinc oxide to imidazole ligand. For reactions with **HMeim** at 10 gram scale 3.47 g (42.6 mmol) ZnO was mixed with 7.01 g (85.3 mmol) **HMeim** and 0.52 g (5% w/w) $(NH_4)_2SO_4$. For the 10 gram scale reaction with **HEtim**, 2.96 g (36.4mmol) ZnO was mixed with 7.00 g (72.8mmol) **HEtim** and 0.50 g (5%w/w) $(NH_4)_2SO_4$. Following complete disappearance of ZnO, the samples were washed with distilled water to remove the salt additive or its degradation products and dried in air. Power consumption of the incubator was measured using the BluePlanet energy meter.

Powder X-Ray Diffraction (PXRD): Room temperature PXRD patterns were collected in the 2θ range 4^o to 50^o 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.

Infrared 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}.

Differential Scanning Calorimetry (DSC): DSC measurements were conducted on a TA Instruments Q1000 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 160°C to 200°C depending on the sample, with a constant heating rate of 10°C/min.

Thermogravimetric Analysis (TGA): TGA measurements were conducted on a TA Instruments Q1000 Thermogravimetric System with a Pt pan under dynamic atmosphere of N_2 with 40ml/min balance flow and 60ml/min purge flow. The upper temperature limit ranged from 300°C to 900°C depending on the sample, with a heating rate of 10°C/min.

Solid-state NMR experiments: Solid-state NMR ^{13}C experiments were performed at Bruker UK in Coventry, UK 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. The ^{13}C spectrum of the Zn(**Meim**)$_2$ *dia* framework was acquired in

4096 scans using cross-polarization for 2 ms and a recycle delay of 3 s. The spectrum of the ZIF-8 framework was acquired in 128 scans using cross-polarization for 500 μs and a recycle delay of 5 s.

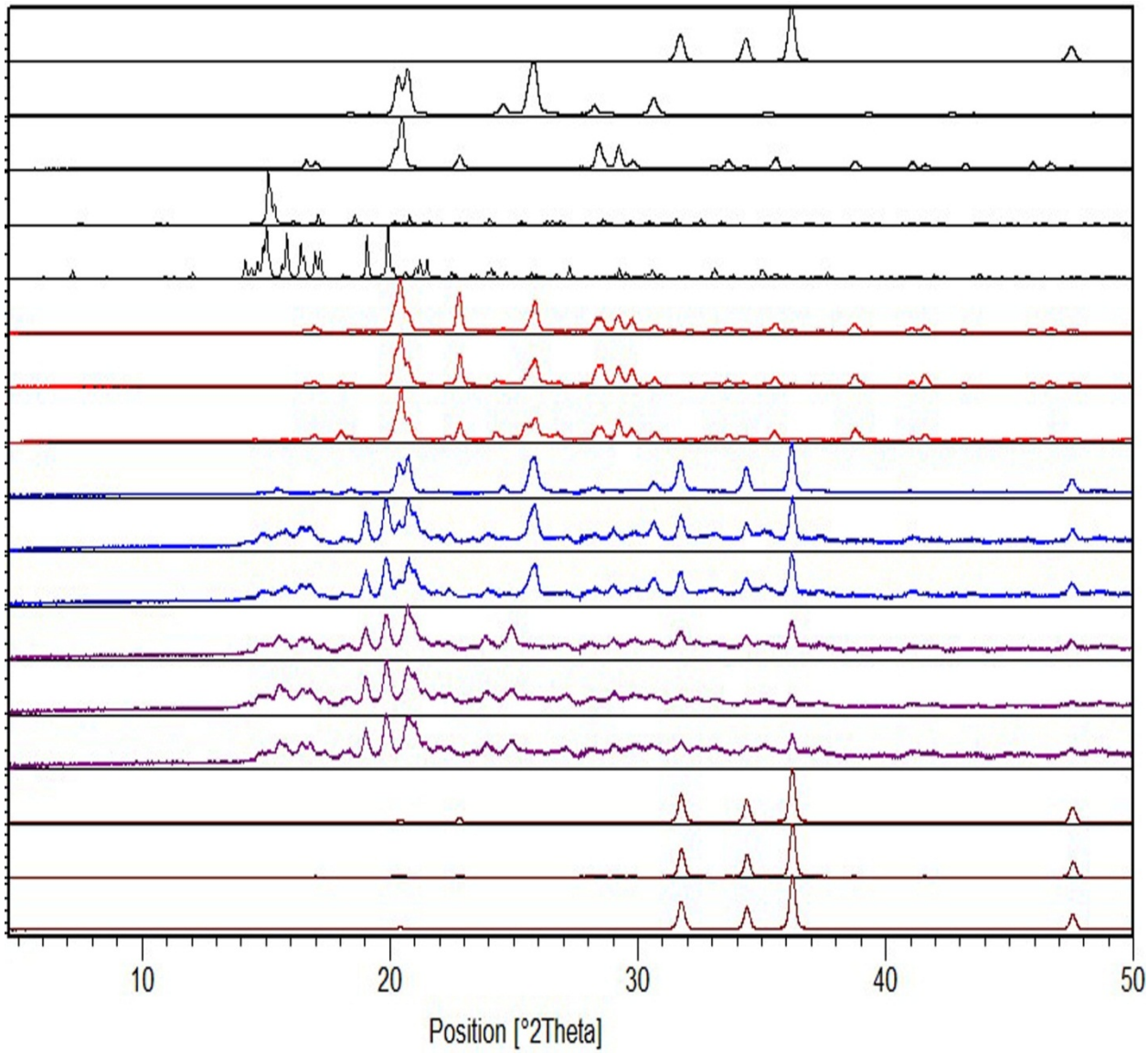

Figure S1. PXRD patterns for the aging reactions of ZnO and **Him** at room temperature and ambient humidity. From top to bottom: commercial ZnO; commercial **Him**; commercial $(NH_4)_2SO_4$; simulated pattern for Zn_4(**im**)$_8$(**Him**) (CCDC code KUMXEW); fresh mixture of $(NH_4)_2SO_4$ and **Him**; mixture of $(NH_4)_2SO_4$ and **Him** after 3 days aging; mixture of $(NH_4)_2SO_4$ and **Him** after 6 days aging; fresh mixture of ZnO and **Him**; mixture of ZnO and **Him** after 3 days aging; mixture of ZnO and **Him** after 6 days aging; fresh mixture of ZnO and **Him** (4 mol% $(NH_4)_2SO_4$); mixture of ZnO and **Him** (4 mol% $(NH_4)_2SO_4$) after 3 days aging; mixture of ZnO and **Him** (4 mol% $(NH_4)_2SO_4$) after 6 days aging; fresh mixture of ZnO and $(NH_4)_2SO_4$; mixture of ZnO and $(NH_4)_2SO_4$ after 3 days aging; mixture of ZnO and $(NH_4)_2SO_4$ after 6 days aging.

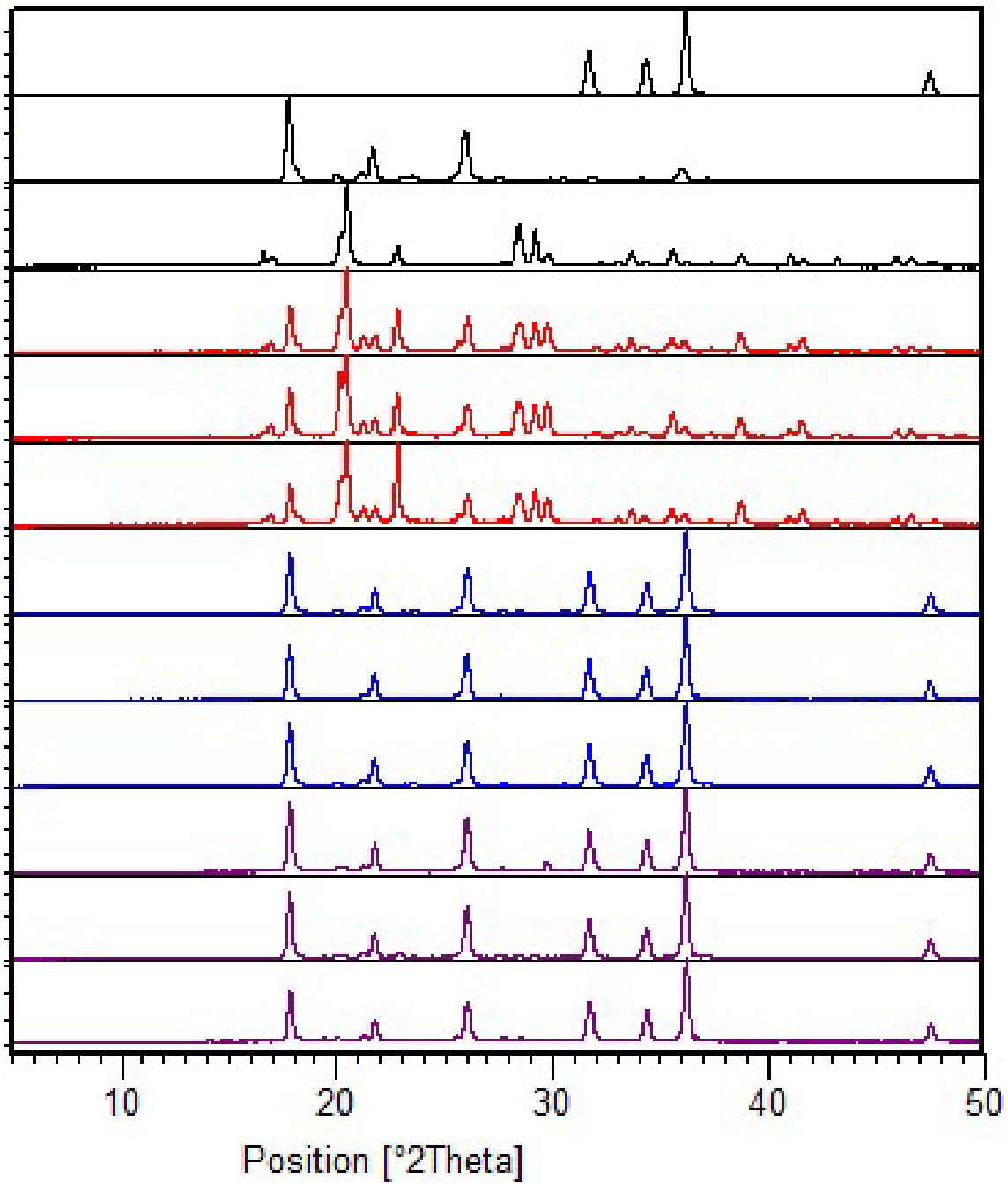

Figure S2. PXRD patterns for the aging reactions of ZnO and **HMeim** at room temperature and ambient humidity. From top to bottom: commercial ZnO; commercial **HMeim**; commercial $(NH_4)_2SO_4$; fresh mixture of $(NH_4)_2SO_4$ and **HMeim**; mixture of $(NH_4)_2SO_4$ and **HMeim** after 3 days aging; mixture of $(NH_4)_2SO_4$ and **HMeim** after 6 days aging; fresh mixture of ZnO and **HMeim**; mixture of ZnO and **HMeim** after 3 days aging; mixture of ZnO and **HMeim** after 6 days aging; fresh mixture of ZnO and **HMeim** (4 mol% $(NH_4)_2SO_4$); mixture of ZnO and **HMeim** (4 mol% $(NH_4)_2SO_4$) after 3 days aging; mixture of ZnO and **HMeim** (4 mol% $(NH_4)_2SO_4$) after 6 days aging.

