

Supplementary Information

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

Angelica Orsi,^a David J. Price,^a Jürgen Kahr,^a Renjith S. Pillai,^b Scott Sneddon,^a Shuai Cao,^c Virginie Benoit,^d Magdalena M. Łozińska,^a David B. Cordes,^a Alexandra M. Z. Slawin,^a Philip L. Llewellyn,^d Ian Casely,^c Sharon E. Ashbrook,^a Guillaume Maurin,^b and Paul A. Wright,^{a,*}

^a EaStCHEM School of Chemistry, University of St Andrews, Purdie Building, North Haugh, St Andrews, Fife, KY16 9ST, United Kingdom.

^b Institut Charles Gerhardt Montpellier, UMR-5253, Université de Montpellier, CNRS, ENSCM, Place E. Bataillon, 34095 Montpellier cedex 05, France.

^c Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH, UK.

^d Aix-Marseille University, CNRS, MADIREL (UMR 7246), Centre de St Jérôme, 13397 Marseille cedex 20, France.

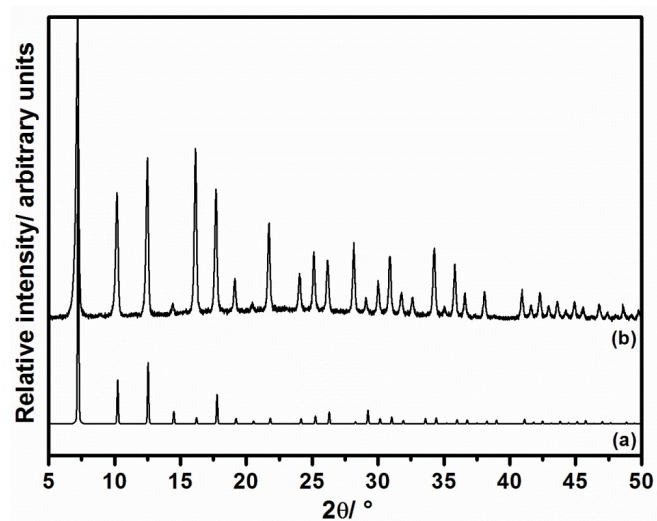


Figure S1. PXRD patterns of (a) the simulated PXRD from single crystal XRD data of ZIF-65(Zn) and (b) as-prepared ZIF-65(Zn).

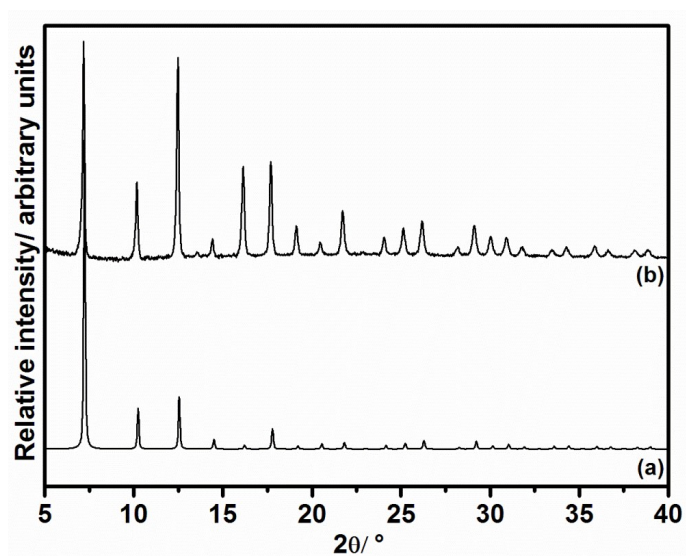


Figure S2. PXRD patterns of (a) the simulated PXRD from single crystal XRD data of ZIF-65(Co) and (b) as-prepared ZIF-65(Co).

