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Supplementary Information

Porous zinc and cobalt 2-nitroimidazolate frameworks with six-membered ring windows and a layered cobalt 2-nitroimidazolate polymorph

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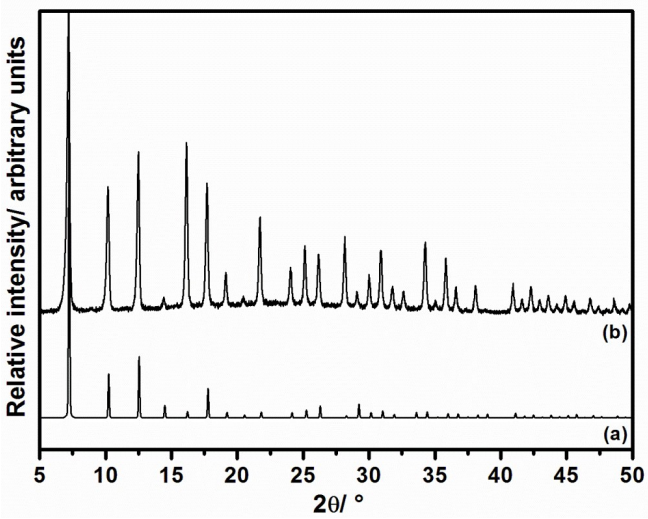

Figure S1. PXRD patterns of (a) the simulated PXRD from single crystal XRD data of ZIF-65(Zn) and (b) as-prepared ZIF-65(Zn).

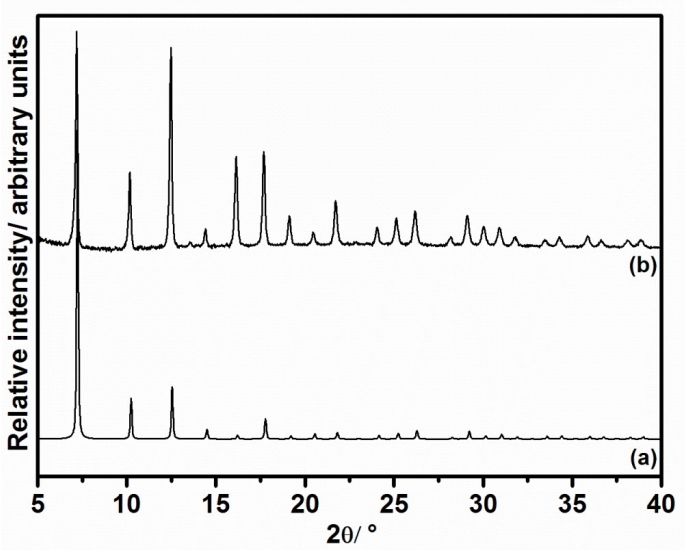

Figure S2. PXRD patterns of (a) the simulated PXRD from single crystal XRD data of ZIF-65(Co) and (b) as-prepared ZIF-65(Co).

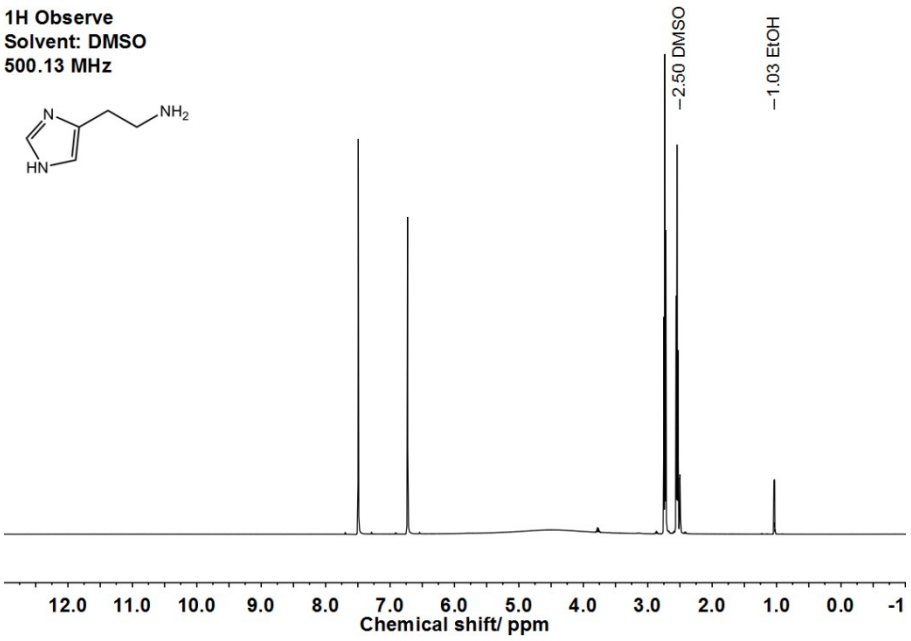

Figure S3. ^{1}H NMR spectrum of histamine (500 MHz, DMSO-d_6) δ 7.49 (d, J = 1.1 Hz, 1H, CH), 6.73 (d, J = 1.0 Hz, 1H, CH), 2.73 (t, J = 7.1 Hz, 2H, CH_2), 2.55 (t, J = 7.1 Hz, 2H, CH_2).

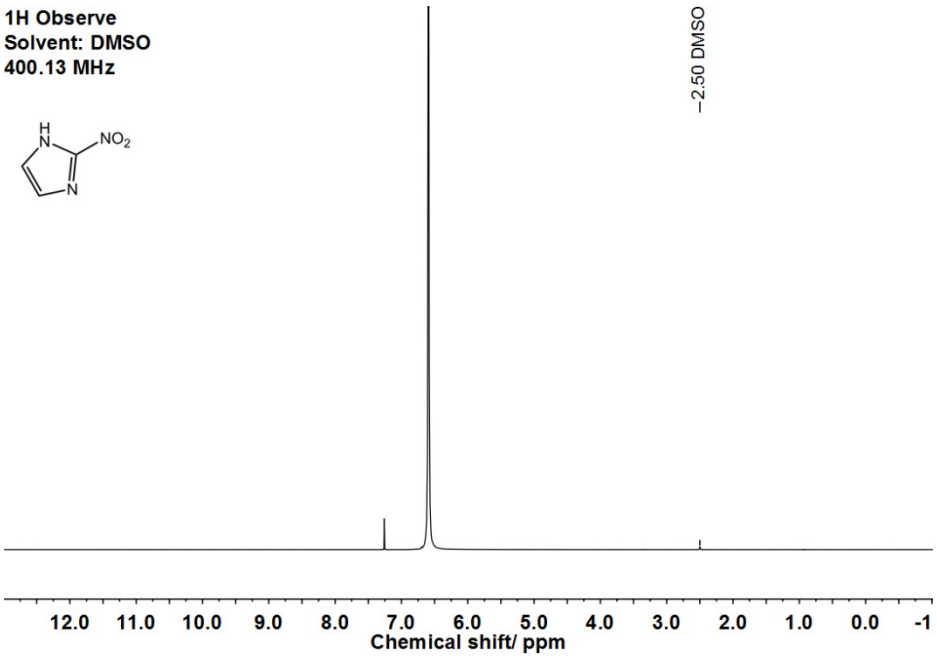

Figure S4. ^{1}H NMR spectrum of 2-nitroimidazole (400 MHz, DMSO-d_6) δ 7.26 (s, 2H, CH), 6.59 (s, HCl).

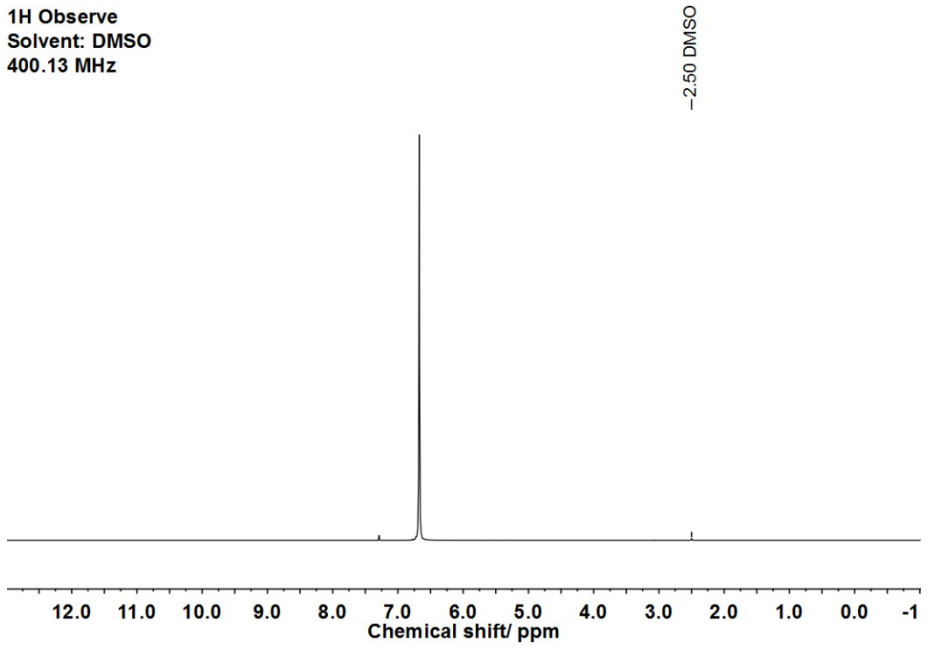

Figure S5. ^{1}H NMR spectrum of compound **1** from solvothermal preparation, dissolved (400 MHz, DMSO-d_6) δ 7.29 (s, 2H, CH), 6.67 (s, HCl).