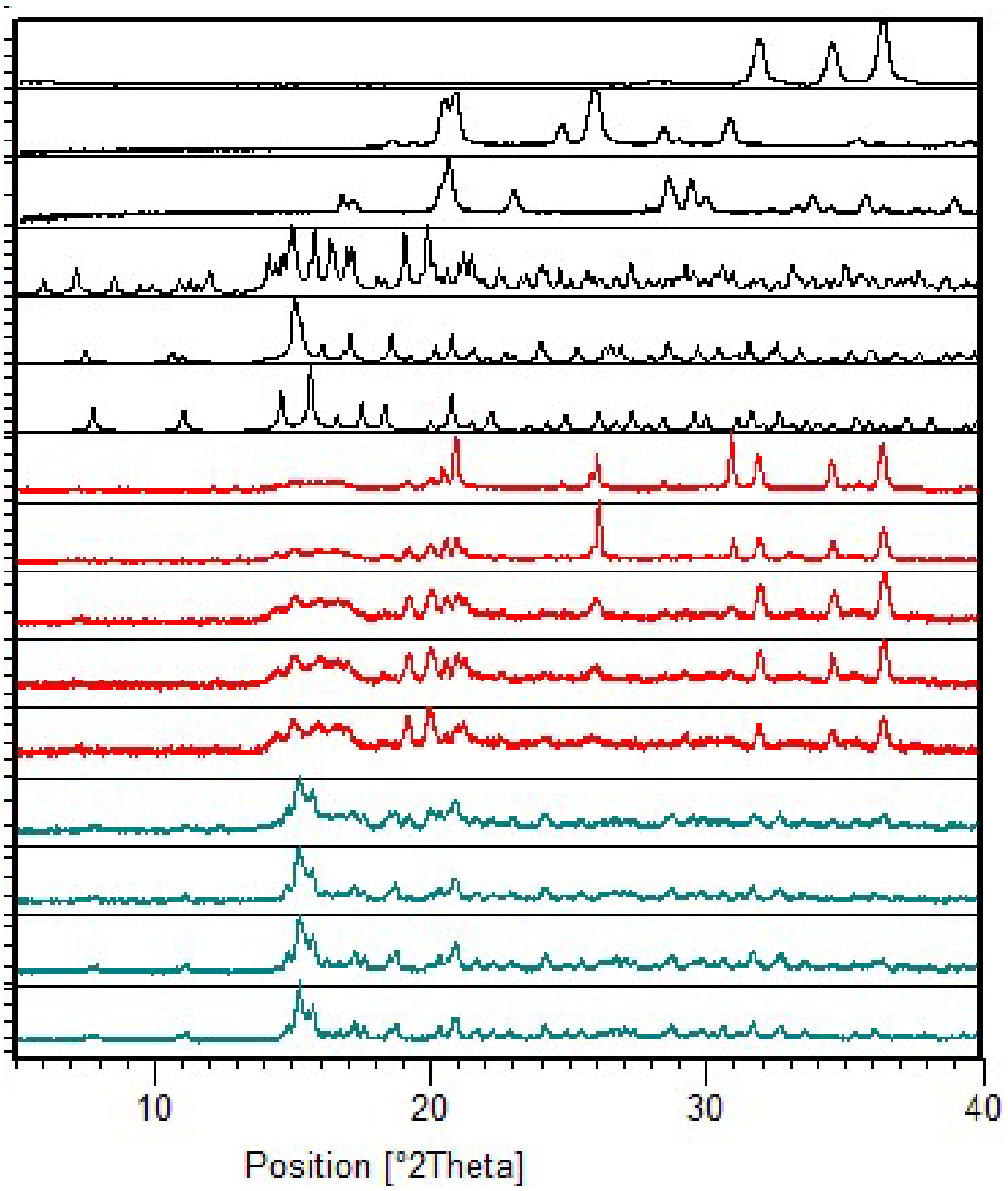

Figure S3. PXRD patterns for the aging reactions of ZnO and **Him** at room temperature and 98% RH. From top to bottom: commercial ZnO; commercial **Him**; commercial $(NH_4)_2SO_4$; simulated pattern for Zn_4(**im**)$_8$(**Him**) (CCDC code KUMXEW); simulated pattern for the zni-type Zn(**im**)$_2$ (CCDC codeIMIDZB03); simulated pattern for the high-pressure Zn(**im**)$_2$ (CCDC code IMIDZB09); fresh mixture of ZnO and **Him**; mixture of ZnO and **Him** after 1 day aging; mixture of ZnO and **Him** after 2 days aging; mixture of ZnO and **Him** after 4 days aging; mixture of ZnO and **Him** after 10 days aging; mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 1 day aging; mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 2 days aging; mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 3 days aging; mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 6 days aging.

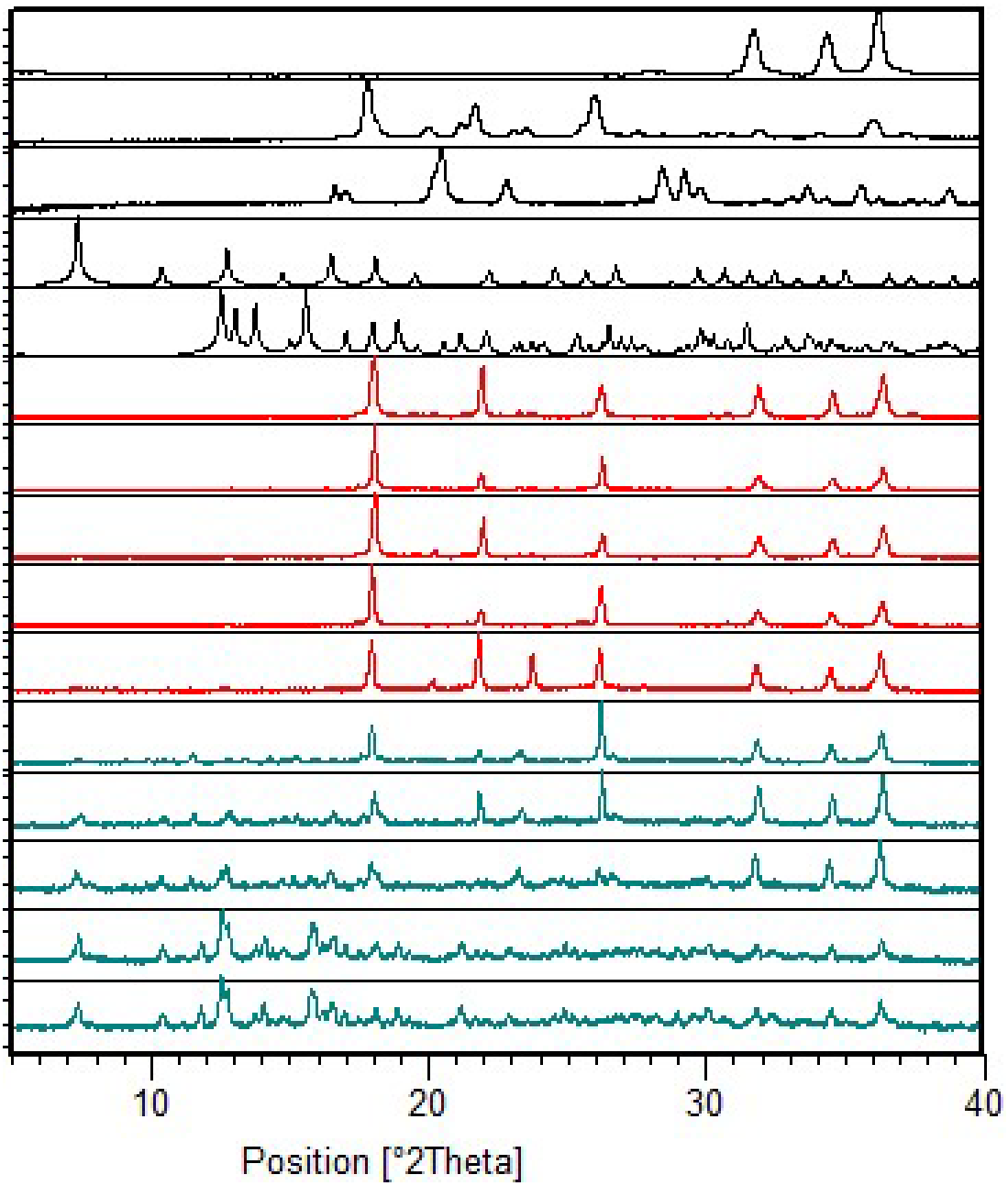

Figure S4. PXRD patterns for the aging reactions of ZnO and **HMeim** at room temperature and 98% RH. From top to bottom: commercial ZnO; commercial **HMeim**; commercial $(NH_4)_2SO_4$; simulated pattern for the porous Zn(**Meim**)$_2$ (ZIF-8, CCDC code VELVOY); simulated pattern for the diamondoid (dia) Zn(**Meim**)$_2$ framework (CCDC code OFERUN10); fresh mixture of ZnO and **HMeim**; mixture of ZnO and **HMeim** after 1 day aging; mixture of ZnO and **HMeim** after 2 days aging; mixture of ZnO and **HMeim** after 4 days aging; mixture of ZnO and **HMeim** after 10 days aging; mixture of ZnO and **HMeim** with $(NH_4)_2SO_4$ additive after 1 day aging; mixture of ZnO and **HMeim** with $(NH_4)_2SO_4$ additive after 2 days aging; mixture of ZnO and **HMeim** with $(NH_4)_2SO_4$ additive after 3 days aging; mixture of ZnO and **HMeim** with $(NH_4)_2SO_4$ additive after 6 days aging; mixture of ZnO and **HMeim** with $(NH_4)_2SO_4$ additive after 7 days aging.

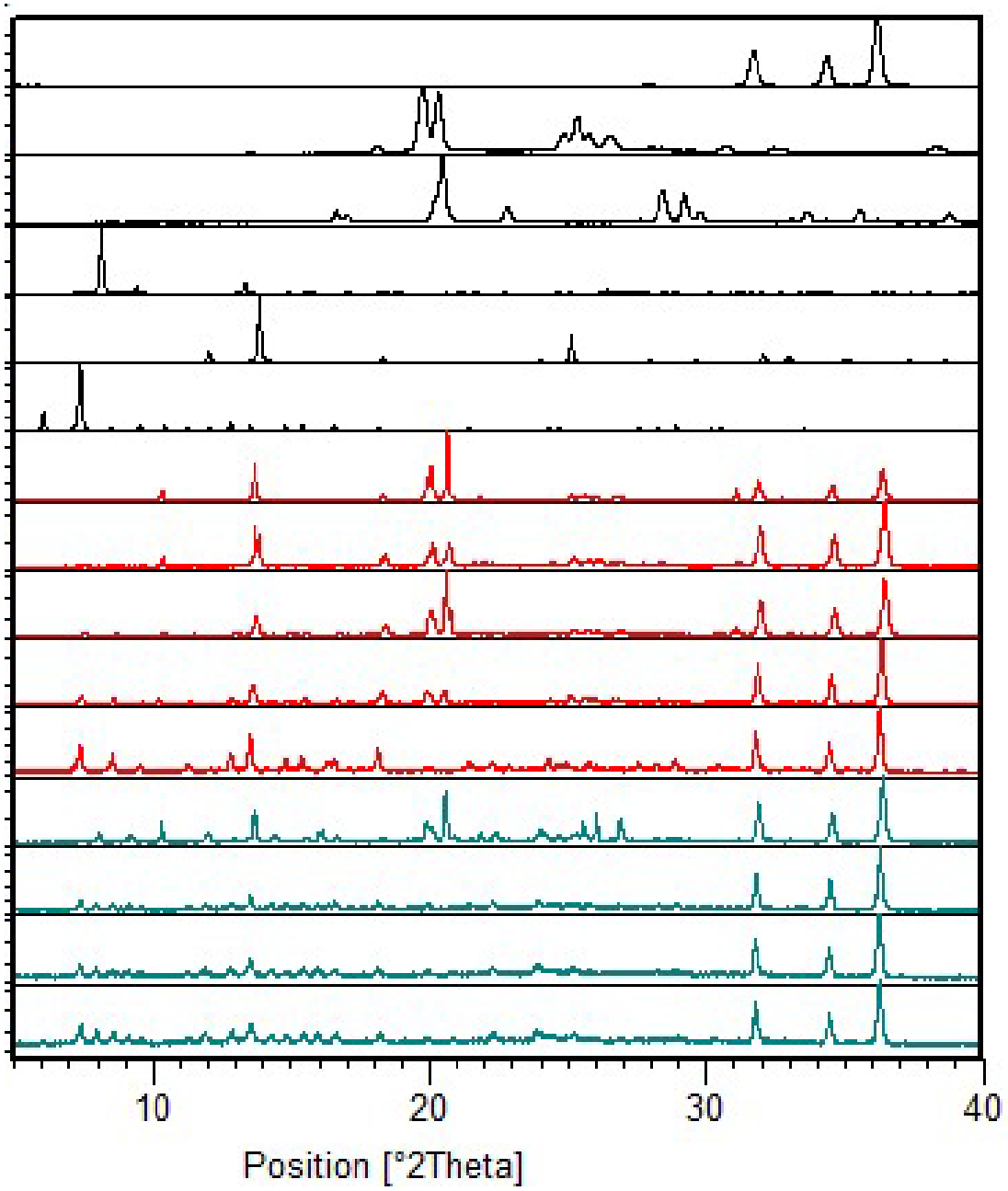

Figure S5. PXRD patterns for the aging reactions of ZnO and **HEtim** at room temperature and 98% RH. From top to bottom: commercial ZnO; commercial **HEtim**; commercial $(NH_4)_2SO_4$; simulated pattern for the analcime-type (ANA) Zn(**Etim**)$_2$ framework (CCDC code MECWIB); simulated pattern for the quartz-type (qtz) Zn(**Etim**)$_2$ framework (CCDC code EHETER); simulated pattern for the zeolite rho-type (RHO) Zn(**Etim**)$_2$ framework (CCDC code MECWOH); fresh mixture of ZnO and **HEtim**; mixture of ZnO and **HEtim** after 1 day aging; mixture of ZnO and **HEtim** after 2 days aging; mixture of ZnO and **HEtim** after 4 days aging; mixture of ZnO and **HEtim** after 10 days aging; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 1 day aging; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 2 days aging; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 3 days aging; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 6 days aging.

