Electronic Supplementary Information

Formate modulated solvothermal synthesis of ZIF-8 investigated using time-resolved *in situ* X-ray diffraction and scanning electron microscopy

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Powder XRD

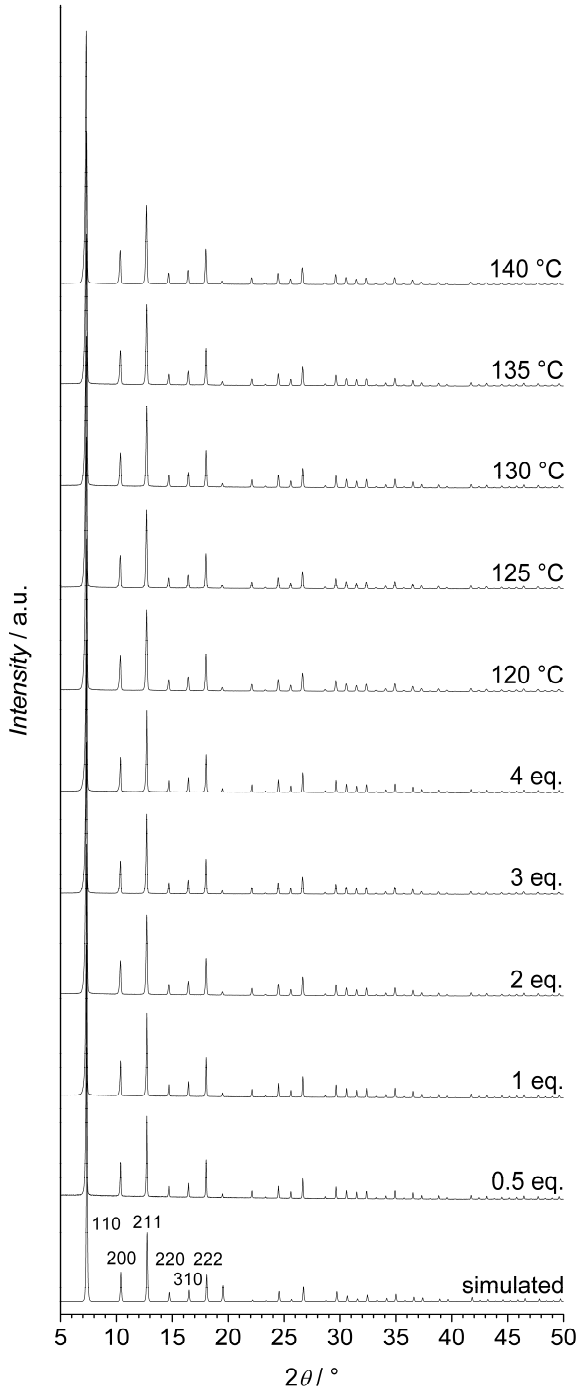

Fig. S1 Powder XRD patterns taken from the final products obtained by the monitored syntheses for the composition Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : 2 : 333 at different temperatures and for the varied compositions Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : x : 333 ($0.5 \leq x \leq 4.0$) at T = 130 °C. A pattern simulated from crystal structure data is also shown.