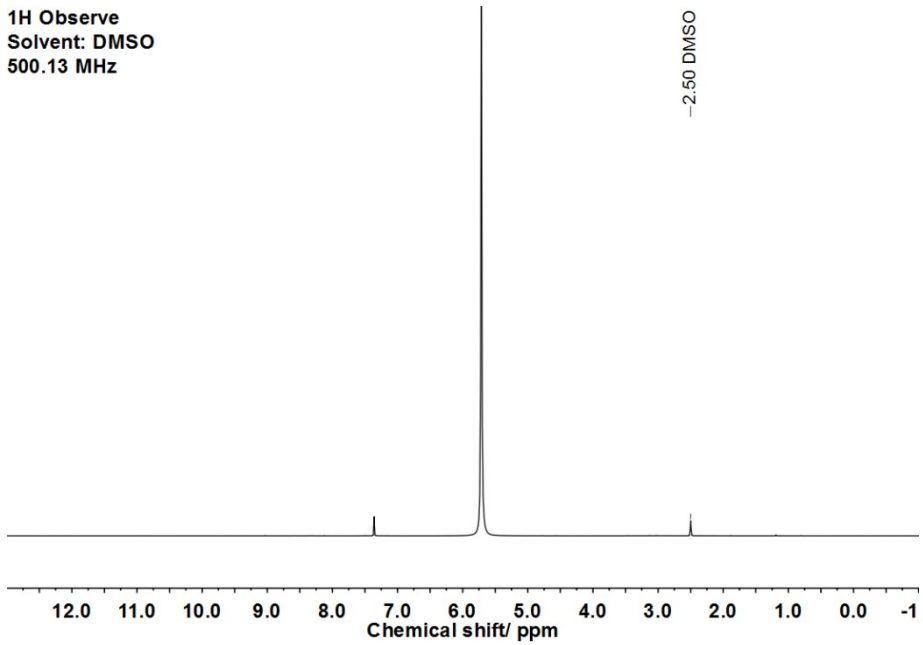

Figure S6. ^{1}H NMR spectrum of compound **2** from solvothermal preparation, dissolved (500 MHz, DMSO-d_6) δ 7.36 (s, 2H, CH), 5.71 (s, HCl).

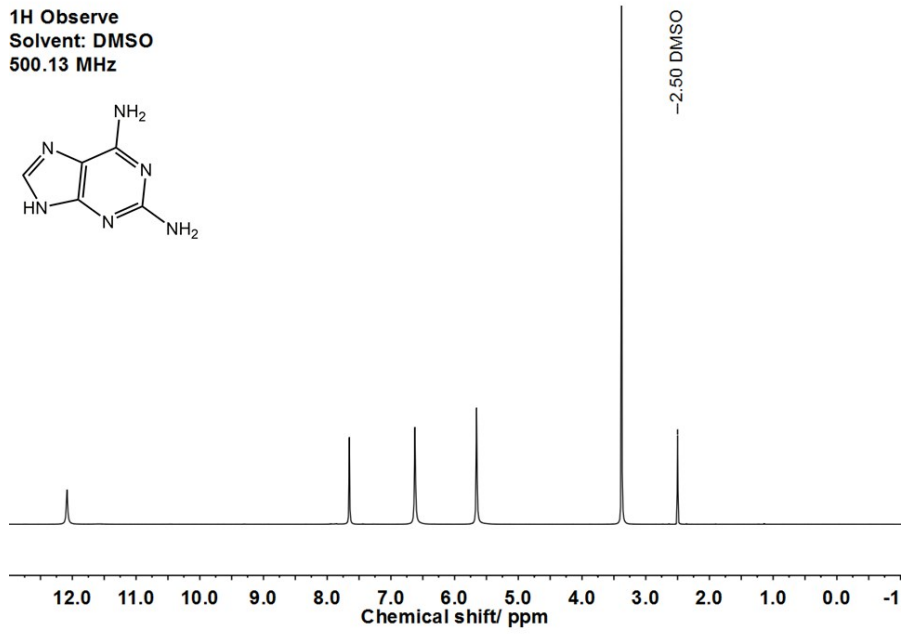

Figure S7. ^{1}H NMR spectrum of 2,6-diaminopurine (500 MHz, DMSO-d_6) δ 12.09 (s, 1H, NH), 7.65 (s, 1H, CH), 6.62 (s, 2H, NH_2), 5.66 (s, 2H, NH_2), 3.38 (s, H_2O).

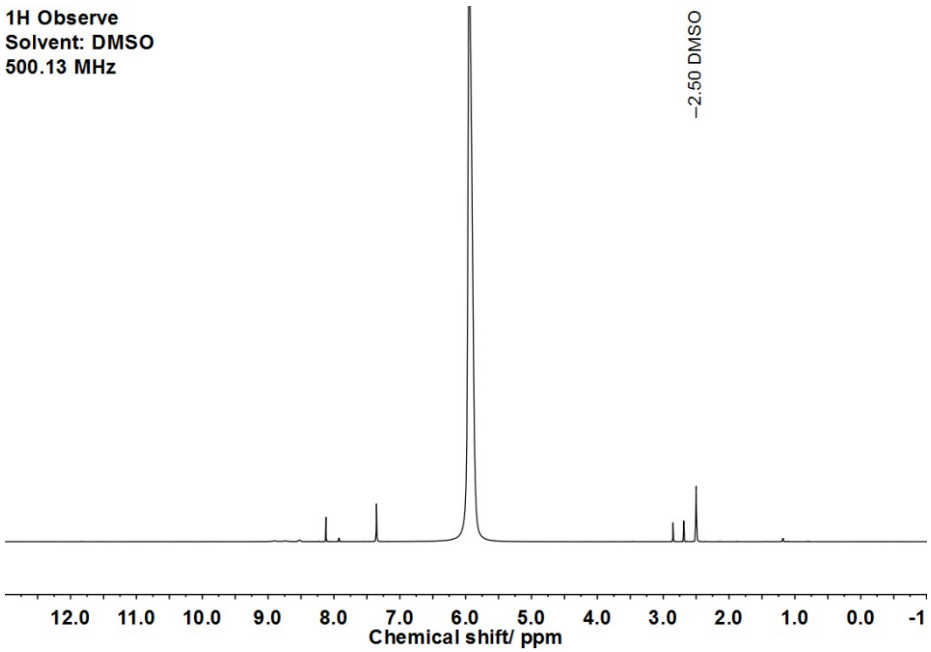

Figure S8. ^{1}H NMR spectrum of compound **3** from solvothermal preparation, dissolved (500 MHz, DMSO-d_6) δ 8.12 (s, DMF), 7.35 (s, 2H, CH), 5.95 (s, HCl), 2.85 (s, DMF), 2.96 (s, DMF).

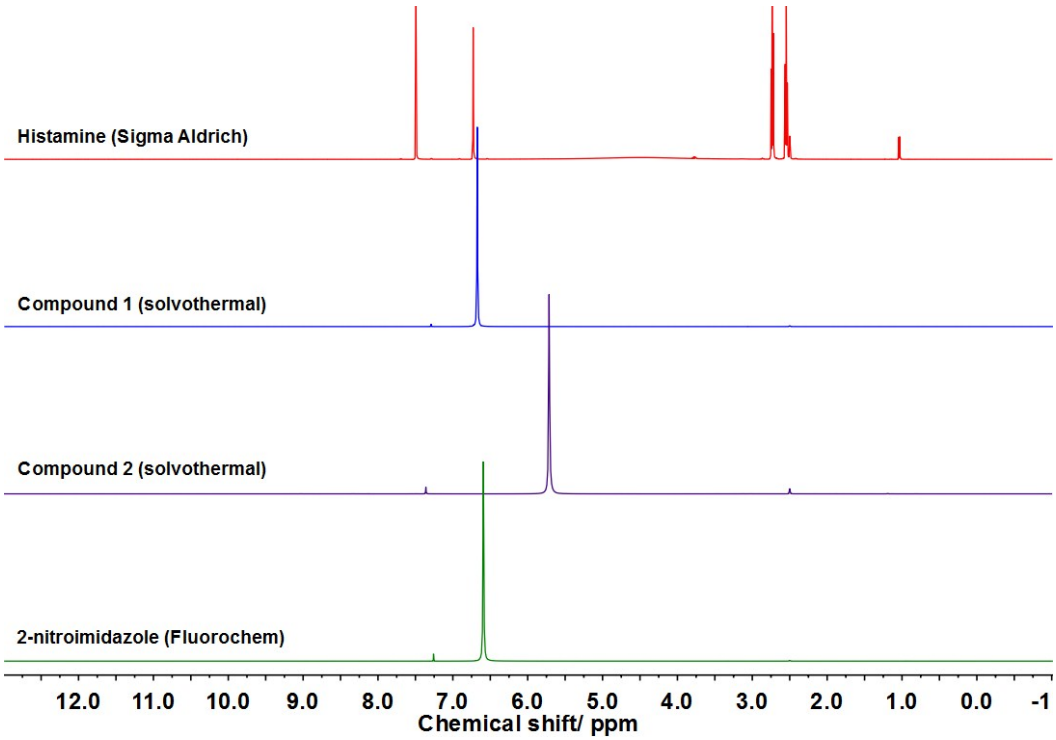

Figure S9. Stacked ^{1}H NMR of histamine (red) and dissolved compound **1** (blue), compound **2** (purple) and 2-nitroimidazole (green).