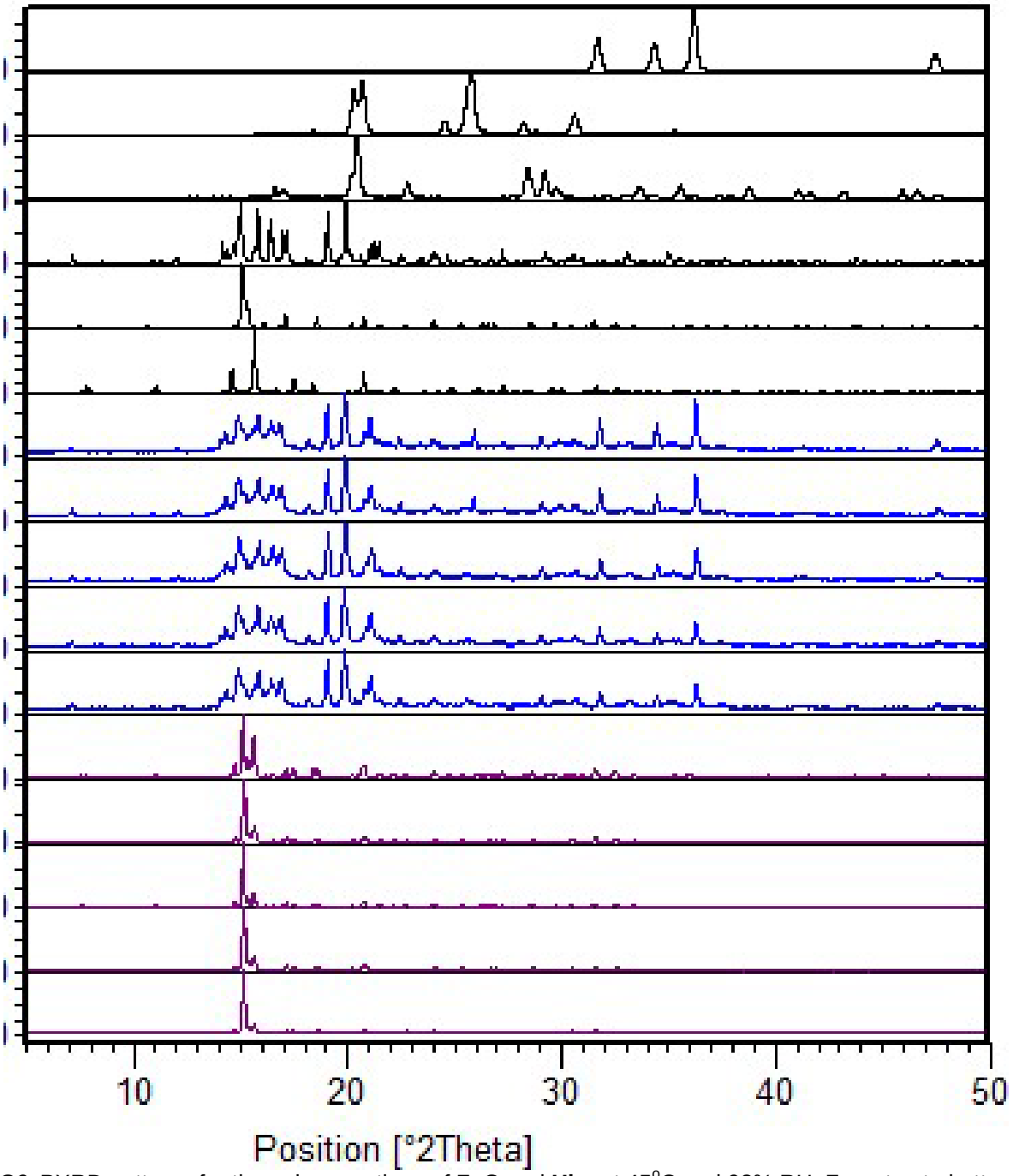

Figure S6. PXRD patterns for the aging reactions of ZnO and **Him** at 45°C and 98% RH. From top to bottom: commercial ZnO; commercial **Him**; commercial $(NH_4)_2SO_4$; simulated pattern for Zn_4(**im**)$_8$(**Him**) (CCDC code KUMXEW); simulated pattern for the zni-type Zn(**im**)$_2$ (CCDC code IMIDZB03); simulated pattern for the high pressure Zn(**im**)$_2$ (CCDC code IMIDZB09); mixture of ZnO and **Him** after 3 days; mixture of ZnO and **Him** after 6 days; mixture of ZnO and **Him** after 9 days; mixture of ZnO and **Him** after 12 days; mixture of ZnO and **Him** after 15 days; mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 3 days aging; mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 6 days aging; mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 9 days aging; mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 12 days aging and mixture of ZnO and **Him** with $(NH_4)_2SO_4$ additive after 15 days aging.

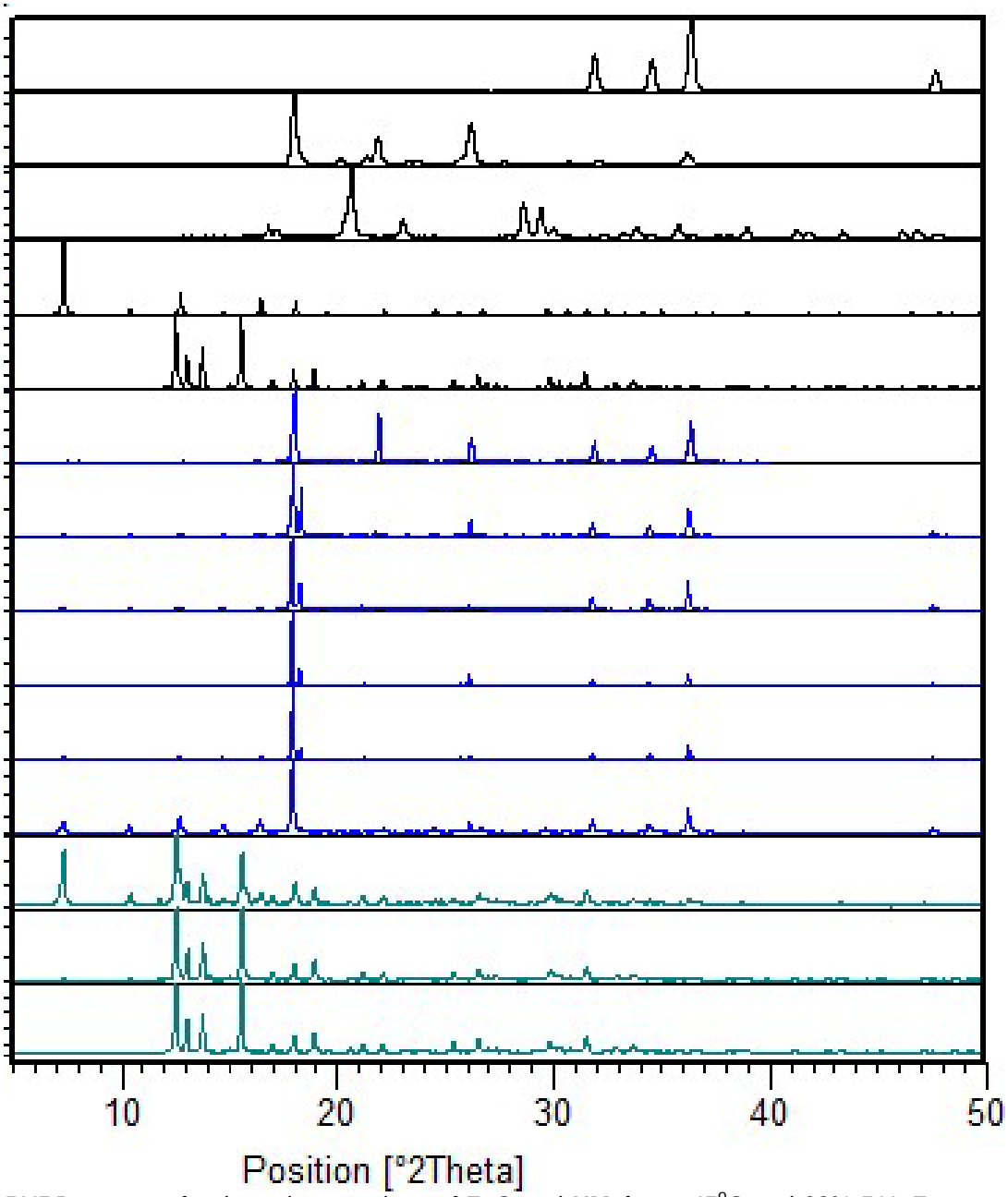

Figure S7. PXRD patterns for the aging reactions of ZnO and **HMeim** at 45°C and 98% RH. From top to bottom: commercial ZnO; commercial **HMeim**; commercial $(NH_4)_2SO_4$; simulated pattern for the open framework Zn(**Meim**)$_2$ (ZIF-8, CCDC code VELVOY); simulated pattern for the diamondoid (dia) structure Zn(**Meim**)$_2$ (CCDC code OFERUN01); fresh mixture of ZnO and **HMeim**; mixture of ZnO and **HMeim** after 3 days; mixture of ZnO and **HMeim** after 6 days; mixture of ZnO and **HMeim** after 9 days; mixture of ZnO and **HMeim** after 12 days; mixture of ZnO and **HMeim** after 15 days; mixture of ZnO and **HMeim** with $(NH_4)_2SO_4$ additive after 3 days aging; mixture of ZnO and **HMeim** with $(NH_4)_2SO_4$ additive after 6 days aging; mixture of ZnO and **HMeim** with $(NH_4)_2SO_4$ additive after 9 days aging.