Sharp-Hancock Plots

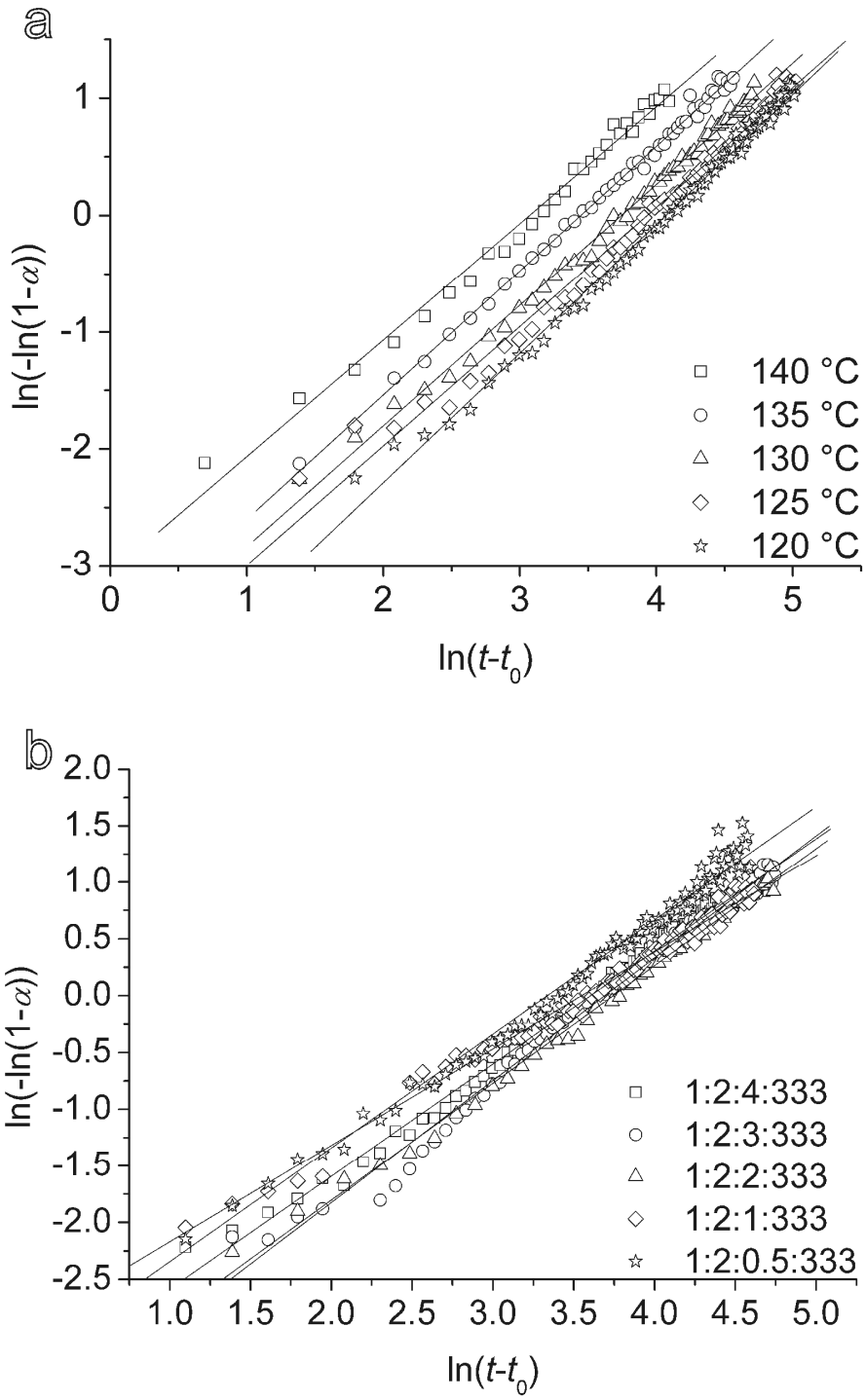

Fig. S2 Sharp-Hancock plots (a) for the composition Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : 2 : 333 at different temperatures and (b) for the varied compositions Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : x : 333 ($0.5 \leq x \leq 4.0$) at T = 130 °C.

Non-linear Avrami Erofe'ev Fits

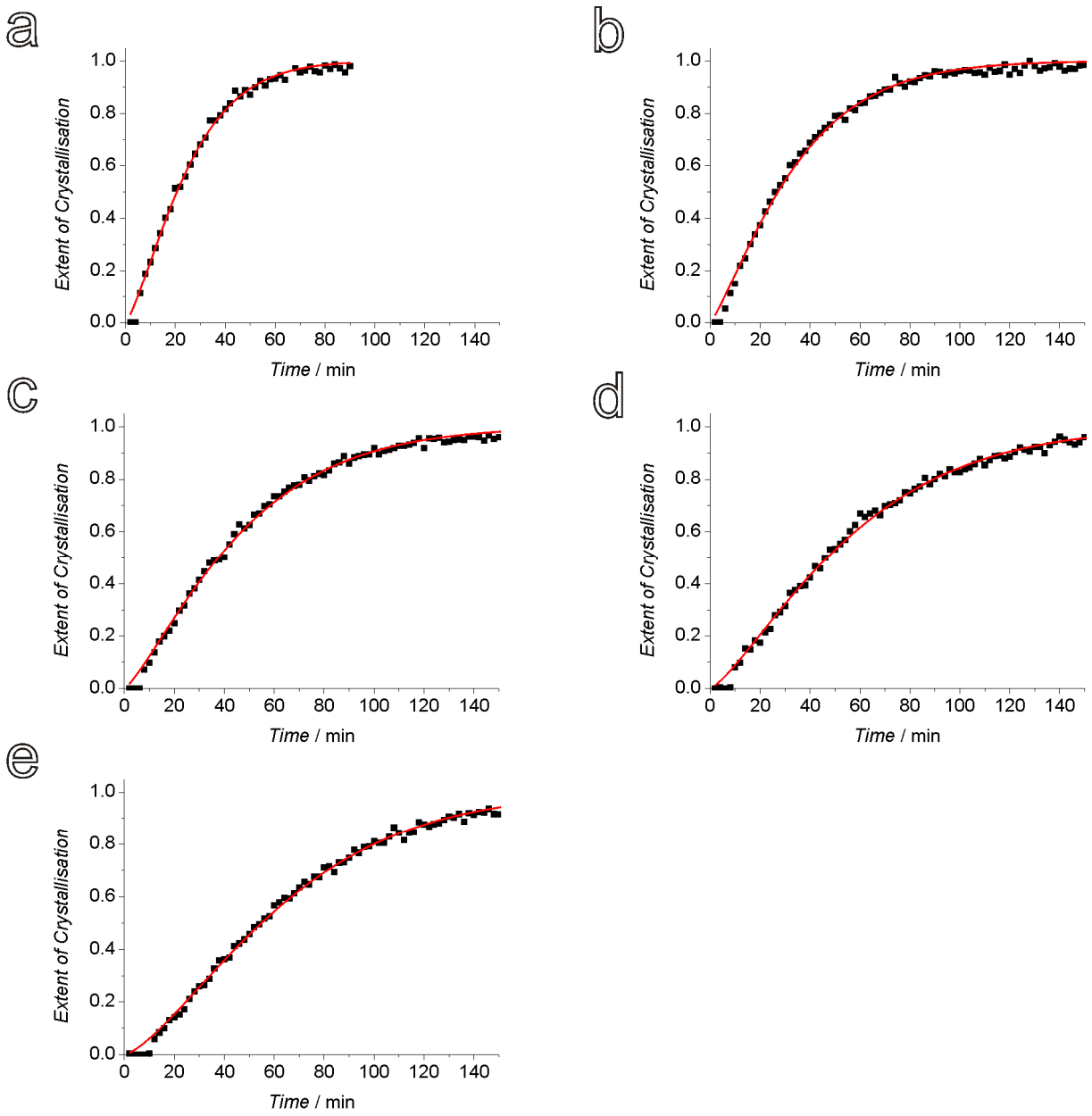

Fig. S3 Extent of crystallisation *vs.* time (black squares) for the composition Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : 2 : 333 at different temperatures [(a) 140 °C, (b) 135 °C, (c) 130 °C, (d) 125 °C and (e) 120 °C] and corresponding non-linear least-squares fits with the Avrami-Erofe'ev equation (red line).