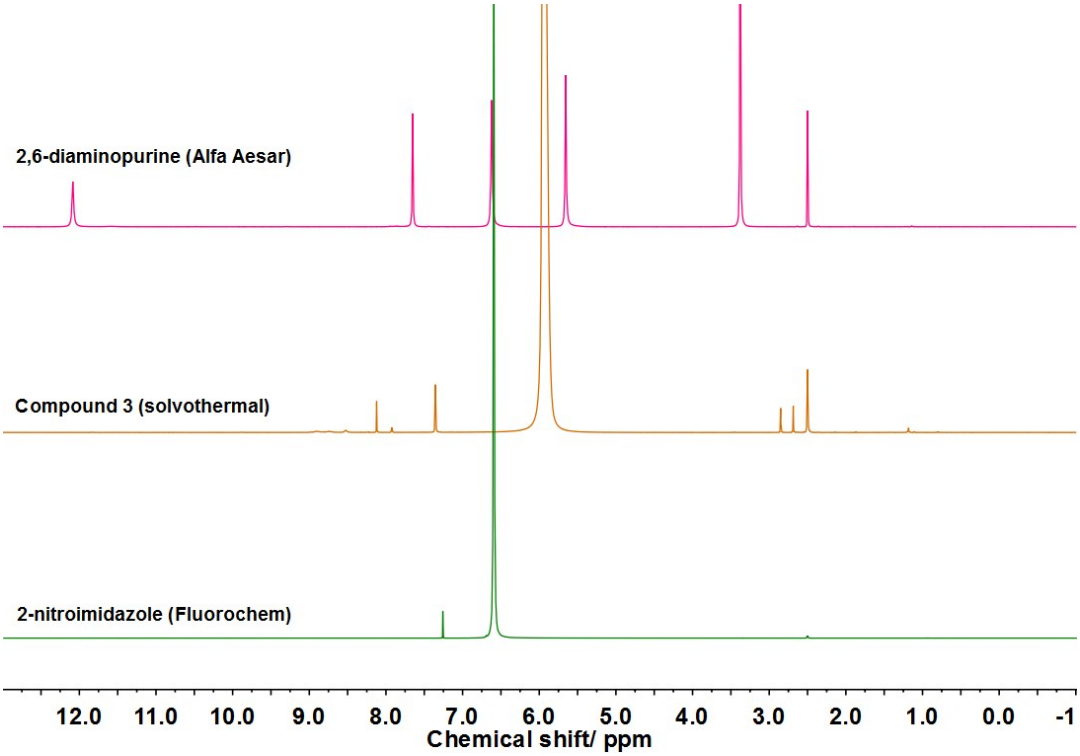

Figure S10. Stacked ^{1}H NMR of 2,6-diaminopurine (pink), dissolved compound **3** (orange) and 2-nitroimidazole (green).

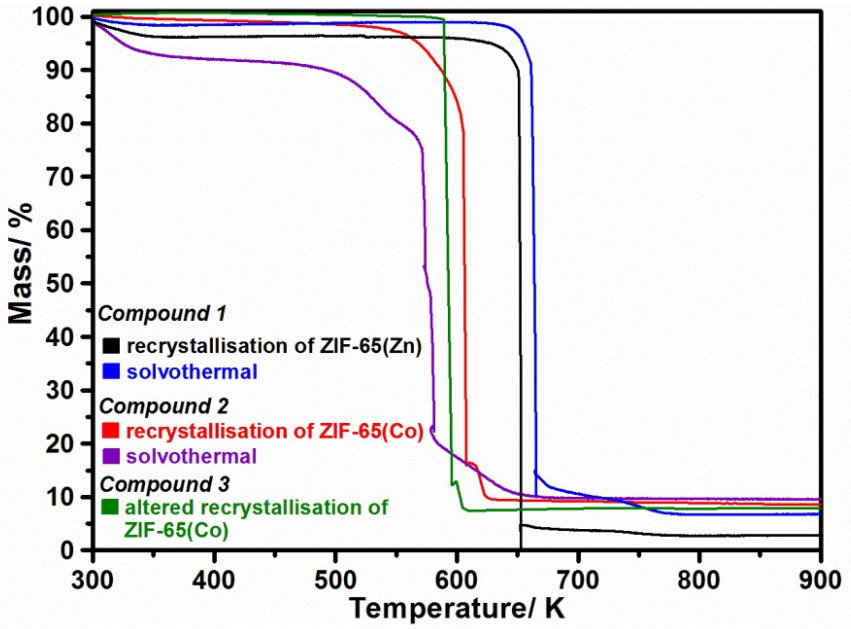

Figure S11. TGA (flowing air, ramp rate 5 °C min^{-1}) of as-prepared compound **1**, **2** and **3** from the described synthetic procedures.

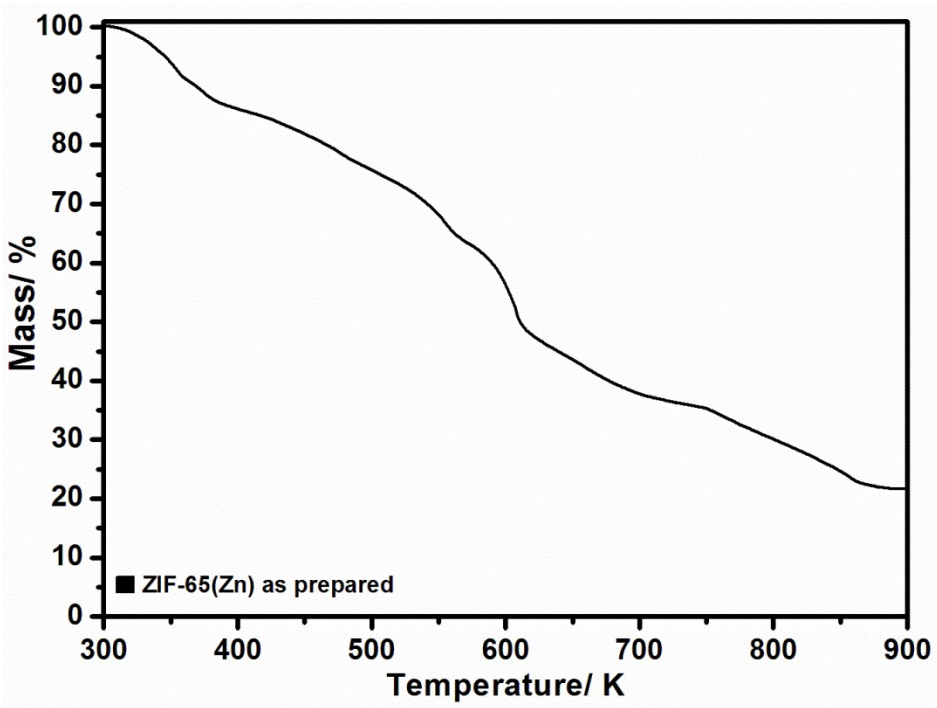

Figure S12. TGA (flowing air, ramp rate 5 °C min^{-1}) of as-prepared ZIF-65(Zn).