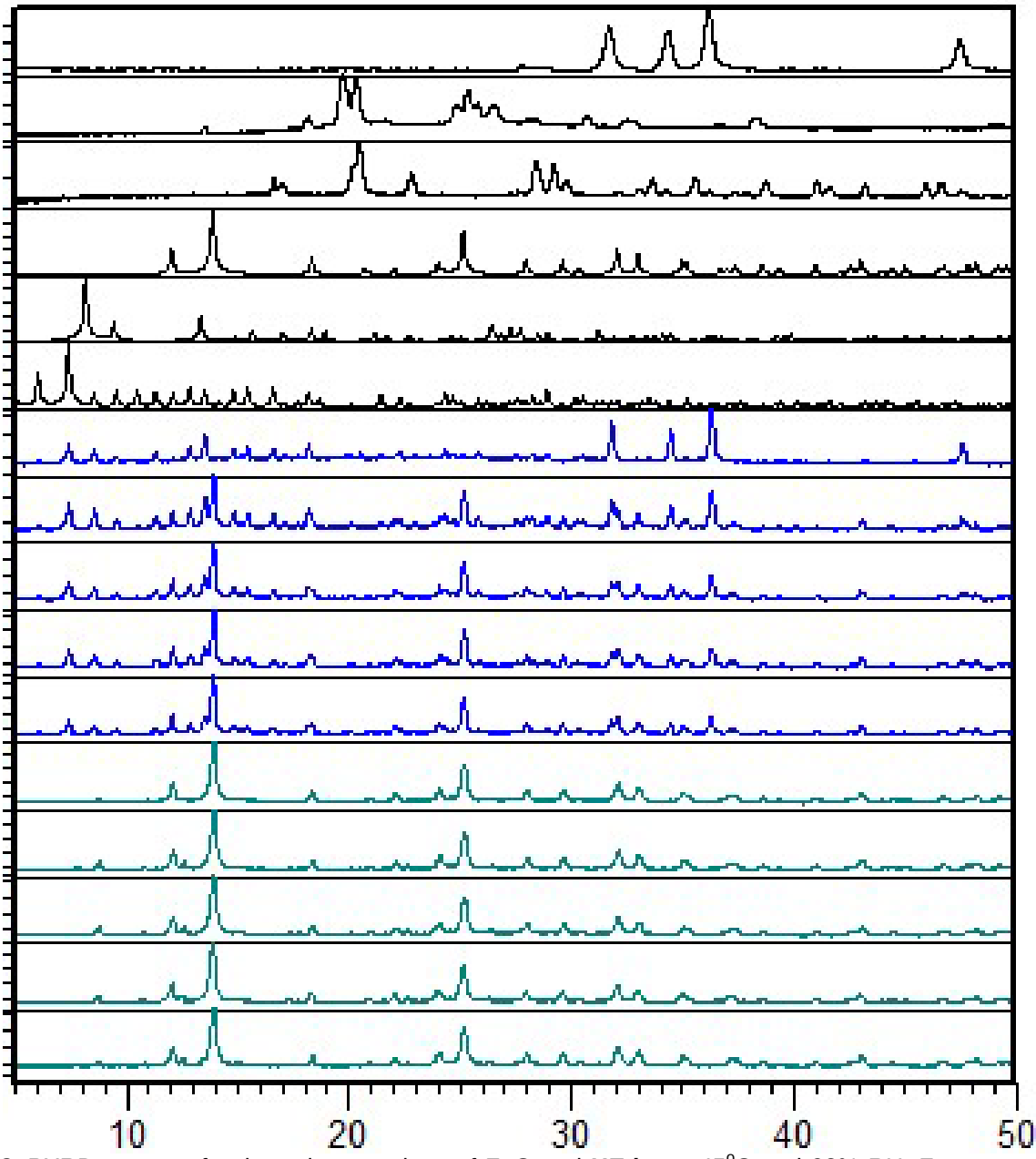

Figure S8. PXRD patterns for the aging reactions of ZnO and **HEtim** at 45°C and 98% RH. From top to bottom: commercial ZnO; commercial **HEtim**; commercial $(NH_4)_2SO_4$; simulated pattern for the quartz-type (qtz) close-packed framework Zn(**Etim**)$_2$ (CCDC code EHETER); simulated pattern for the analcime-type (ANA) Zn(**Etim**)$_2$ framework (CCDC code MECWIB); simulated pattern for the zeolite rho-type (RHO) Zn(**Etim**)$_2$ framework (CCDC code MECWOH); mixture of ZnO and **HEtim** after 3 days aging; mixture of ZnO and **HEtim** after 6 days aging; mixture of ZnO and **HEtim** after 9 days aging; mixture of ZnO and **HEtim** after 12 days aging; mixture of ZnO and **HEtim** after 15 days aging; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 3 days aging; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 6 days aging; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 9 days aging; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 12 days aging and; mixture of ZnO and **HEtim** with $(NH_4)_2SO_4$ additive after 15 days aging.

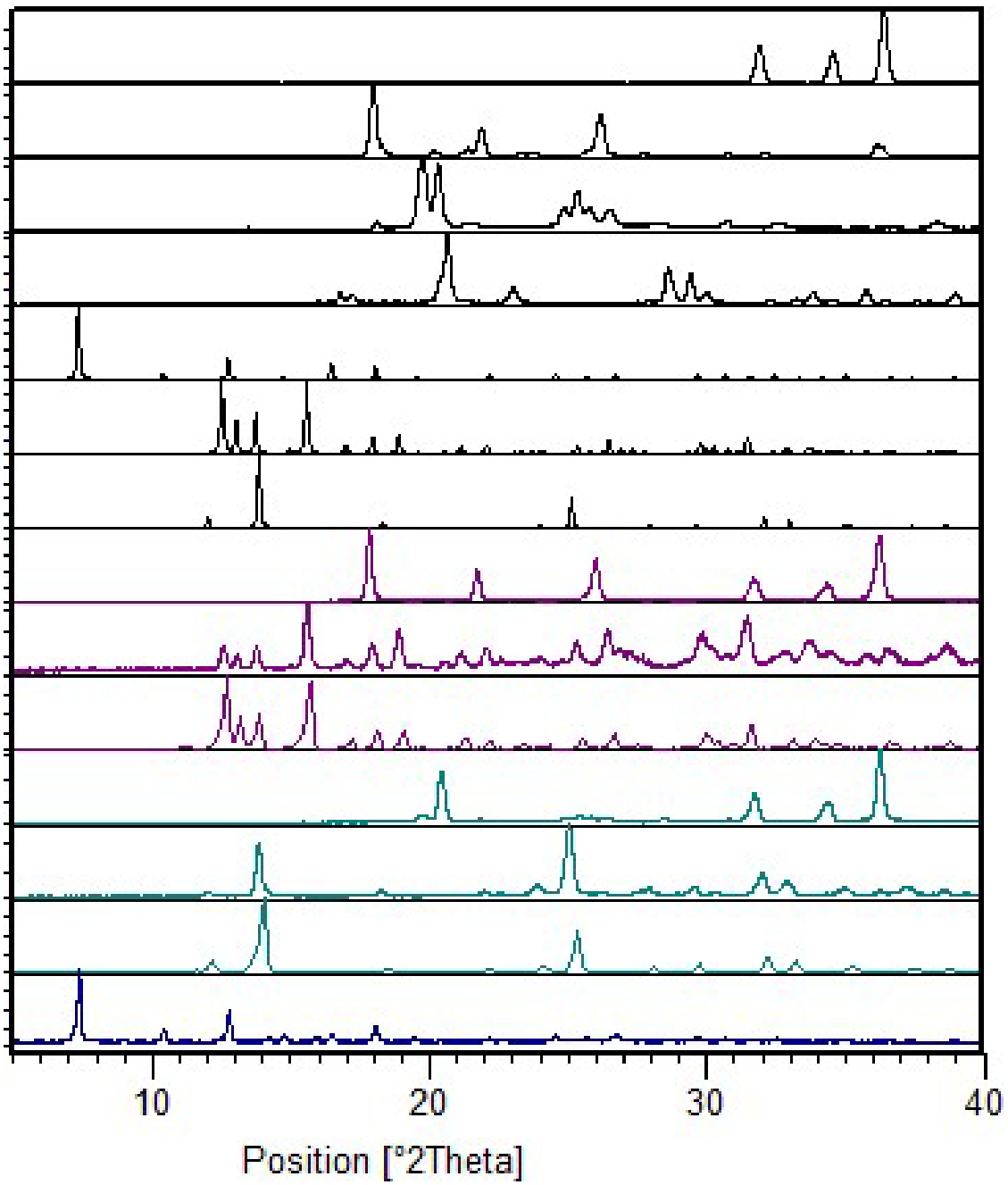

Figure S9. PXRD patterns for the aging reactions at 10 grams scale and the transformation of *dia*-Zn(**Meim**)$_2$ into open ZIF-8 structure. From top to bottom: commercial ZnO; commercial **HMeim**; commercial **HEtim**; commercial $(NH_4)_2SO_4$; simulated pattern for the open framework Zn (**Meim**)$_2$ (ZIF-8, CCDC code VELVOY); simulated pattern for the diamondoid (dia) structure Zn(**Meim**)$_2$ (CCDC code OFERUN01); simulatd pattern for the quartz (qtz) topology Zn(**Etim**)$_2$ (CCDC code EHETER); fresh mixture of ZnO and **HMeim** (added $(NH_4)_2SO_4$); mixture of ZnO and **HMeim** (added $(NH_4)_2SO_4$) after 35 days aging; mixture of ZnO and **HMeim** (added $(NH_4)_2SO_4$) after 35 days aging and washing with water; fresh mixture of ZnO and **HEtim** (added $(NH_4)_2SO_4$); mixture of ZnO and **HEtim** (added $(NH_4)_2SO_4$) after 35 days aging; mixture of ZnO and **HEtim** (added $(NH_4)_2SO_4$) after 35 days aging and washing with water and ZIF-8 made by exposing *dia*-Zn(**Meim**)$_2$ to ethanol vapour.

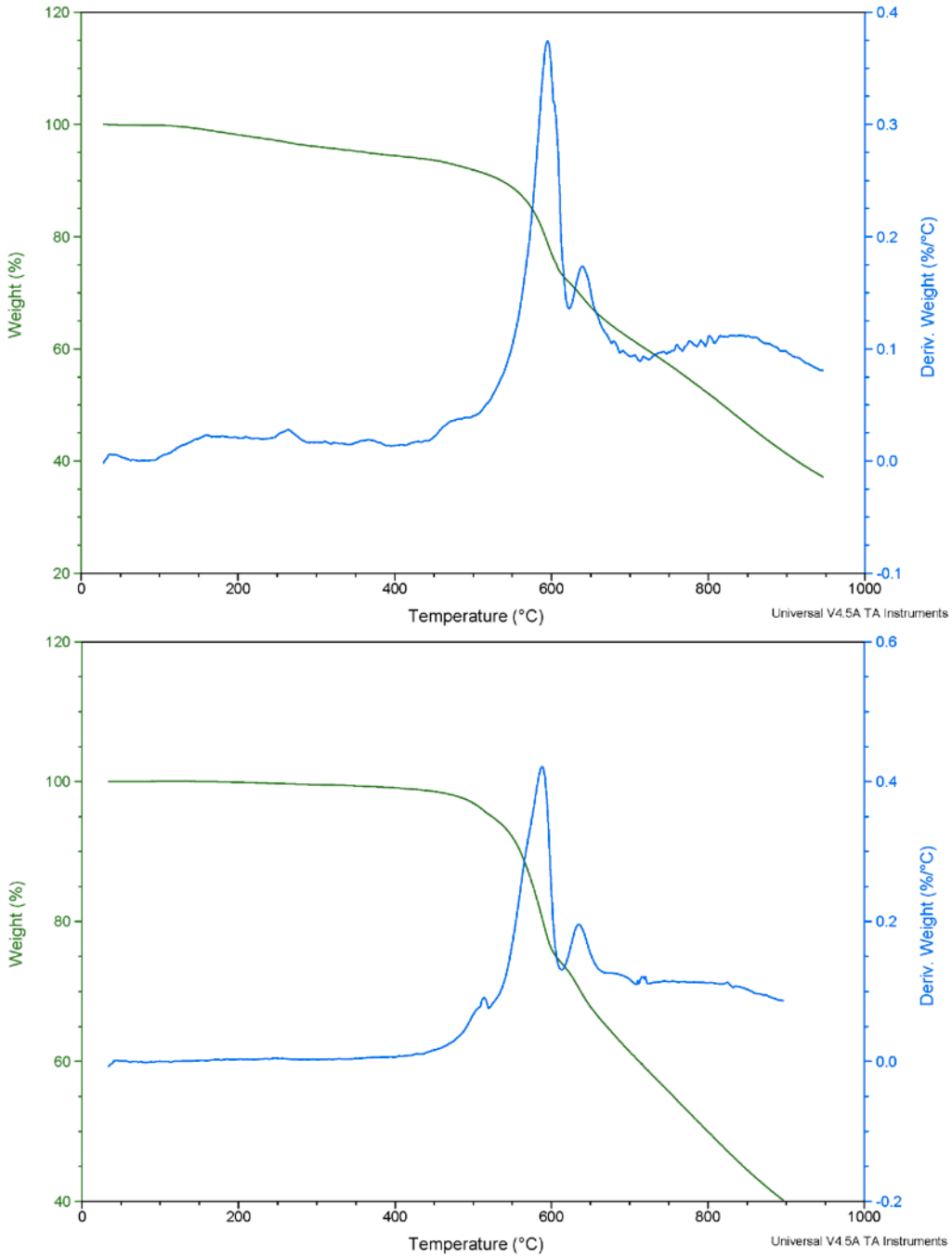

Figure S10. TGA thermogram of the product of "accelerated aging" reaction of ZnO and **HMeim** on 10 grams scale: (a) before washing with water and (b) after washing with water.