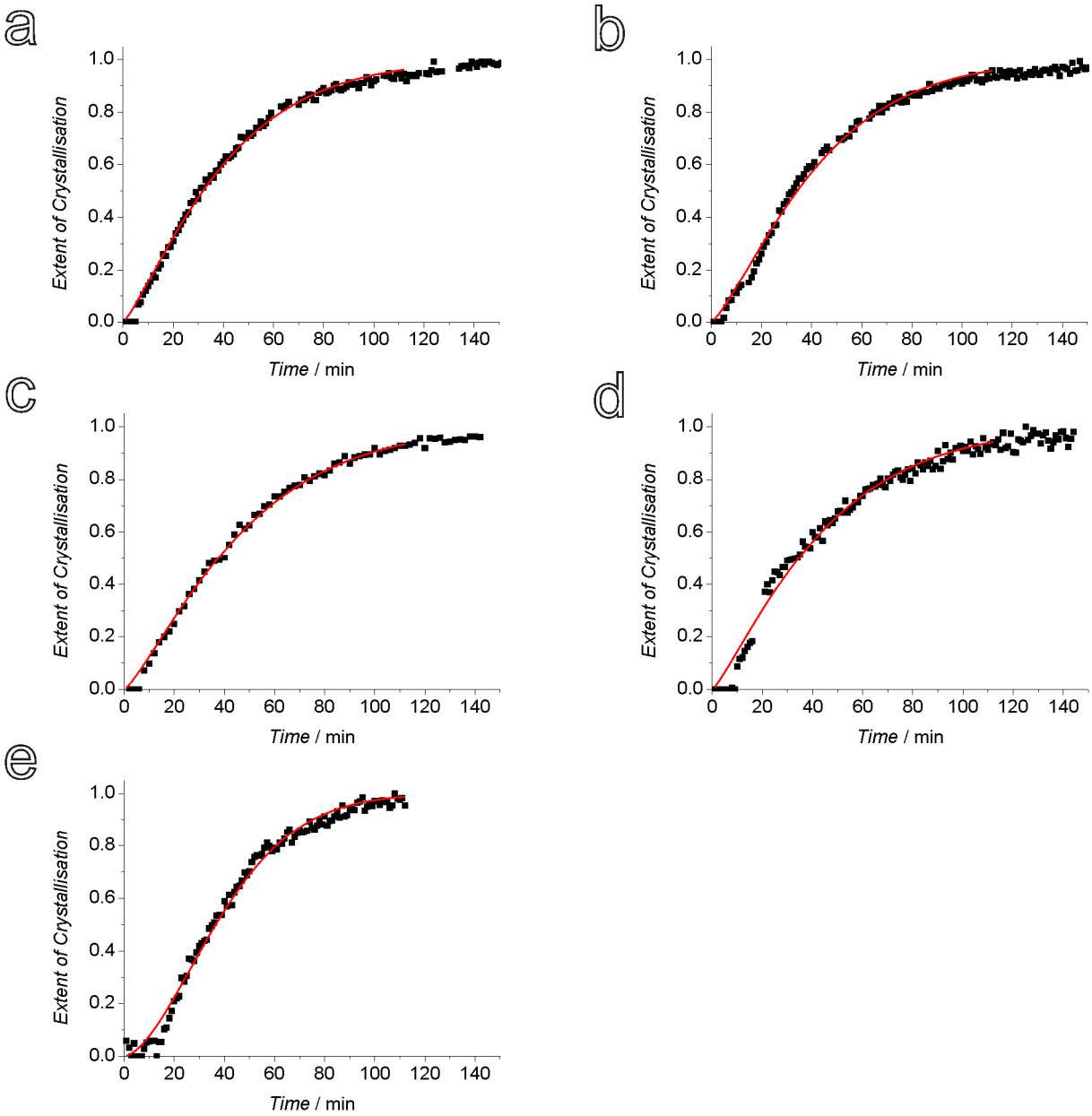

Fig. S4 Extent of crystallisation *vs.* time (black squares) for the varied compositions Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : *x* : 333 [(a) *x* = 4.0, (b) *x* = 3.0, (c) *x* = 2.0, (d) *x* = 1.0 and (e) *x* = 0.5] and corresponding non-linear least-squares fits with the Avrami-Erofe'ev equation (red line).