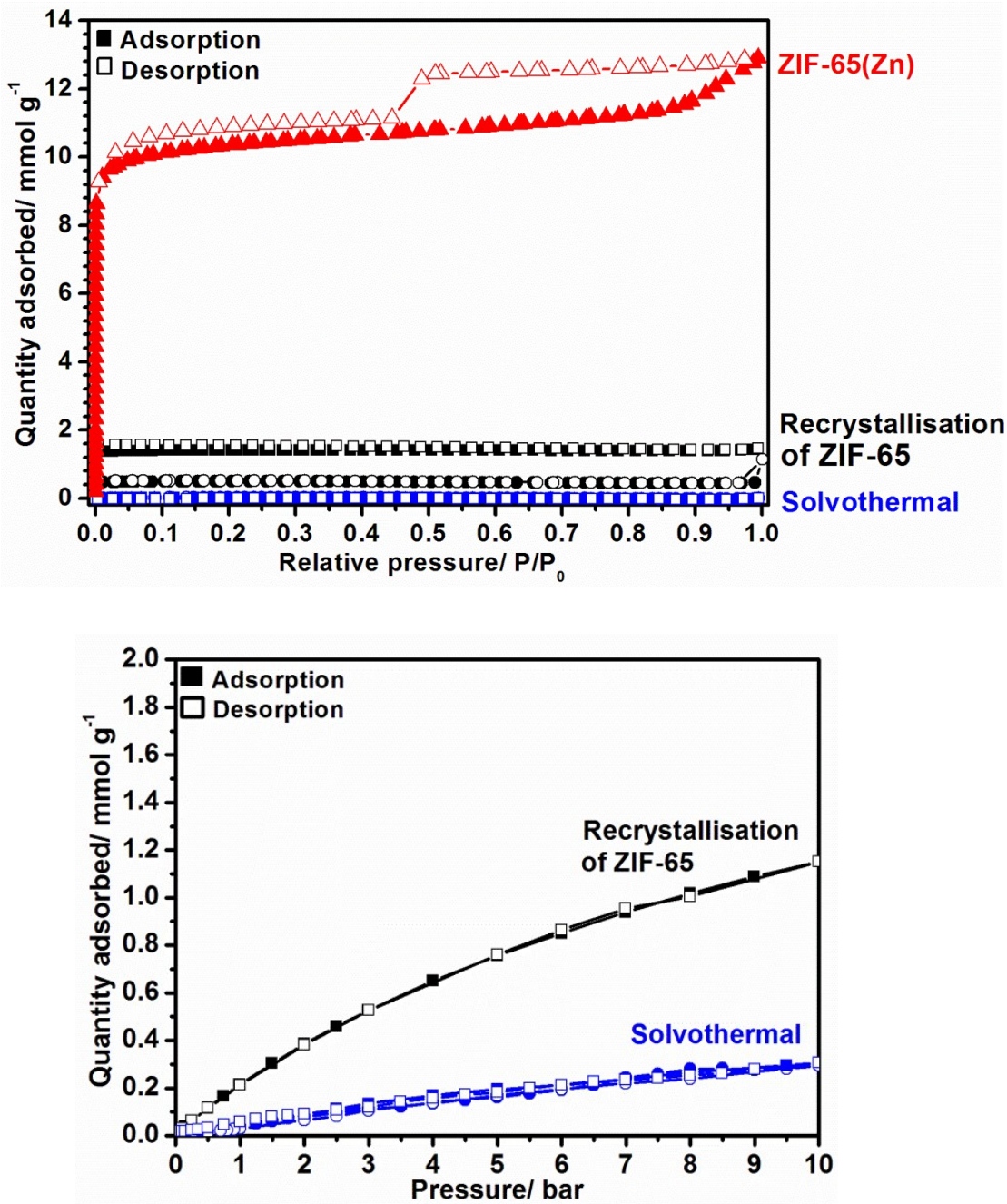

Figure S13. N_2 adsorption isotherms (-196 °C (top) and 25 °C (bottom)) for ZIF-65(Zn) (red) and compound **1** samples from the recrystallisation of ZIF-65(Zn) (black) and from direct solvothermal synthesis (blue). Activation conditions: 110 °C (circles), 140 °C (squares) and 200 °C (triangles) for 6 hours.

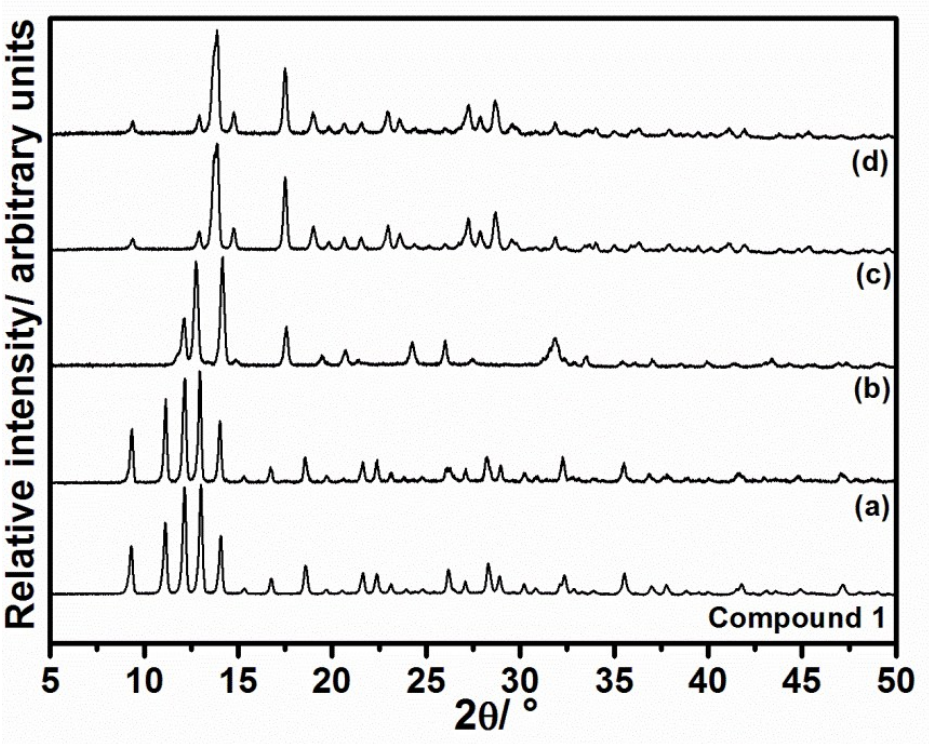

Figure S14. PXRD patterns of as-prepared compound **1** (bottom) and after various stability tests: (a) furnace heated (60 °C, 18 h, N_2+H_2O flow), (b) immersion in water (room temperature, 72 h), (c) water reflux (24 h) followed by (d) re-immersion in MeOH (room temperature 48 h).

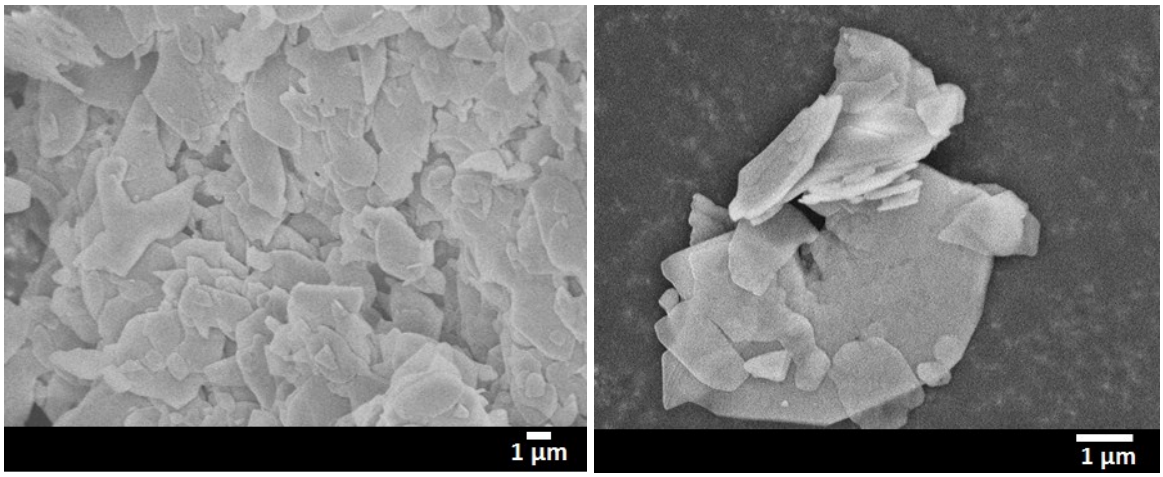

Figure S15. SEM images of compound **1** after refluxing in water (24 h).