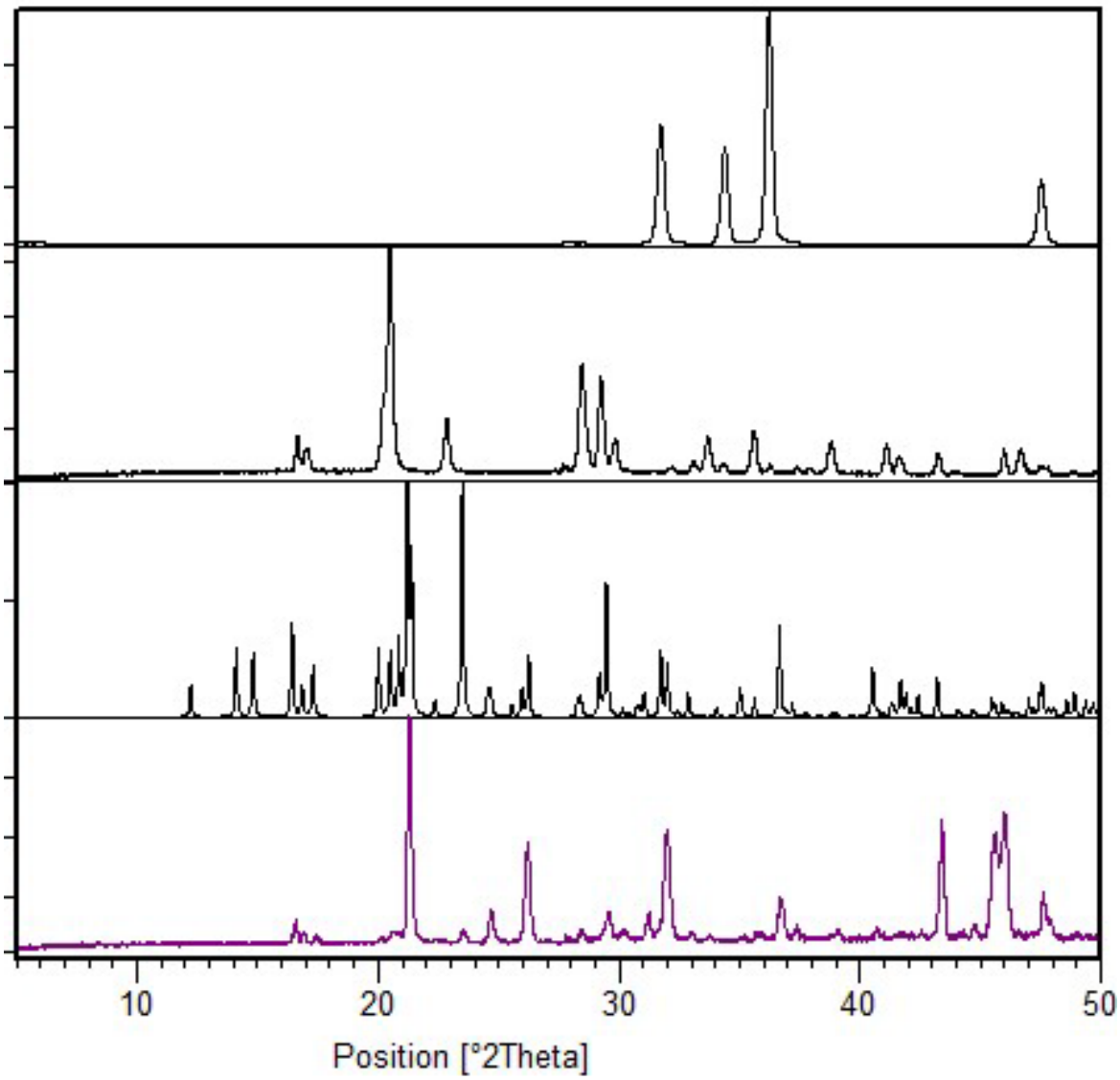

Figure S11. PXRD patterns for the aging reactions of ZnO and $(NH_4)_2SO_4$ at 45°C and 98% RH. From top to bottom: commercial ZnO; commercial $NH_4)_2SO_4$; simulated pattern for Tutton's salt $Zn(H_2O)_6(NH_4)_2(SO_4)_2$ and pattern of a mixture of ZnO and $(NH_4)_2SO_4$ after 7 days aging. The discrepancy between intensities of simulated and experimental patterns is tentatively explained by preferred orientation effects.

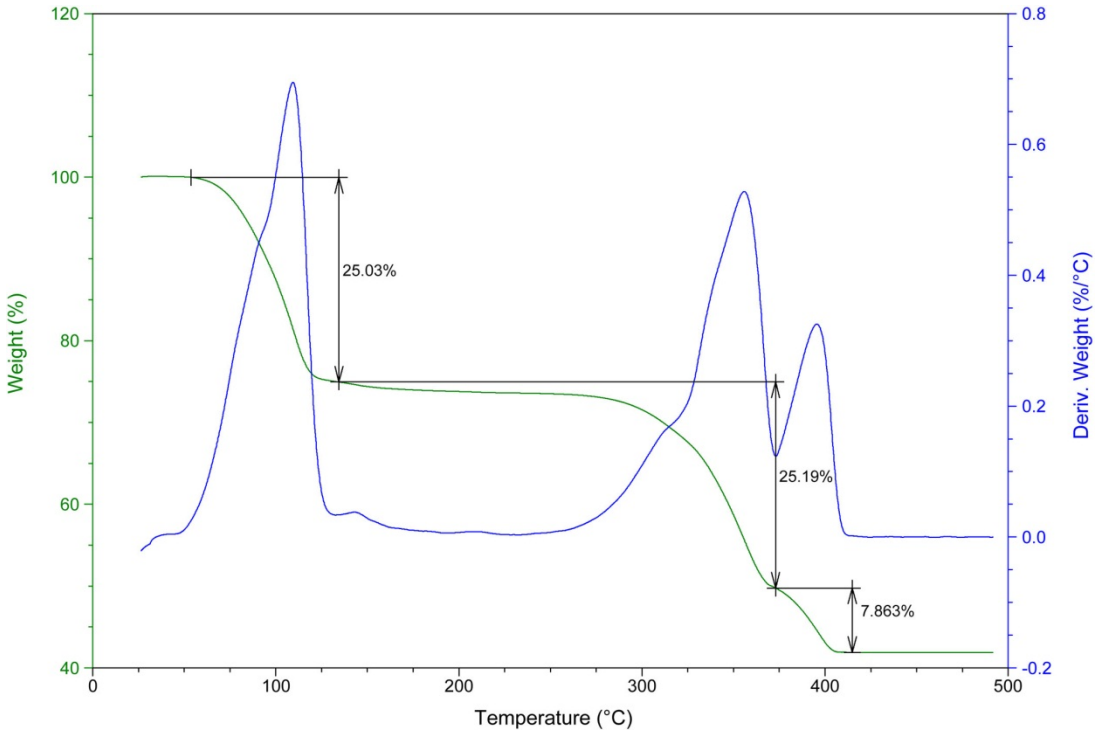

Figure S12. TGA thermogram of Tutton's salt $Zn(H_2O)_6(NH_4)_2(SO_4)_2$ prepared by aging of a mixture of ZnO and $(NH_4)_2SO_4$. Expected water content: 26.9 % Water content as determined by the first step in thermal decomposition: 25.0%.

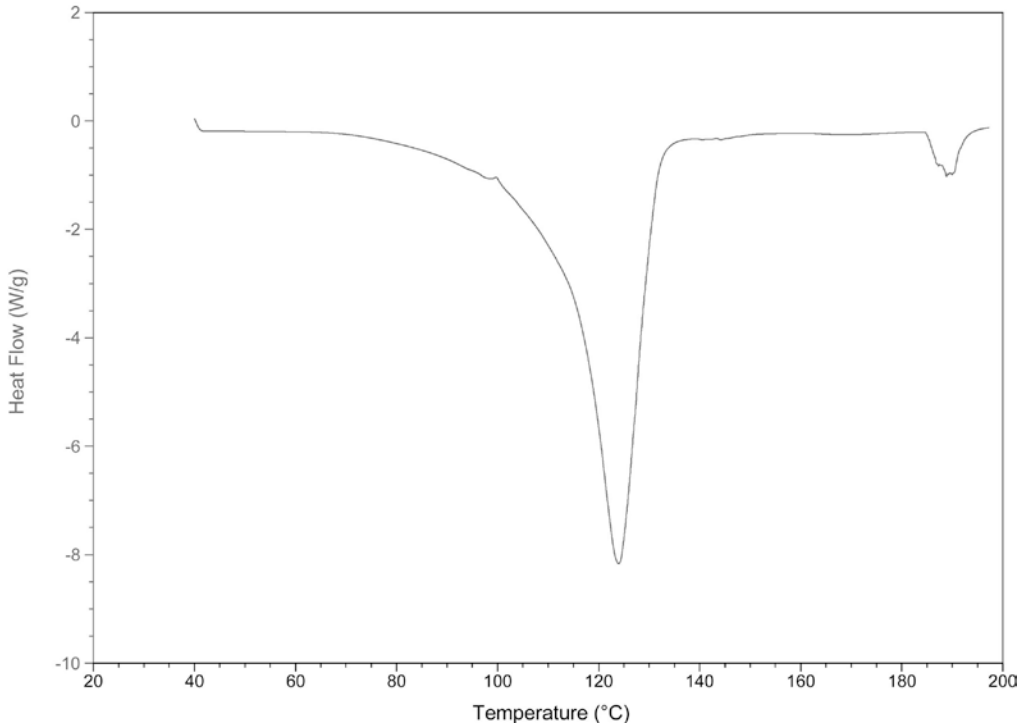

Figure S13. DSC thermogram of Tutton's salt $Zn(H_2O)_6(NH_4)_2(SO_4)_2$ prepared by aging of a mixture of ZnO and $(NH_4)_2SO_4$.