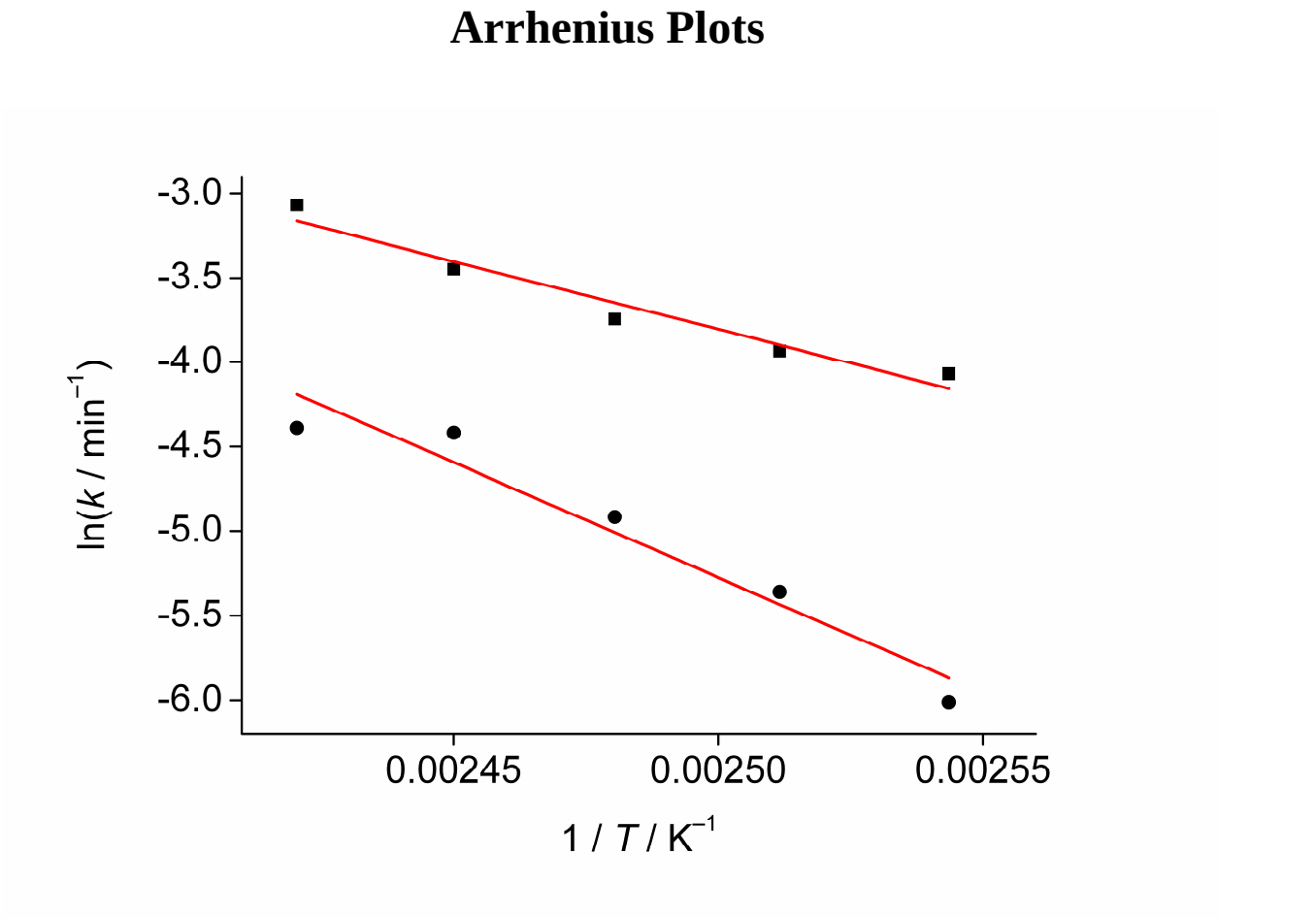

Fig. S5 Arrhenius plots for the temperature-dependent rate constants of the Sharp-Hancock anaylsis (black squares) and non-linear least-squares fitting with the Avrami-Erofe'ev equation (black circles).