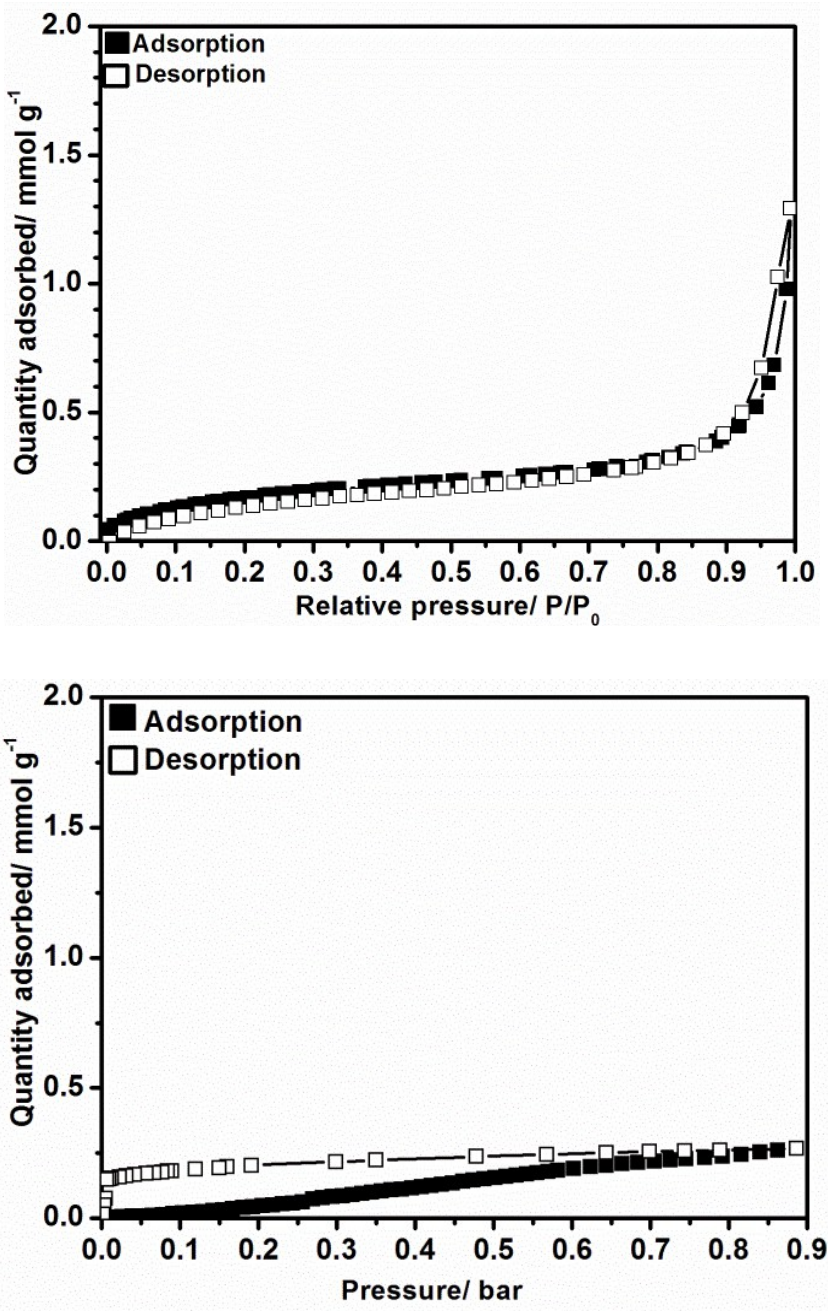

Figure S16. N_2 (-196 °C, top) and CO_2 (25 °C, bottom) isotherms of a dense phase achieved from refluxing compound **1** in water. Activation conditions: 140 °C for 6 hours.

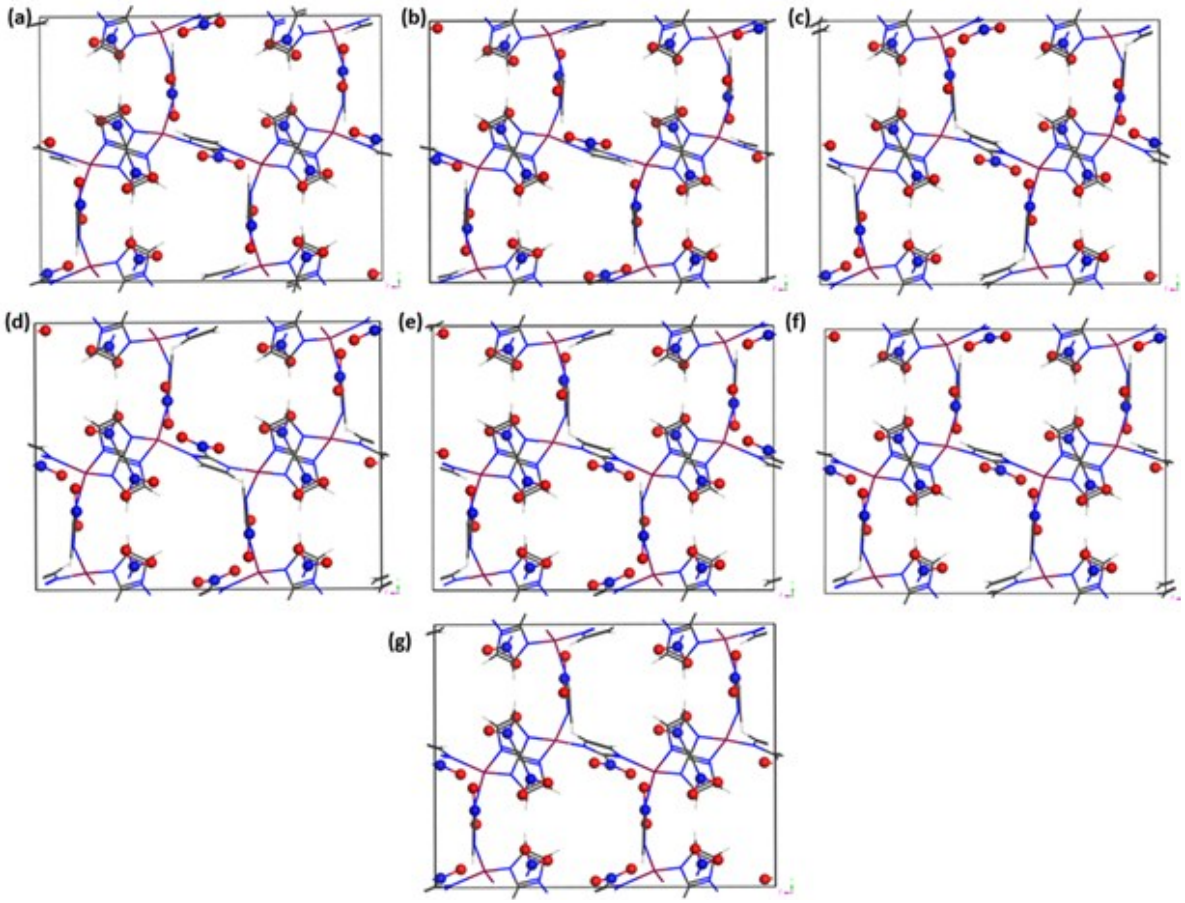

Figure S17. DFT-geometry optimized structures of the seven plausible models of compound **1** viewed along the *a* vector direction. Models: 1 (a), 2 (b), 3 (c), 4 (d), 5 (e), 6 (f) and 7 (g). Zn, orange; C, grey; O, red; N, blue; H, white.

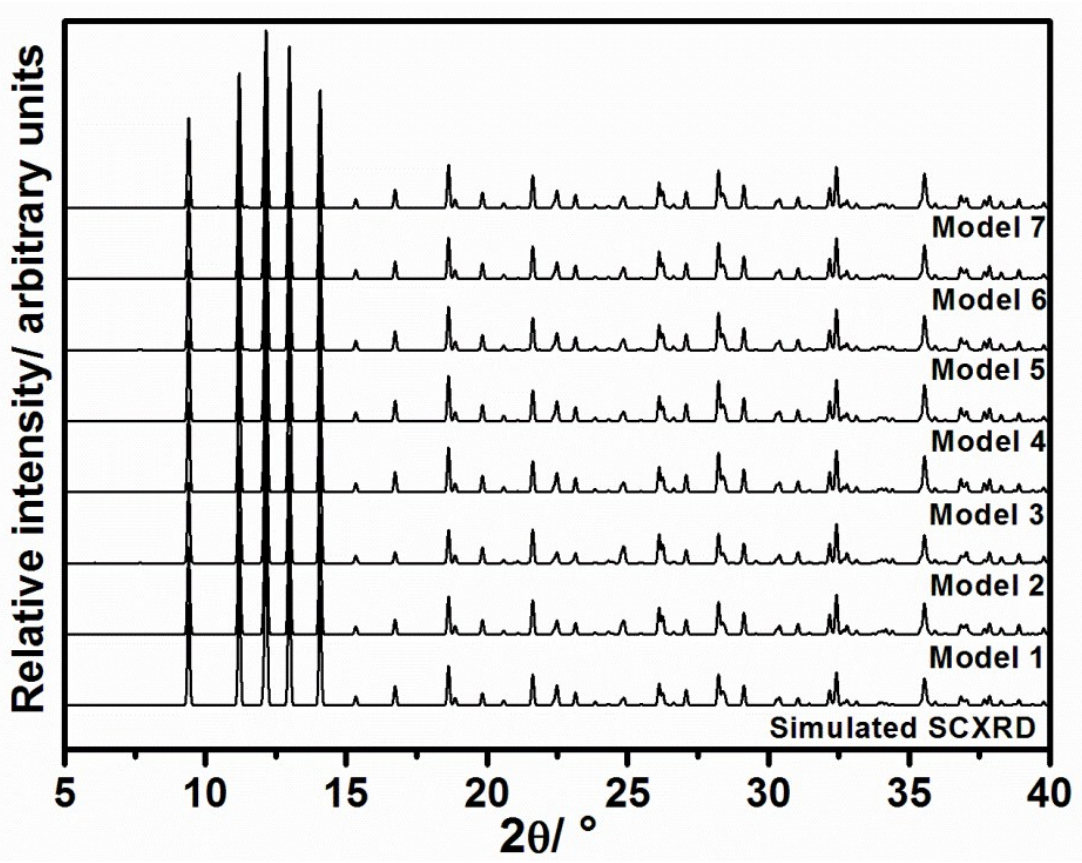

Figure S18. SCXRD of compound **1** compared to the calculated PXRD patterns for the seven DFT-geometry optimized structures of compound **1**.

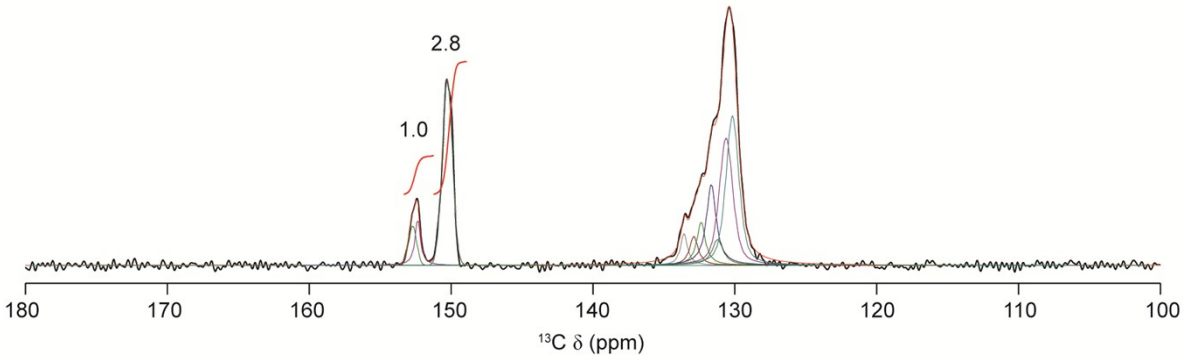

Figure S19. Fitting of the ^{13}C (9.4 T, 12.5 kHz MAS) CP MAS NMR spectrum of compound **1**, performed using dmfit, with the (integrated) intensity ratio of the two **C**−NO_2 resonances (1.0:2.8) shown.