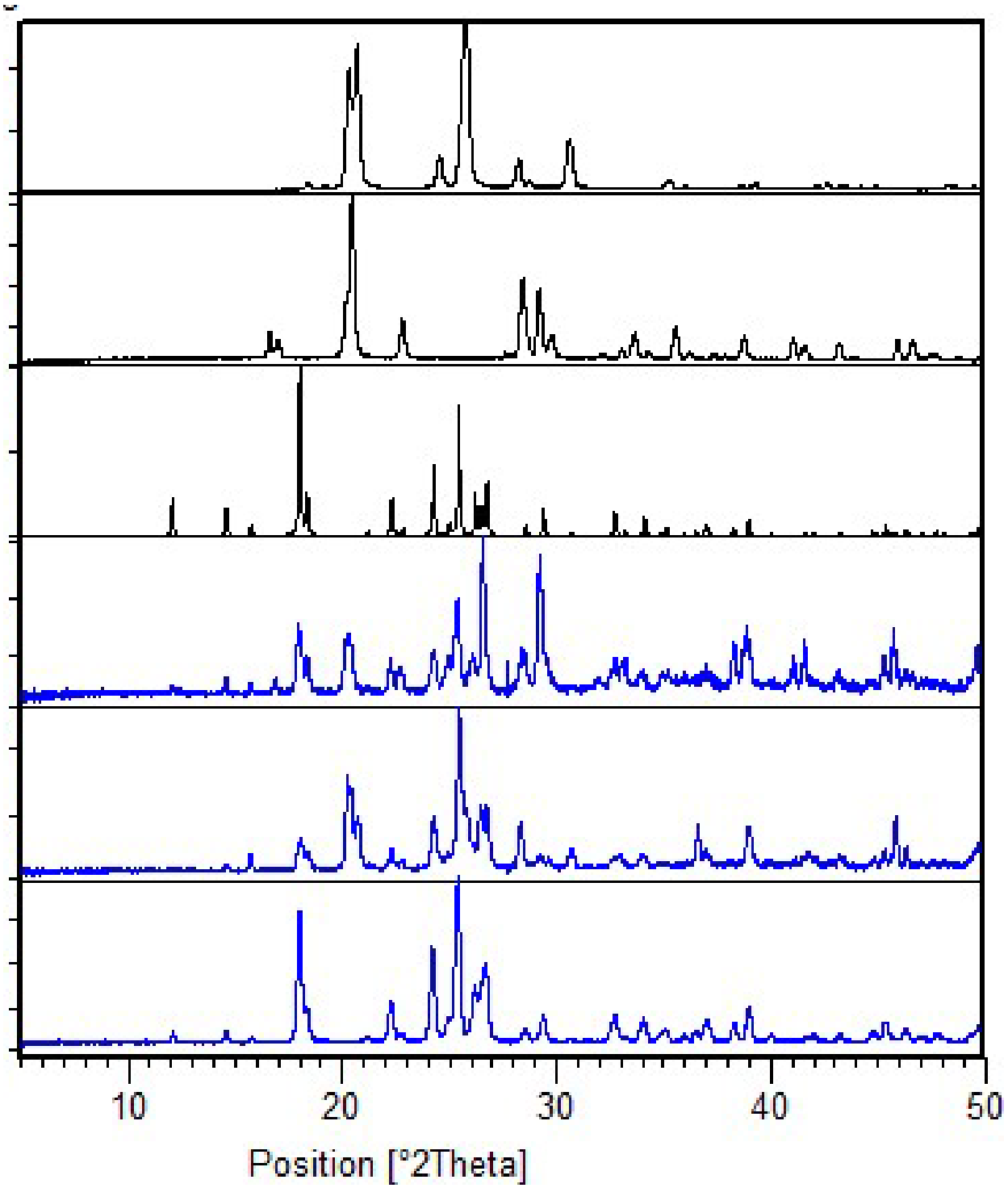

Figure S14. PXRD patterns for the aging reactions of **Him** and$(NH_4)_2SO_4$ at 45°C and 98% RH. From top to bottom: commercial **Him**; commercial $NH_4)_2SO_4$; simulated pattern for (**H_2im**)$_2SO_4 \cdot 2H_2O$; mixture of **Him** and $(NH_4)_2SO_4$ in 1:1 stoichiometric ratio after 7 days aging; mixture of **Him** and $(NH_4)_2SO_4$ in 2:1 stoichiometric ratio after 7 days aging and (**H_2im**)$_2SO_4 \cdot 2H_2O$ prepared by the reaction of **Him** and H_2SO_4 in a water:ethanol (1:9 v/v) mixture.

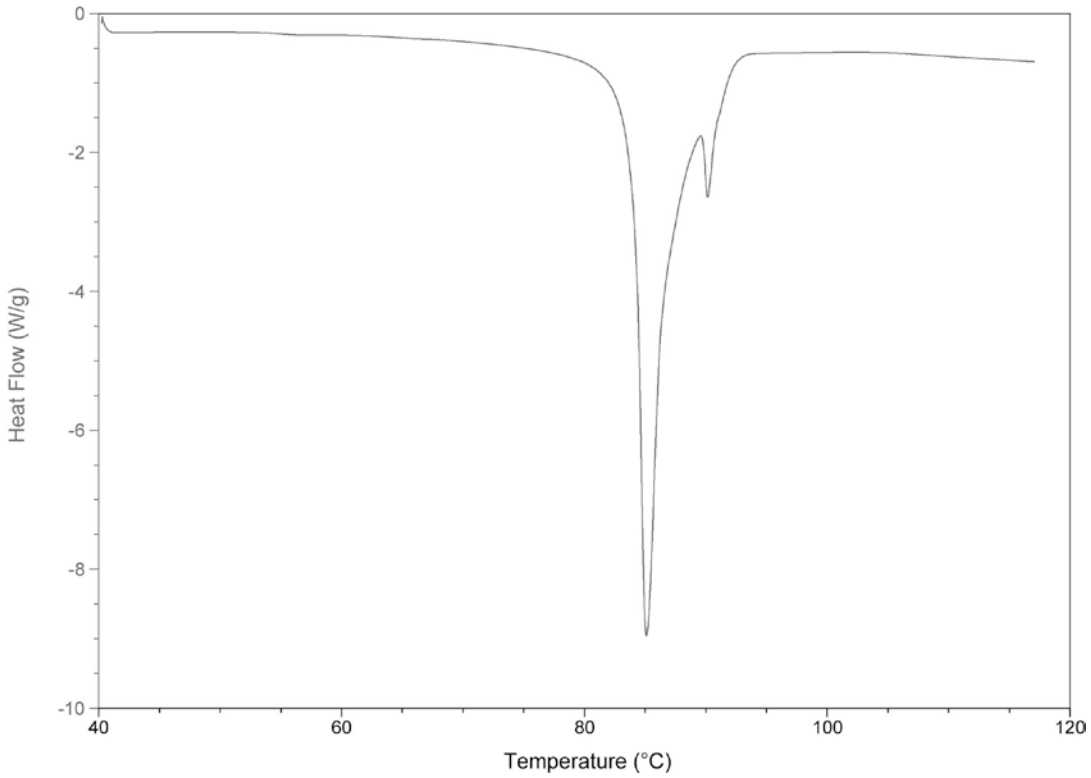

Figure S15. DSC thermogram of $(\mathbf{H_2im})_2SO_4 \cdot 2H_2O$ prepared by the reaction of **Him** and H_2SO_4 in a water:ethanol (1:9 v/v) mixture.

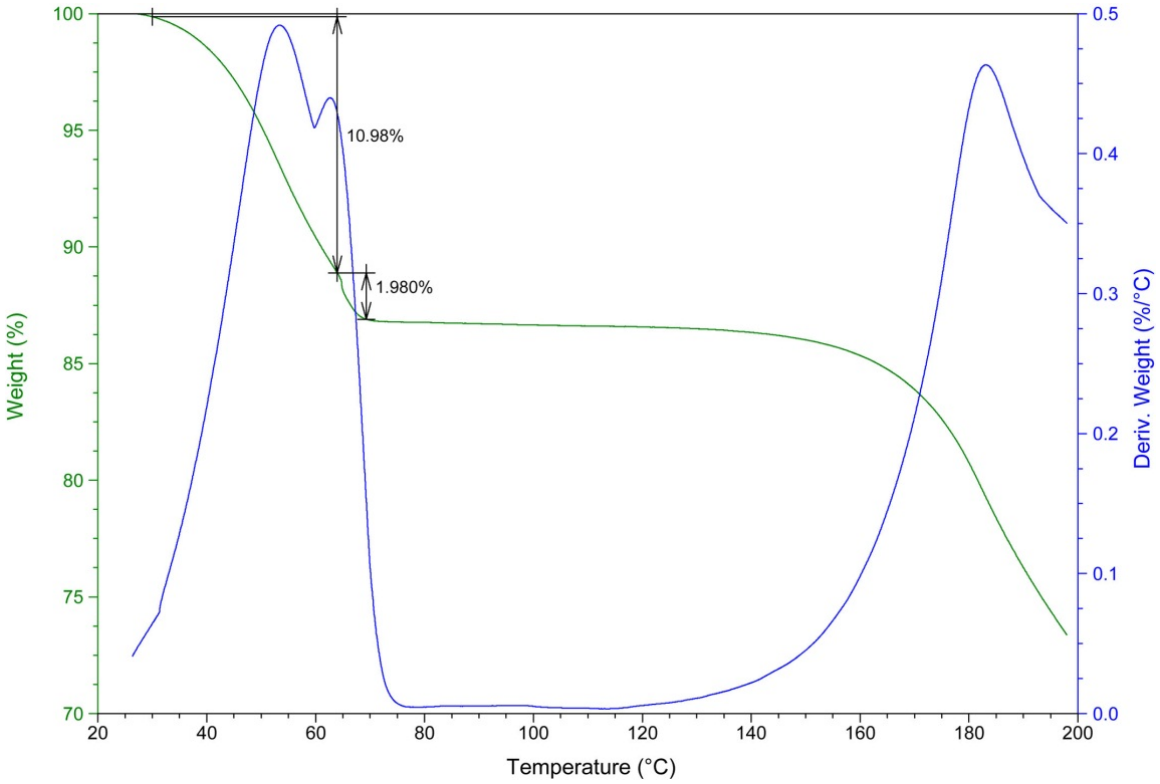

Figure S16. TGA thermogram of $(\mathbf{H_2im})_2SO_4 \cdot 2H_2O$ prepared by the reaction of **Him** and H_2SO_4 in a water:ethanol (1:9 v/v) mixture. Expected content of water: 13.3% Experimental weight loss below 80°C: 13.0%