Non-linear Gualtieri Fits

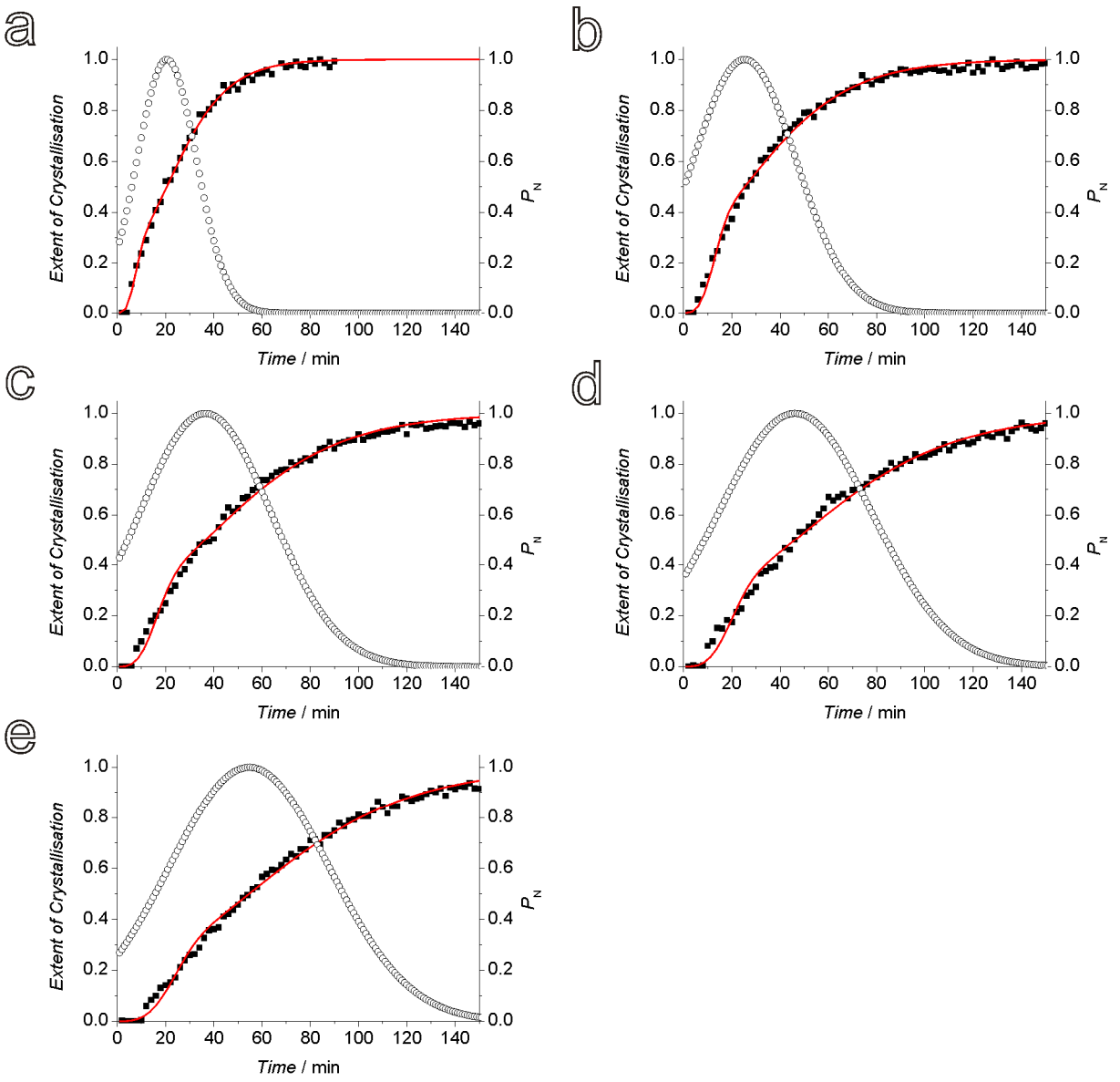

Fig. S6 Extent of crystallisation *vs.* time (black squares) for the composition Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : 2 : 333 at different temperatures [(a) 140 °C, (b) 135 °C, (c) 130 °C, (d) 125 °C and (e) 120 °C] and corresponding non-linear least-squares fits with the Gualtieri equation (red line) as well as probability curves of nucleation P_N (open circles).