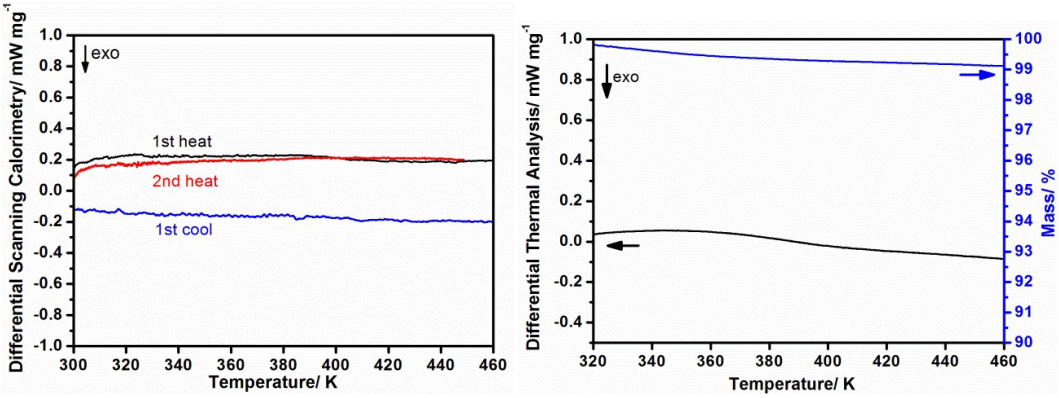

Figure S20. DSC (left) and DTA (right) of compound **1** (in flowing air).

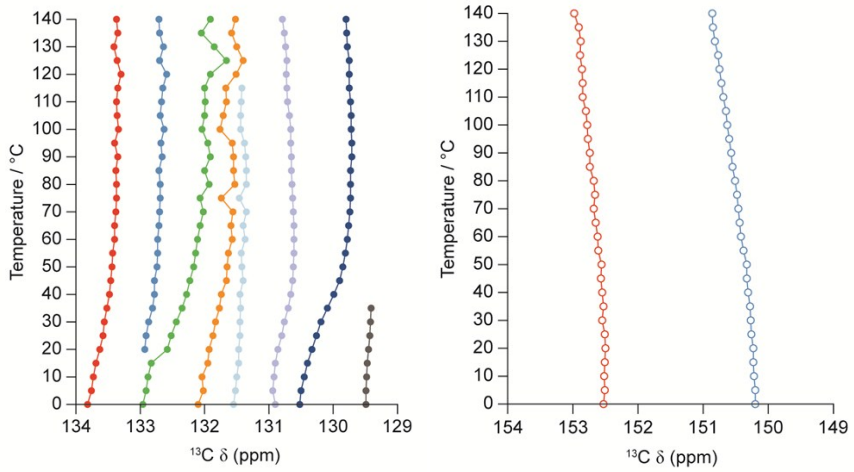

Figure S21. A plot of ^{13}C (9.4 T, 12.5 kHz MAS) chemical shift position as a function of temperature for **C**H (left) and **C**-NO_2 (right) species in compound **1**.

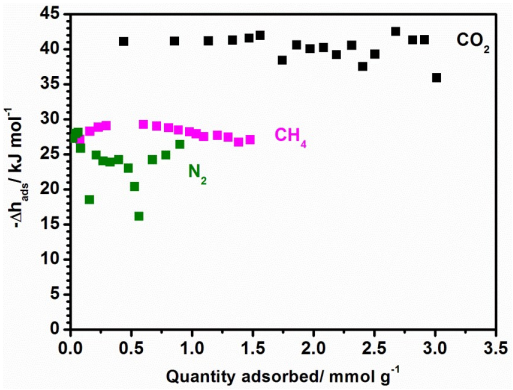

Figure S22. CO_2 (black), CH_4 (pink) and N_2 (green) adsorption enthalpies (0-10 bar, 30 °C) for compound **1** from the recrystallisation of ZIF-65(Zn).

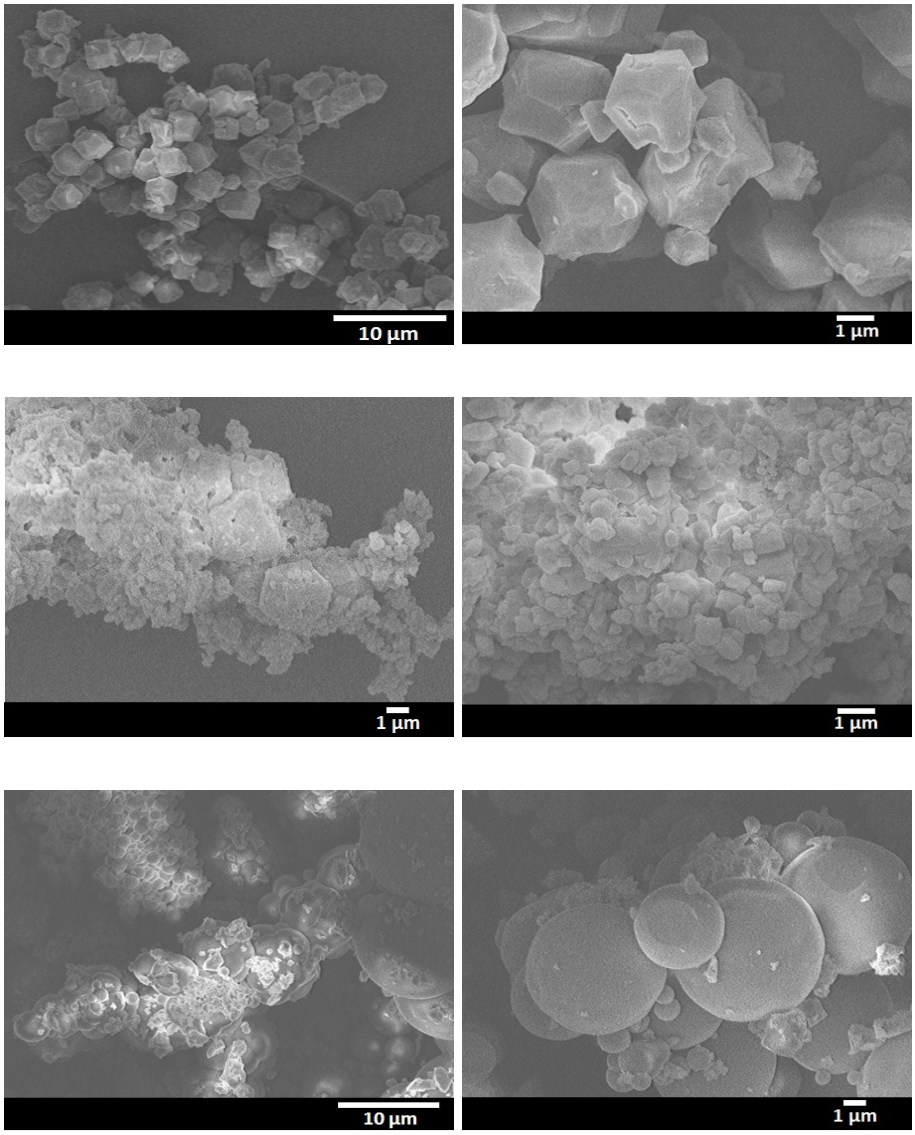

Figure S23. SEM images of as-prepared ZIF-65(Co) (top), compound **2** from the recrystallisation of ZIF-65(Co) (middle) and compound **2** from solvothermal synthesis (bottom).

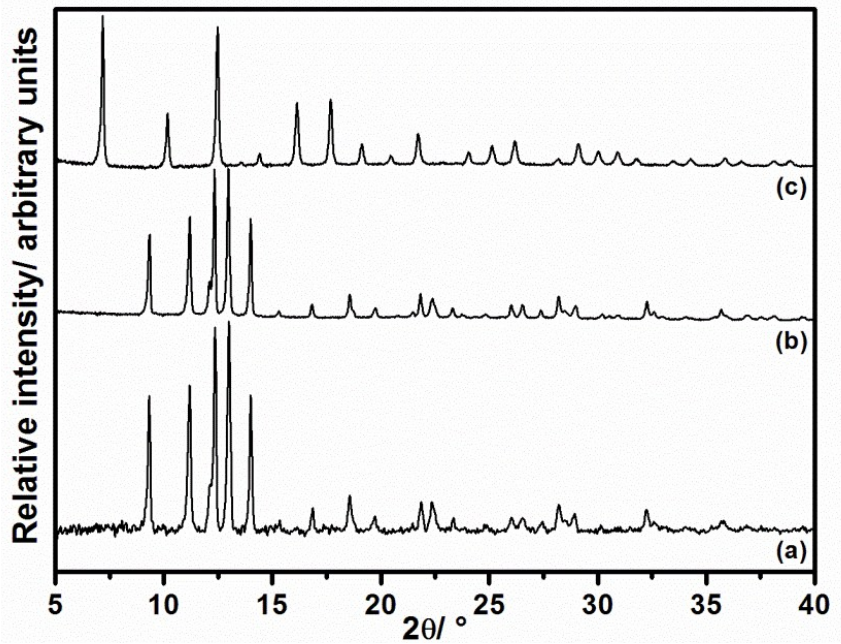

Figure S24. PXRD of compound **2** via (a) direct solvothermal synthesis and (b) recrystallization of ZIF-65(Co), and (c) of as prepared ZIF-65(Co).