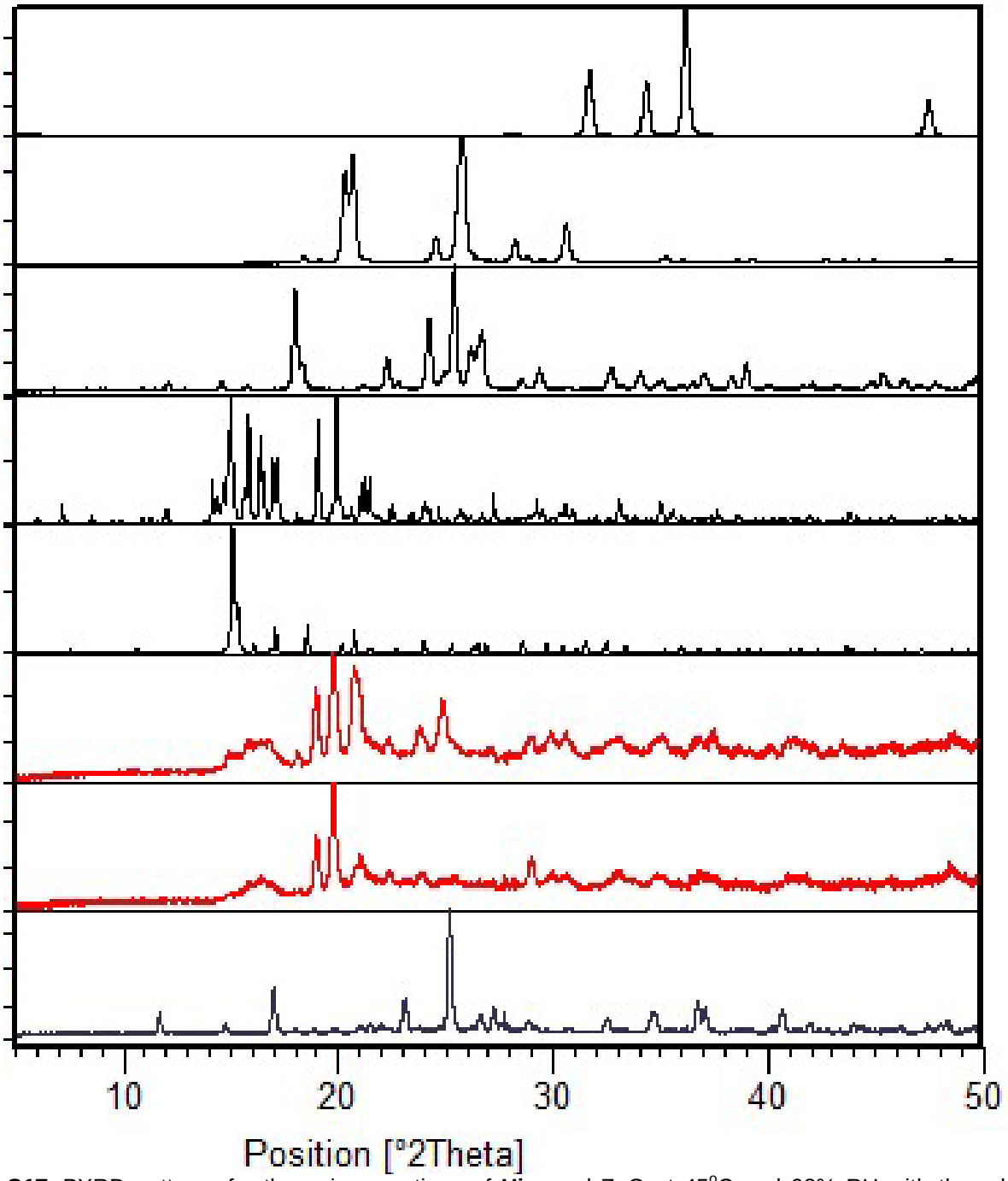

Figure S17. PXRD patterns for the aging reactions of **Him** and ZnO at 45°C and 98% RH with the addition of (**H_2im**)$_2SO_4 \cdot 2H_2O$. From top to bottom: : commercial ZnO; commercial **Him**; (**H_2im**)$_2SO_4 \cdot 2H_2O$ prepared by the reaction of **Him** and H_2SO_4 in a water:ethanol (1:9 v/v) mixture; simulated pattern for Zn_4(**im**)$_8$(**Him**) (CCDC KUMXEW) and simulated pattern for the zni-topology Zn(**im**)$_2$; fresh mixture of ZnO and **Him** with added (**H_2im**)$_2SO_4 \cdot 2H_2O$ and mixture of ZnO; **Him** with added (**H_2im**)$_2SO_4 \cdot 2H_2O$ after 7 days aging and mixture of ZnO and (**H_2im**)$_2SO_4 \cdot 2H_2O$ after 3 days aging.

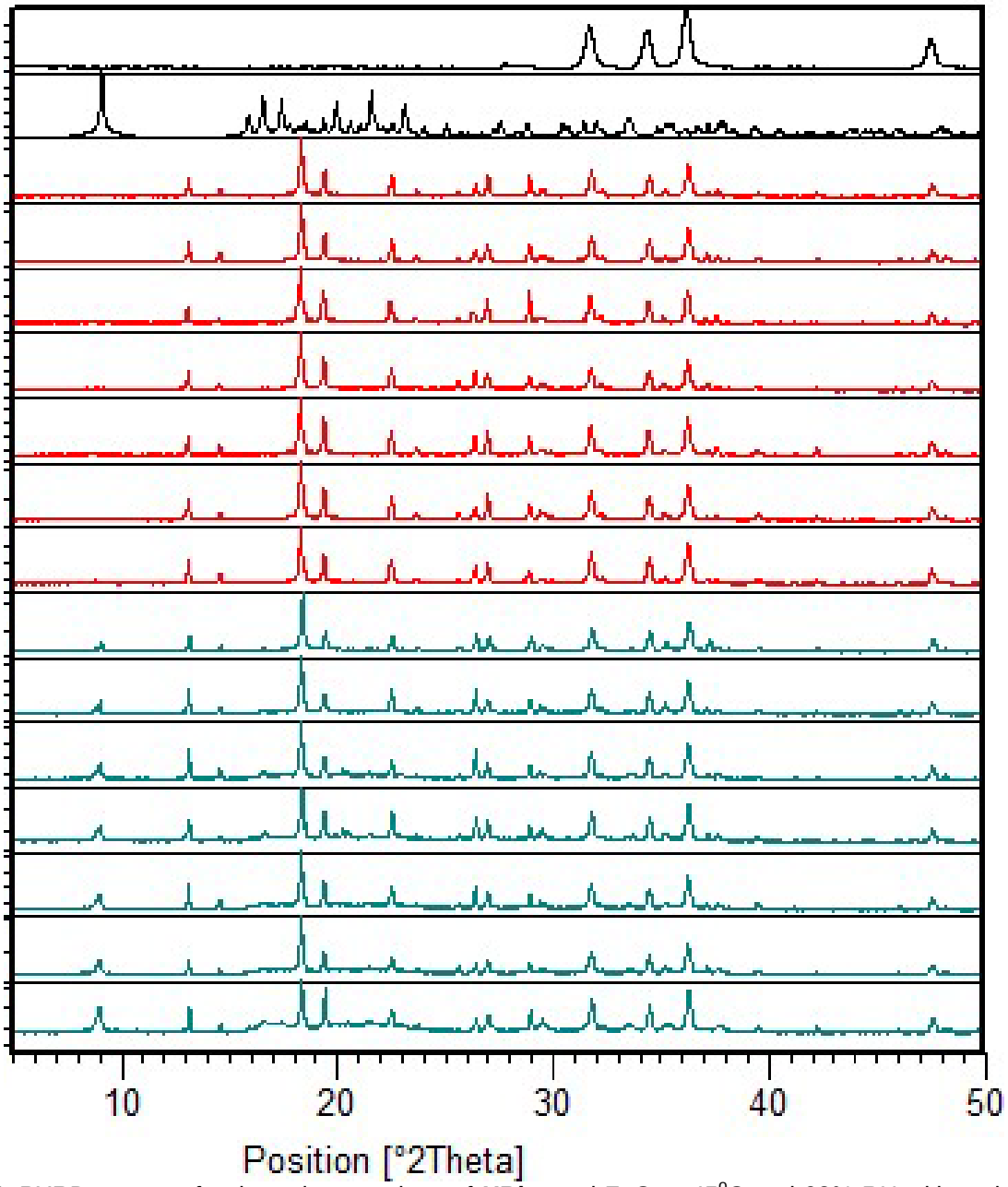

Figure S18. PXRD patterns for the aging reactions of **HBim** and ZnO at 45°C and 98% RH with and without the addition of $(NH_4)_2SO_4$. From top to bottom: : commercial ZnO; simulated pattern for non-porous Zn(**Bim**)$_2$ (CCDC code KOLYAM); mixture of ZnO and **HBim** after 3 days aging; mixture of ZnO and **HBim** after 6 days aging; mixture of ZnO and **HBim** after 9 days aging; mixture of ZnO and **HBim** after 12 days aging; mixture of ZnO and **HBim** after 15 days aging; mixture of ZnO and **HBim** after 19 days aging; mixture of ZnO and **HBim** after 33 days aging; mixture of ZnO and **HBim** with added $(NH_4)_2SO_4$ after 3 days aging; mixture of ZnO and **HBim** with added $(NH_4)_2SO_4$ after 6 days aging; mixture of ZnO and **HBim** with added $(NH_4)_2SO_4$ after 9 days aging; mixture of ZnO and **HBim** with added $(NH_4)_2SO_4$ after 12 days aging; mixture of ZnO and **HBim** with added $(NH_4)_2SO_4$ after 15 days aging; mixture of ZnO and **HBim** with added $(NH_4)_2SO_4$ after 19 days aging and mixture of ZnO and **HBim** with added $(NH_4)_2SO_4$ after 33 days aging.

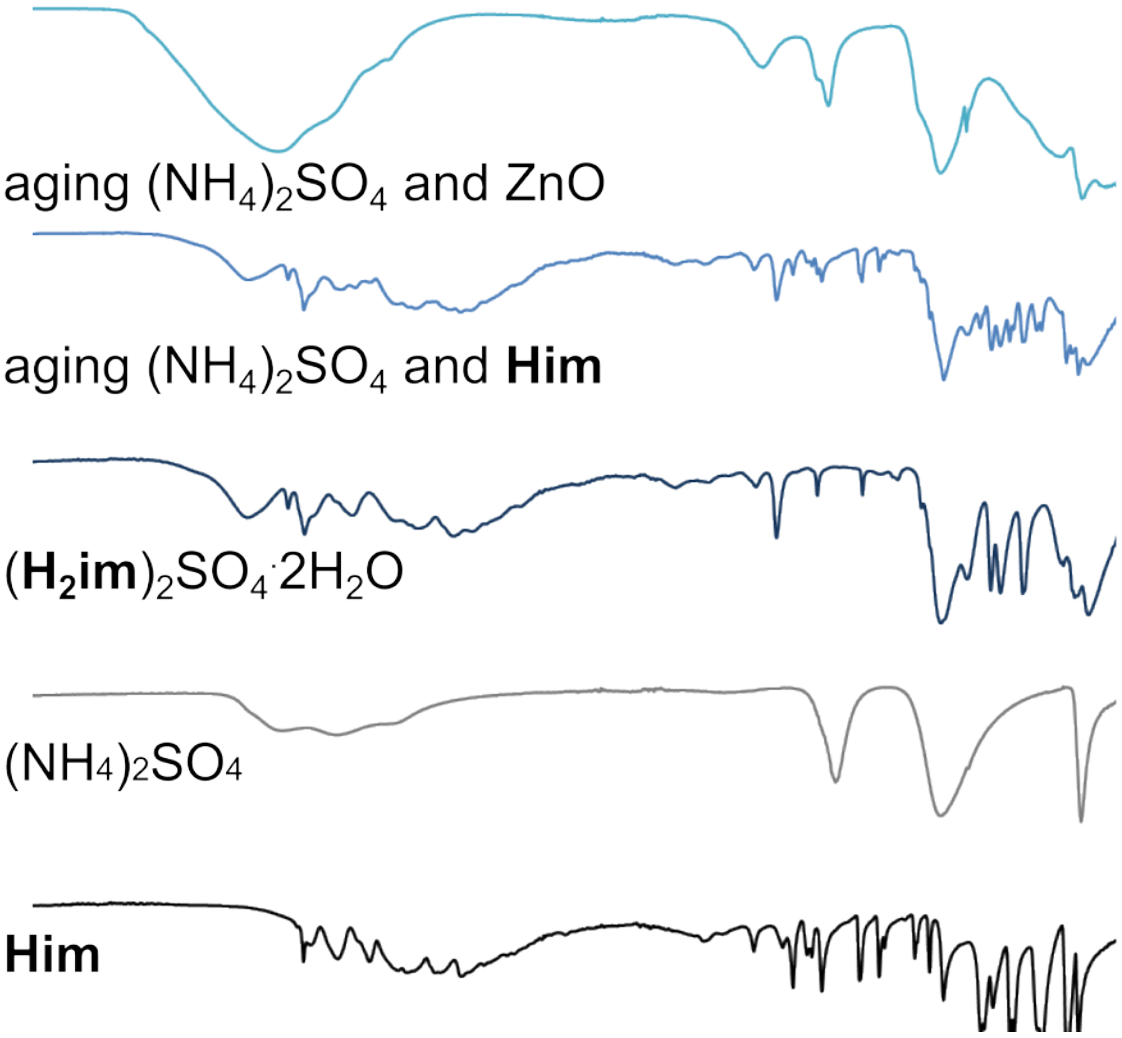

Figure S19. FTIR-ATR spectra of (top to bottom): mixture of ZnO and $(NH_4)_2SO_4$ after aging at 45°C and 98% RH (converted to $Zn(H_2O)_6(NH_4)_2(SO_4)_2$); mixture of **Him** and $(NH_4)_2SO_4$ after aging at 45°C and 98% RH (partially converted to $(\mathbf{H_2im})_2SO_4 \cdot 2H_2O$); $(\mathbf{H_2im})_2SO_4 \cdot 2H_2O$ prepared by the reaction of **Him** and H_2SO_4 in a water:ethanol (1:9 v/v) mixture; commercial $(NH_4)_2SO_4$ and commercial **Him**.