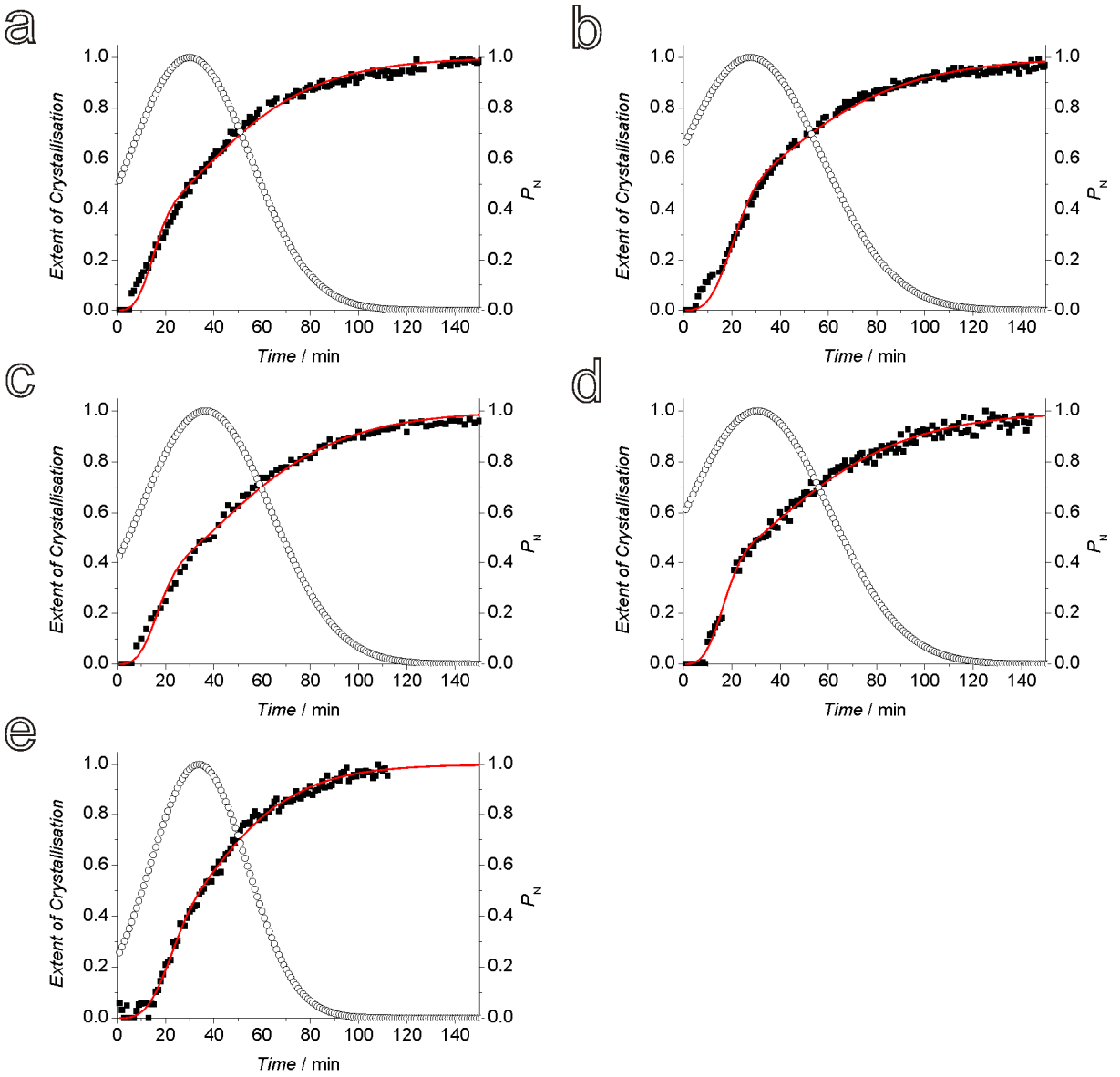

Fig. S7 Extent of crystallisation *vs.* time (black squares) for the varied compositions Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : *x* : 333 [(a) *x* = 4.0, (b) *x* = 3.0, (c) *x* = 2.0, (d) *x* = 1.0 and (e) *x* = 0.5] and corresponding non-linear least-squares fits with the Gualtieri equation (red line) as well as probability curves of nucleation P_N (open circles).

Final Maximum Crystal Size

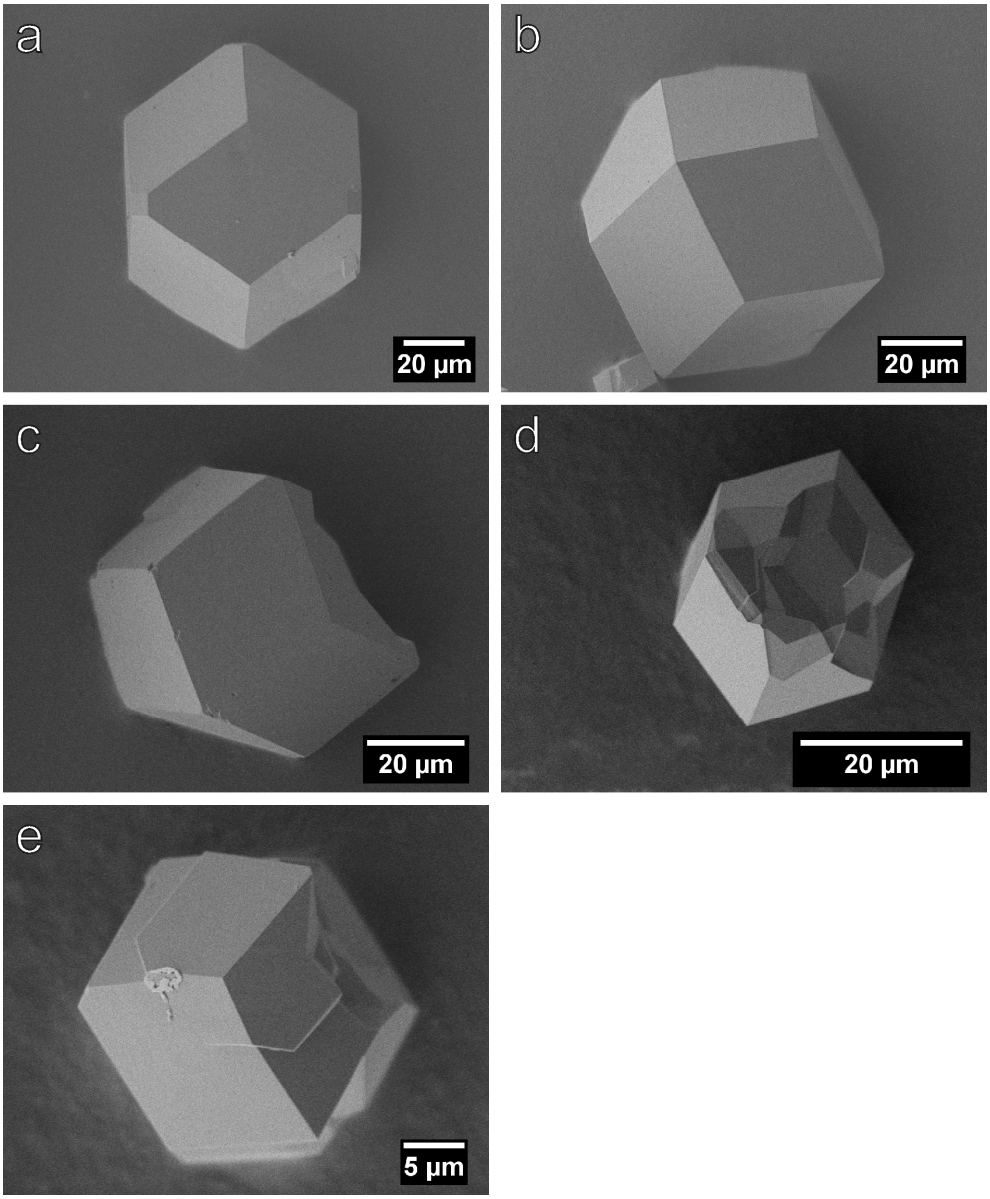

Fig. S8 SEM micrographs showing typical crystals of maximum size as obtained by the monitored syntheses for the compositions Zn/Hmim/$NaHCO_2$/MeOH = 1 : 2 : *x* : 333 [(a) *x* = 0.5, (b) *x* = 1.0, (c) *x* = 2.0, (d) *x* = 3.0 and (e) *x* = 4.0].