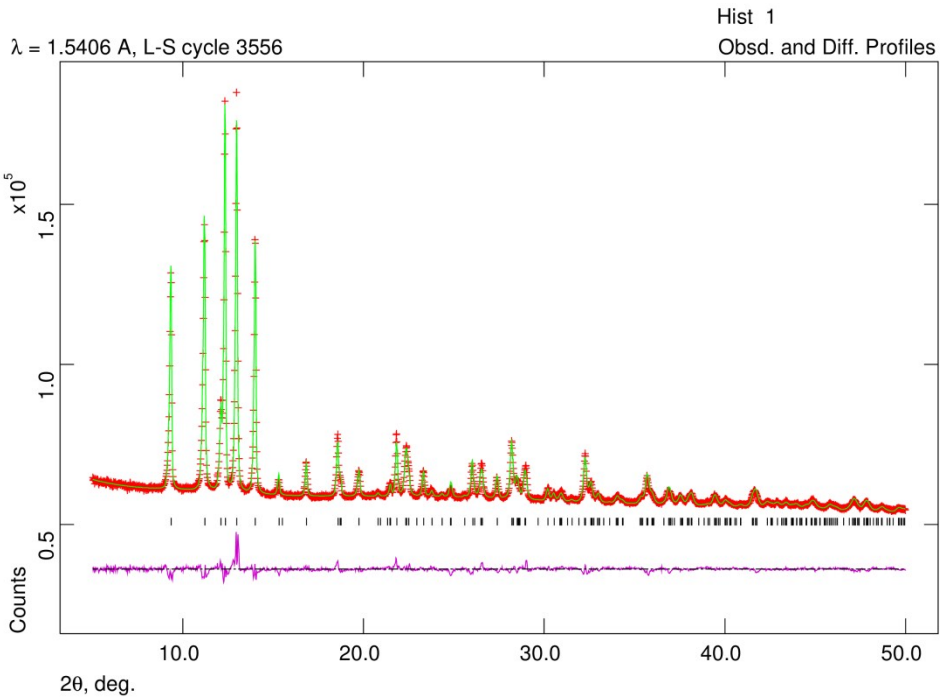

Figure S25. Difference plot (purple) between experimental PXRD profile of compound **2** from the recrystallisation of ZIF-65(Co) (red) and simulated PXRD (green).

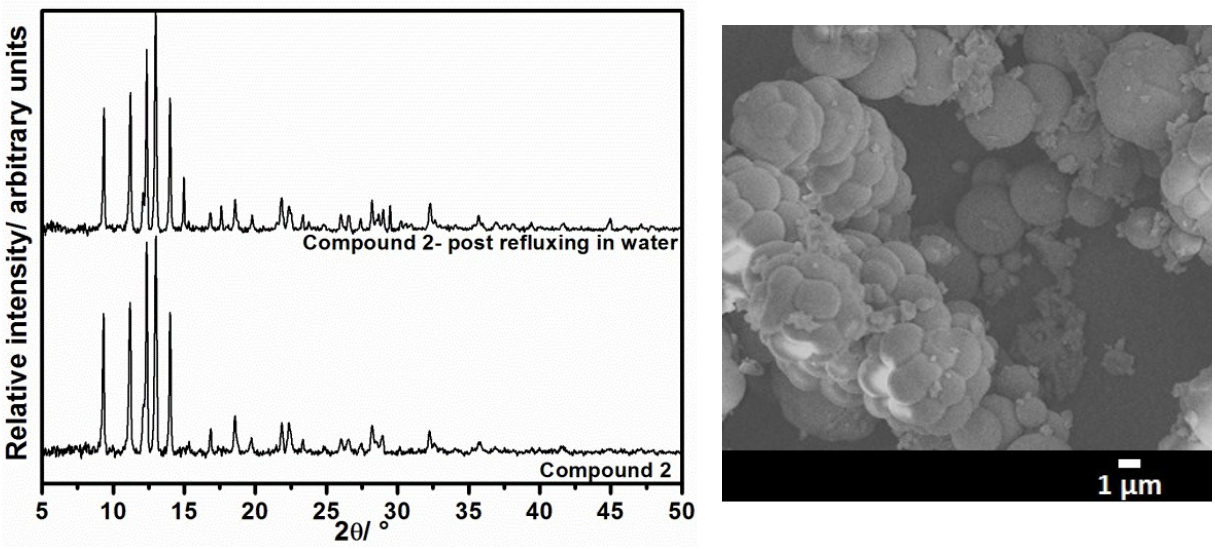

Figure S26. PXRD patterns (left) of as-prepared compound **2** from solvothermal synthesis and the same sample after refluxing in water (8 hours). SEM image (right) of compound **2** particles after refluxing in water.

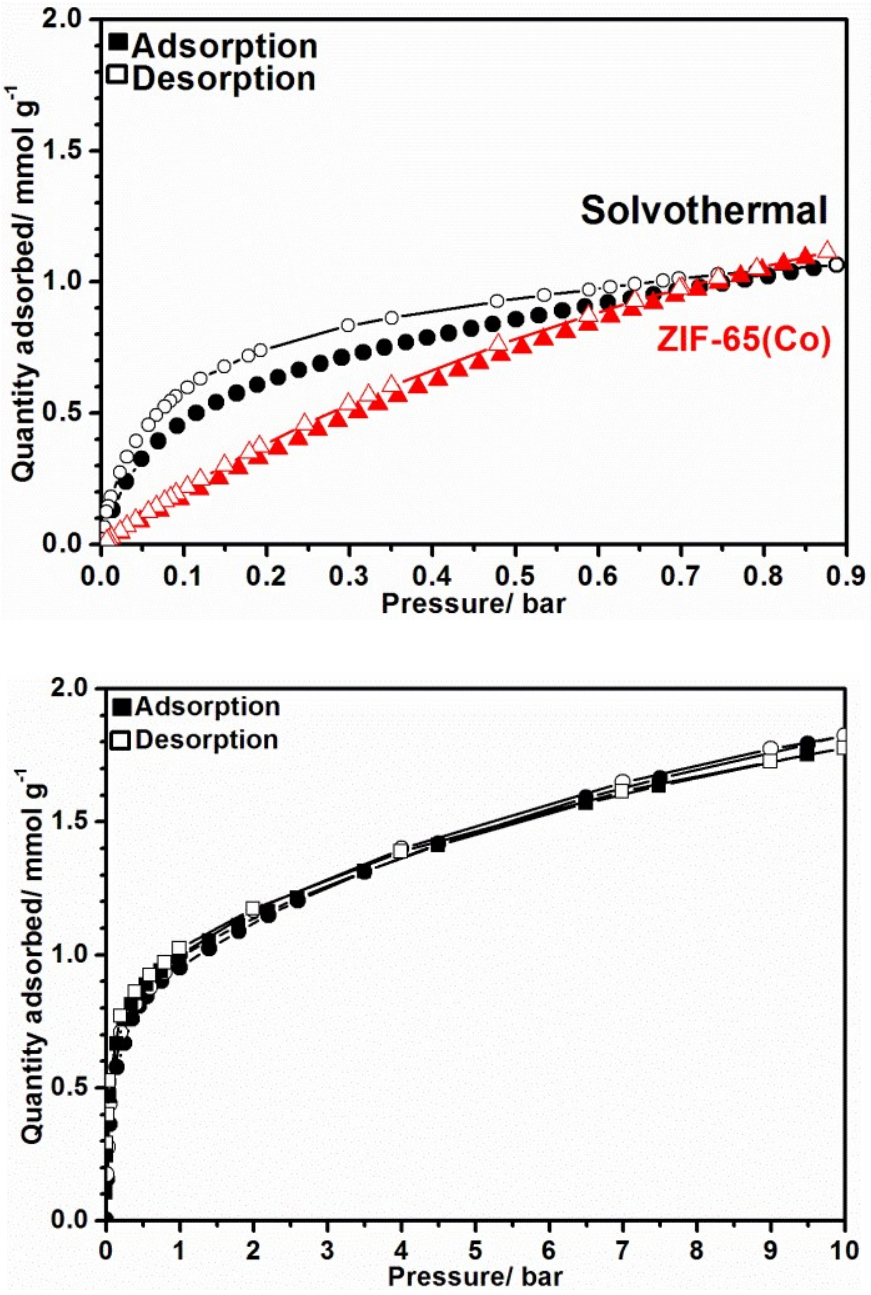

Figure S27. (Above) Low pressure CO_2 single gas adsorption isotherms (298 K, 1 bar, top) for ZIF-65(Co) and compound **2** from direct solvothermal synthesis. (Below) High pressure isotherm for compound 2 from direct synthesis (298 K, 10 bar, bottom) Activation conditions: 110 °C (circles), 150 °C (squares) and 200 °C (triangles) for 6 h.