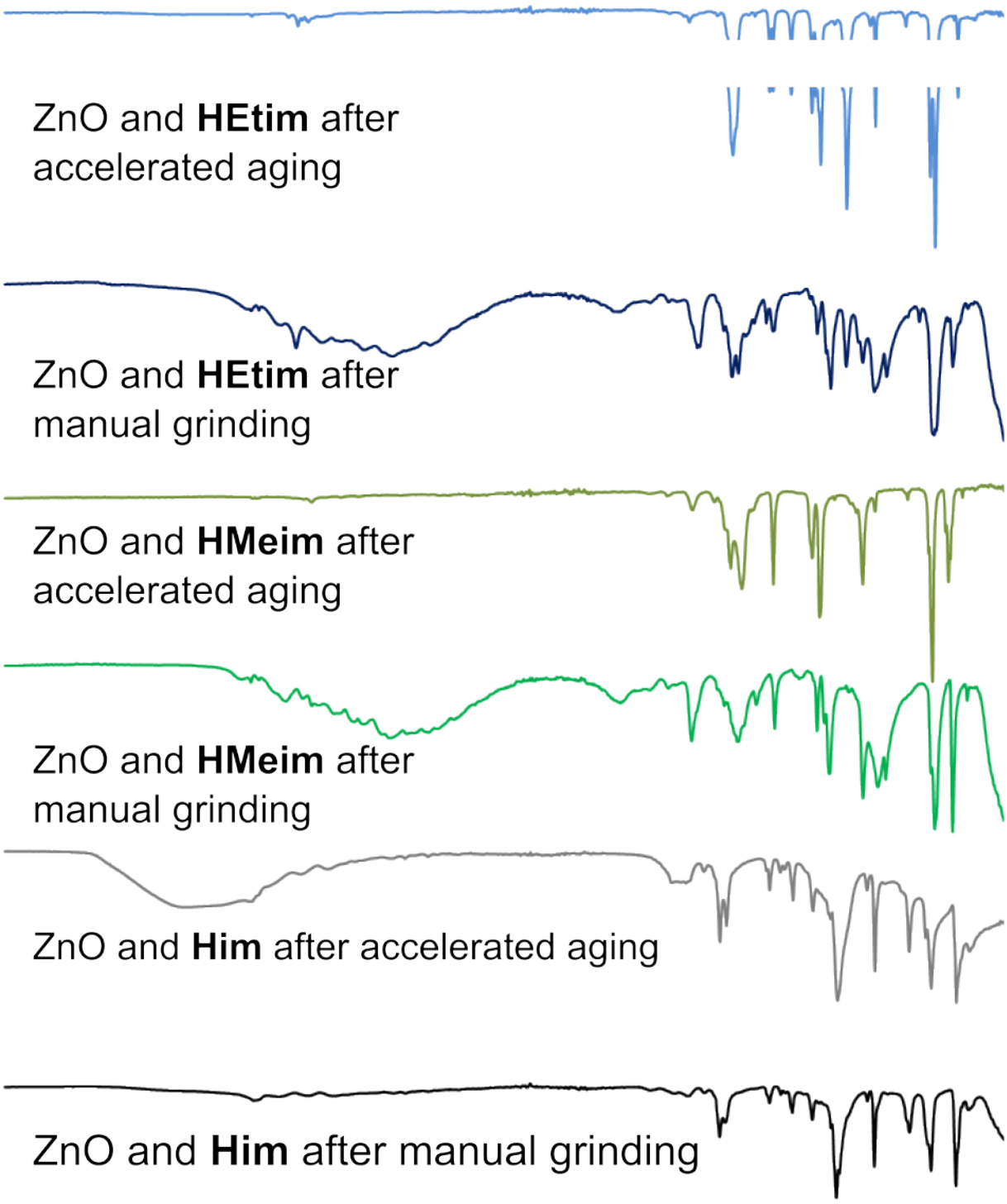

Figure S20. FTIR-ATR spectra of reaction mixtures before and after accelerated aging by exposure to 45oC and 98% RH in the presence of 4 mol% $(NH_4)_2SO_4$. Top to bottom: mixture of **HEtim** and ZnO before aging; mixture of **HEtim** and ZnO after aging; mixture of **HMeim** and ZnO before aging; mixture of **HMeim** and ZnO after aging; mixture of **Him** and ZnO before aging; mixture of **Him** and ZnO after aging. Comparison of the initial reaction mixture involving **Him** with the spectrum of **Him** (Figure S19) reveals reactivity upon manual grinding.

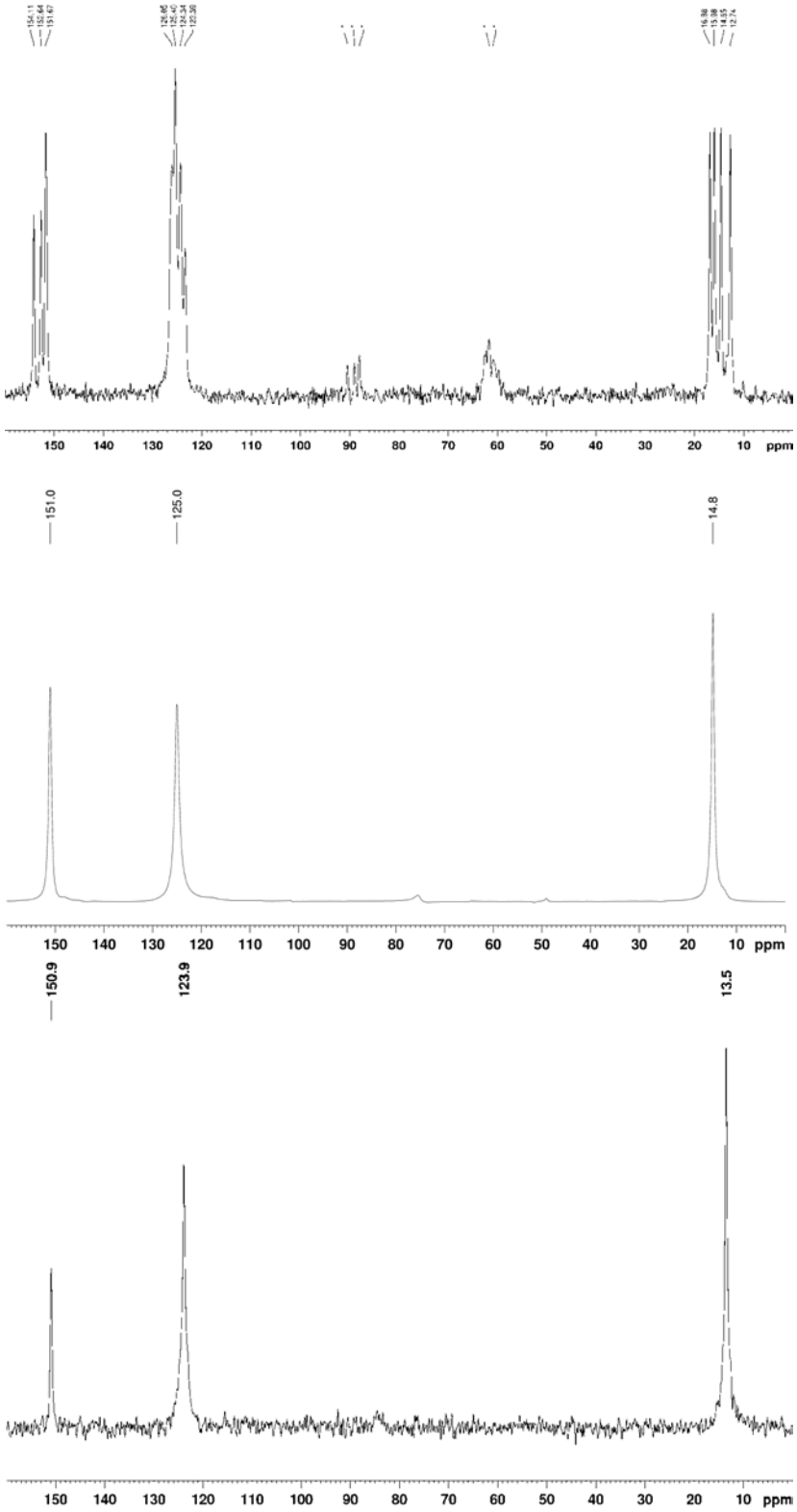

Figure S21. Comparison of solid-state CP-MAS ^{13}C NMR spectra for: (top) the *dia*-framework Zn(**Meim**)$_2$ prepared by "accelerated aging"; the same material after exposure to methanol vapours (middle) and the sodalite-topology ZIF-8 obtained through mechanochemical methods[6a] using DMF (bottom).

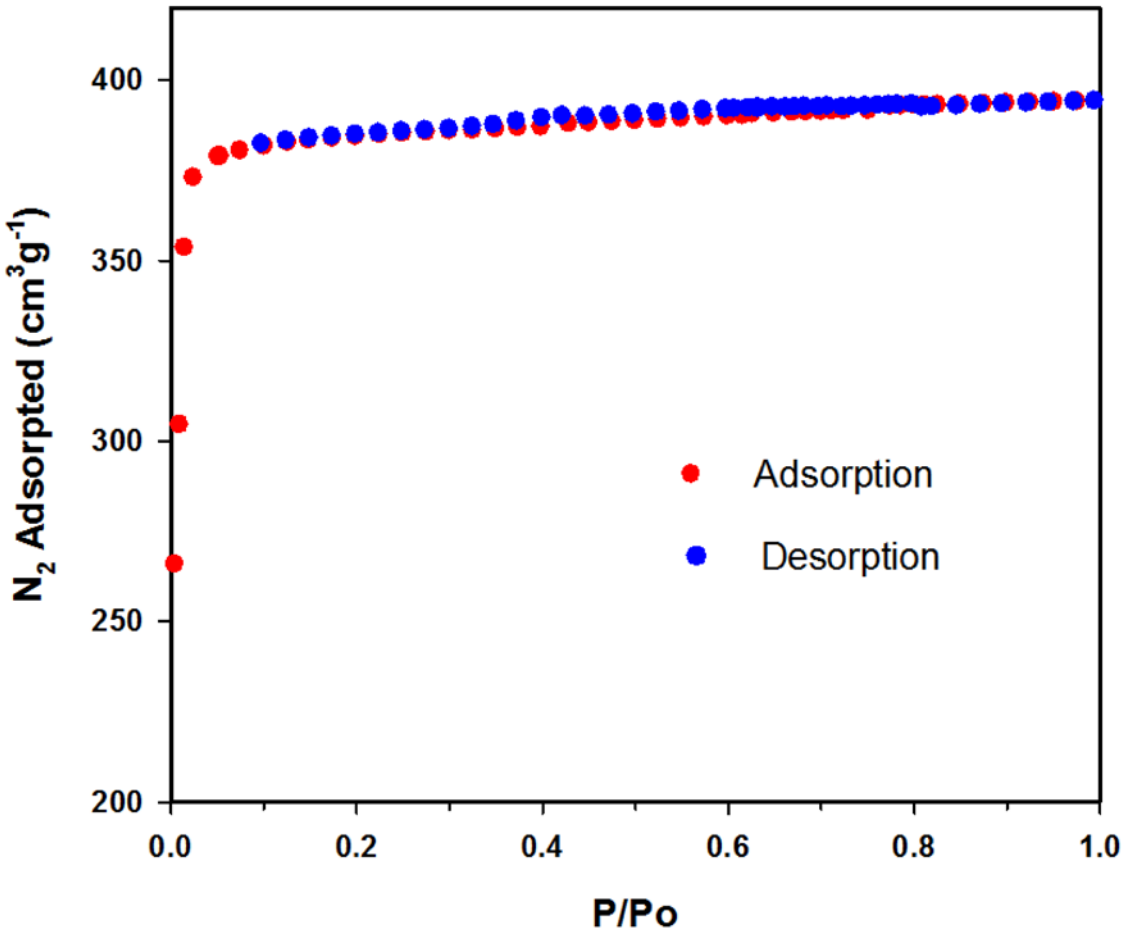

Figure S22. Nitrogen adsorption isotherms for the ZIF-8 material prepared by exposing the *dia*-framework Zn(**Meim**)$_2$ prepared by "accelerated aging" to methanol vapours, measured at 77 K and following overnight sitting *in vacuo* at 80 ^{o}C.