Table S1 Final maximum crystal sizes.

x	0.5	1.0	2.0	3.0	4.0
Crystal Size / µm	71	59	51	25	23

SEM Micrograph from Stirred Synthesis Solution

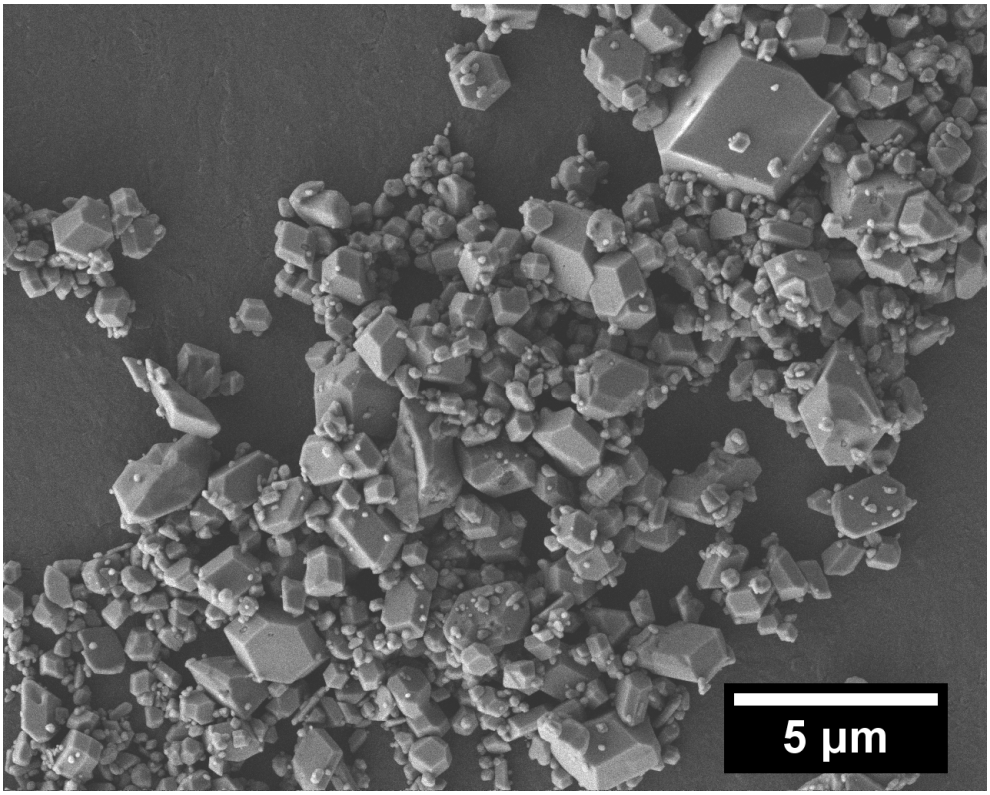

Fig. S9 SEM micrograph taken from solid material obtained from a stirred synthesis solution.