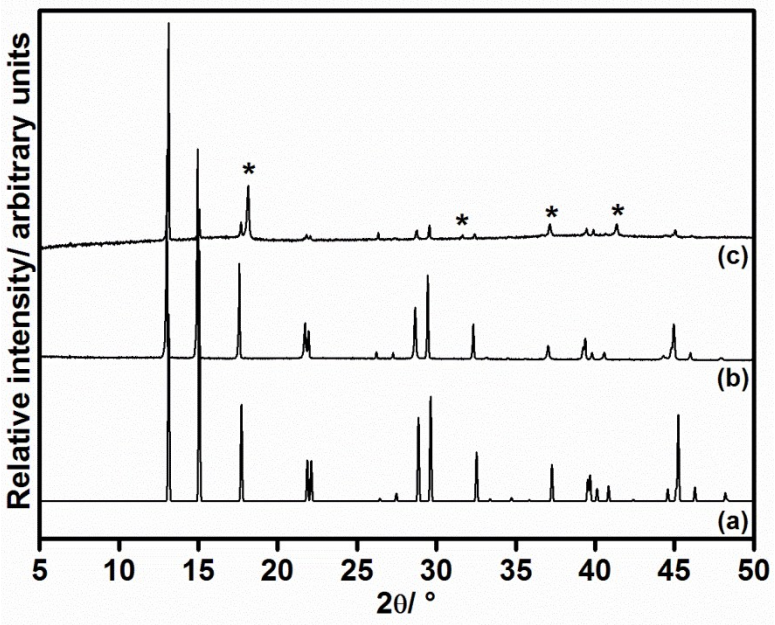

Figure S28. PXRD patterns of compound **3** prepared via two different synthetic routes: (b) recrystallization of ZIF-65(Co) and (c) direct solvothermal synthesis (* Teflon insert), compared to (a) the simulated PXRD from single crystal XRD data of compound **3**

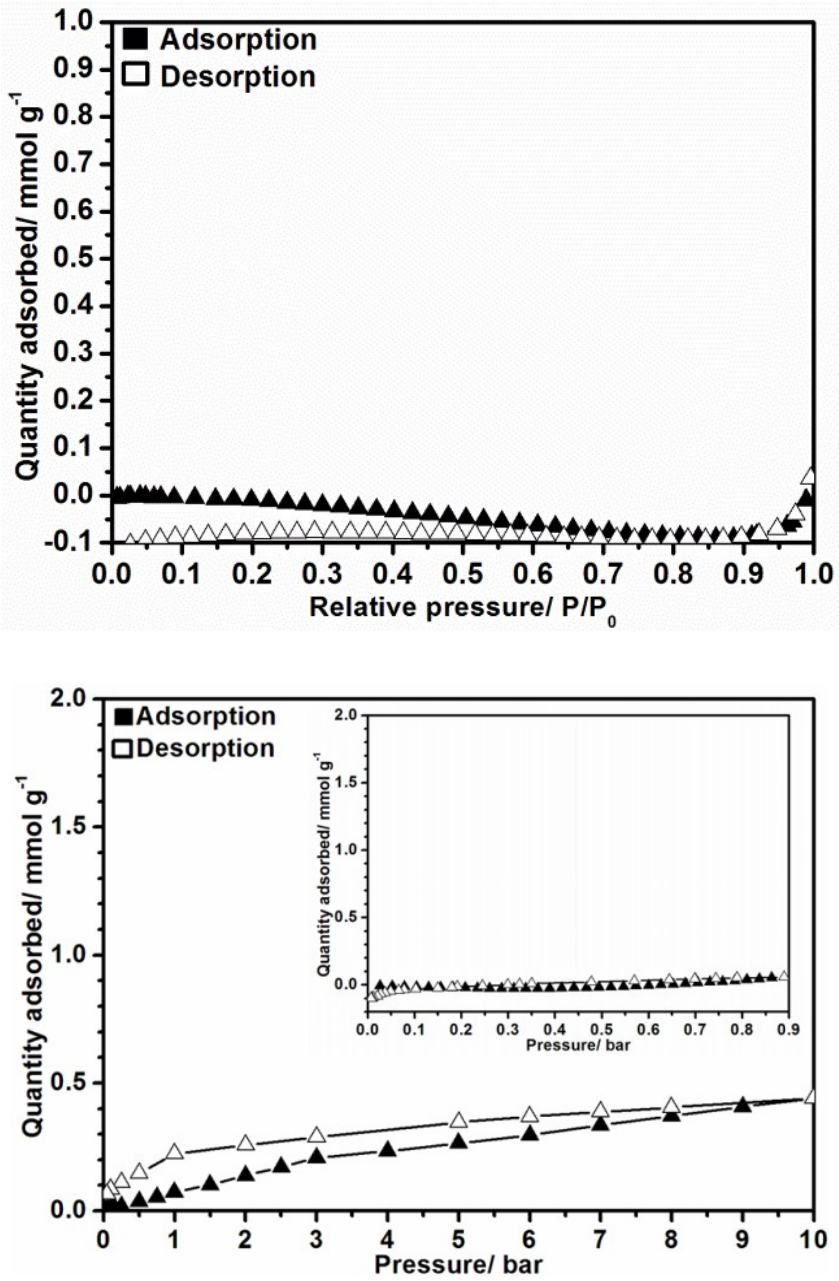

Figure S29. N_2 adsorption isotherm (298 K, top) for compound **3**. High pressure CO_2 single gas adsorption isotherms (298 K, 10 bar, bottom) for compound **3** from recrystallisation of ZIF-65(Co) and inset the low pressure isotherm (298 K, 1 bar). Activation conditions: 120 °C for 6 h.

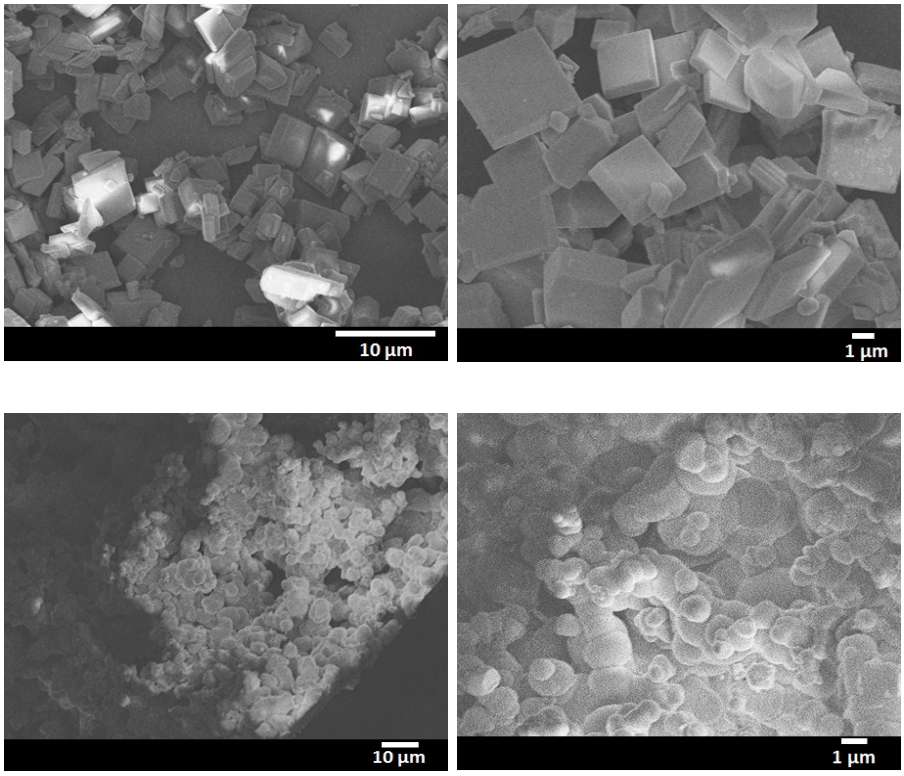

Figure S30. SEM images of compound **3** from the recrystallisation of ZIF-65(Co) (top) and from solvothermal synthesis (bottom).

Table S1. Gas adsorption parameters for compound **1**. Adsorbed quantities (30 °C, 1 bar), Henry's law constants (K_H), enthalpies of adsorption ((-)Δh_{ads}), selectivity (α) CO_2/ N_2 calculated at 1 bar and selectivity (α) CO_2/ CH_4 calculated at 1 and 5 bar.

Gas type	**Amount adsorbed/ mmol g^{-1}**	**K_H/ mmol g^{-1} bar^{-1}**	**(-)Δh_{ads}/ kJ mol^{-1}**	**α CO_2/N_2 (15/85%) 1 bar**	**α CO_2/CH_4 (50/50%) 1 bar**	**α CO_2/CH_4 (50/50%) 5 bar**
CO_2	1.80	35.4	39.5	75	17	10
CH_4	0.45	0.7	26.0			
N_2	0.21	0.2	18.5			