TG/DTA Analysis

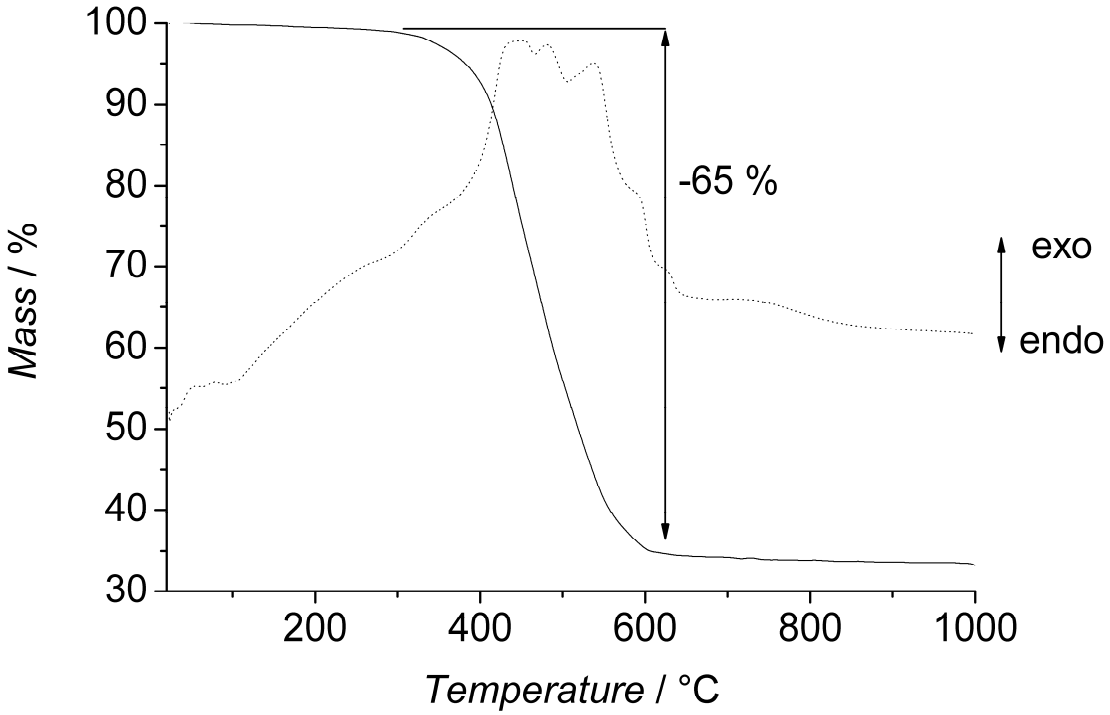

Figure S10 TG (solid line) and DTA curves (dotted line) measured from a sample obtained by the optimised synthesis. Ramp: 5 K / min, flowing air (Netzsch Thermal Analyser STA 429).
The total mass loss (65 %) agrees well with the calculated ones (64 %) assuming decomposition of ZIF-8 [$Zn(mim)_2$] into solid hexagonal ZnO (as verified by XRD) and volatile species stemming from the organic ligand.

Nitrogen Sorption Isotherms

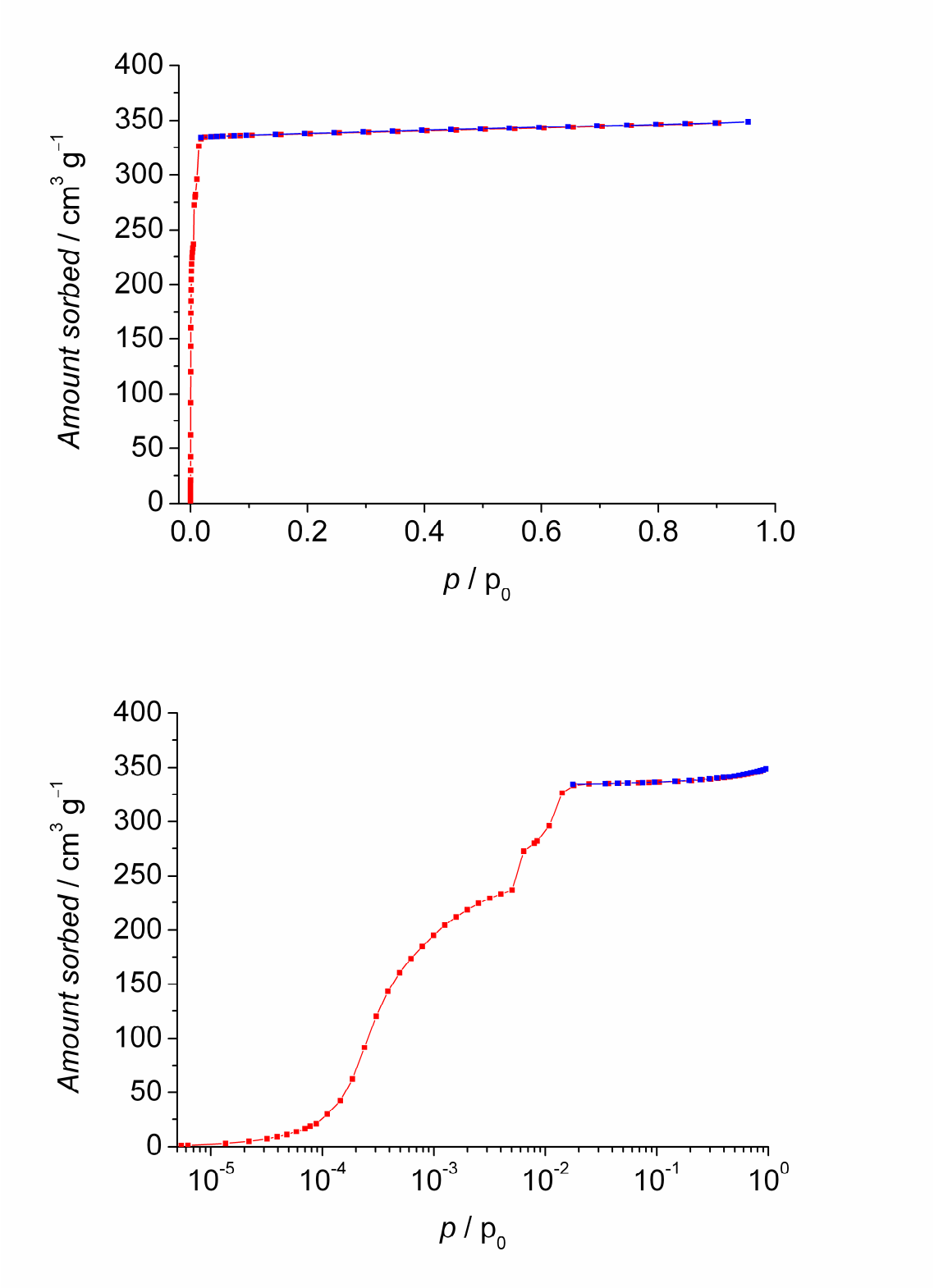

Figure S11 Nitrogen sorption isotherms at 77 K as linear-linear (top) and linear-log plots (bottom). Red and blue data correspond to the adsorption and desorption branches, respectively (Quantachrome Autosorb 1-MP).

The apparent specific surface area was determined by the Brunauer-Emmett-Teller (BET) method: S_{BET} = 1450 m^2/g.