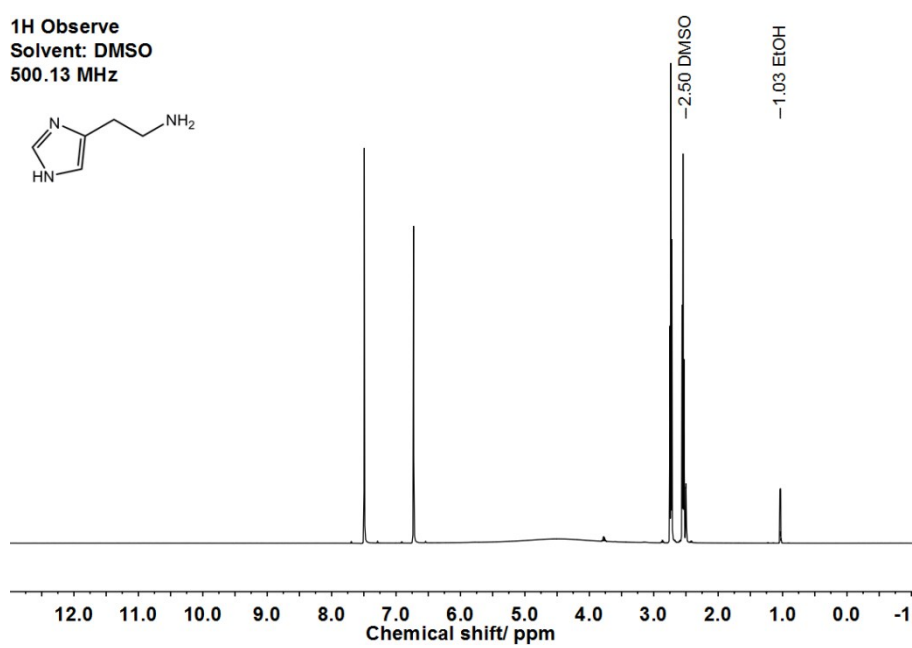


Figure S3. ^1H NMR spectrum of histamine (500 MHz, $\text{DMSO-}d_6$) δ 7.49 (d, $J = 1.1$ Hz, 1H, CH), 6.73 (d, $J = 1.0$ Hz, 1H, CH), 2.73 (t, $J = 7.1$ Hz, 2H, CH_2), 2.55 (t, $J = 7.1$ Hz, 2H, CH_2).

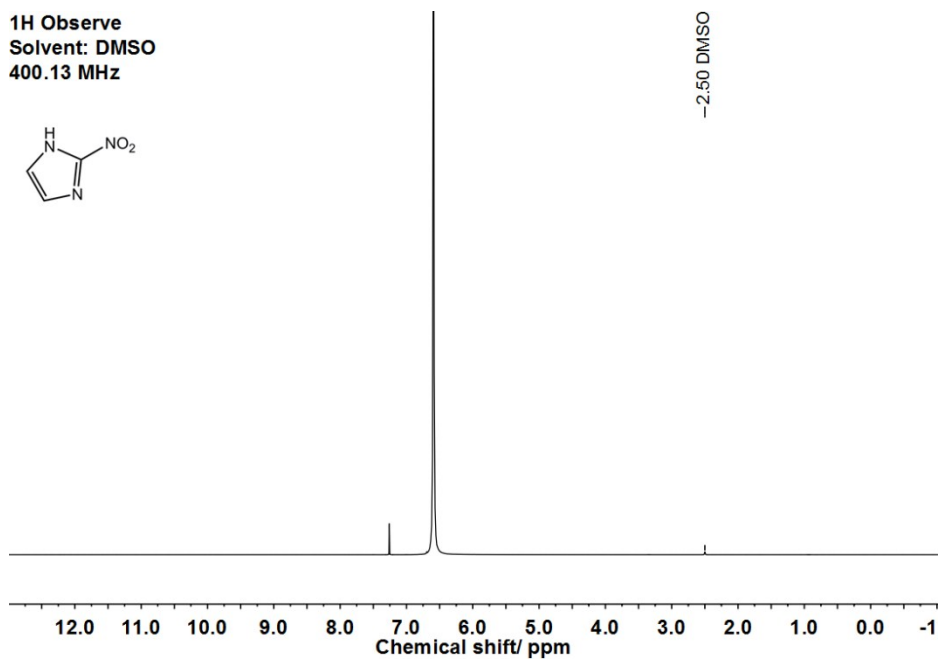


Figure S4. ^1H NMR spectrum of 2-nitroimidazole (400 MHz, $\text{DMSO-}d_6$) δ 7.26 (s, 2H, CH), 6.59 (s, HCl).

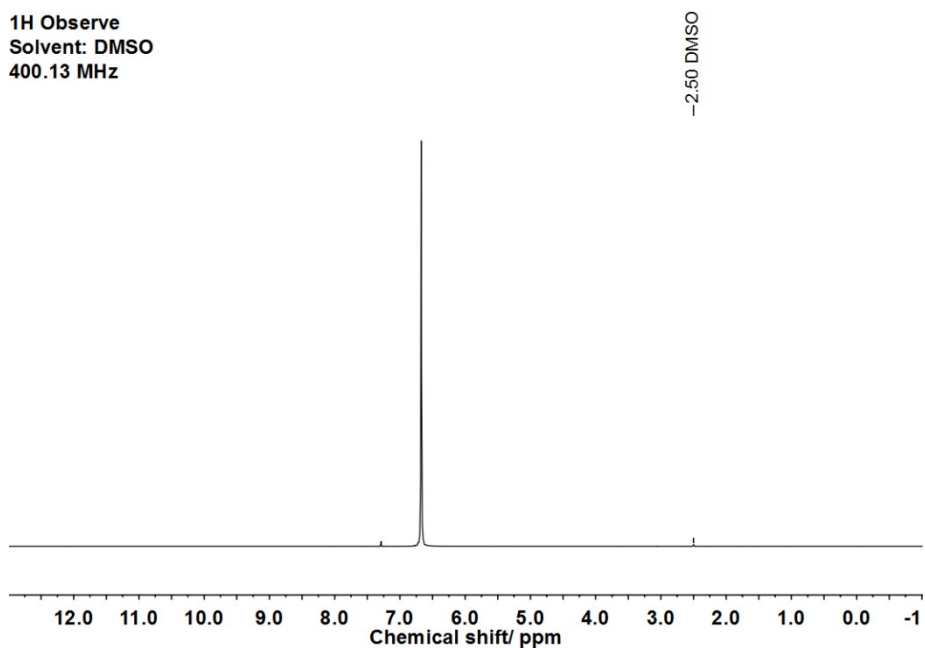


Figure S5. ^1H NMR spectrum of compound **1** from solvothermal preparation, dissolved (400 MHz, $\text{DMSO-}d_6$) δ 7.29 (s, 2H, CH), 6.67 (s, HCl).

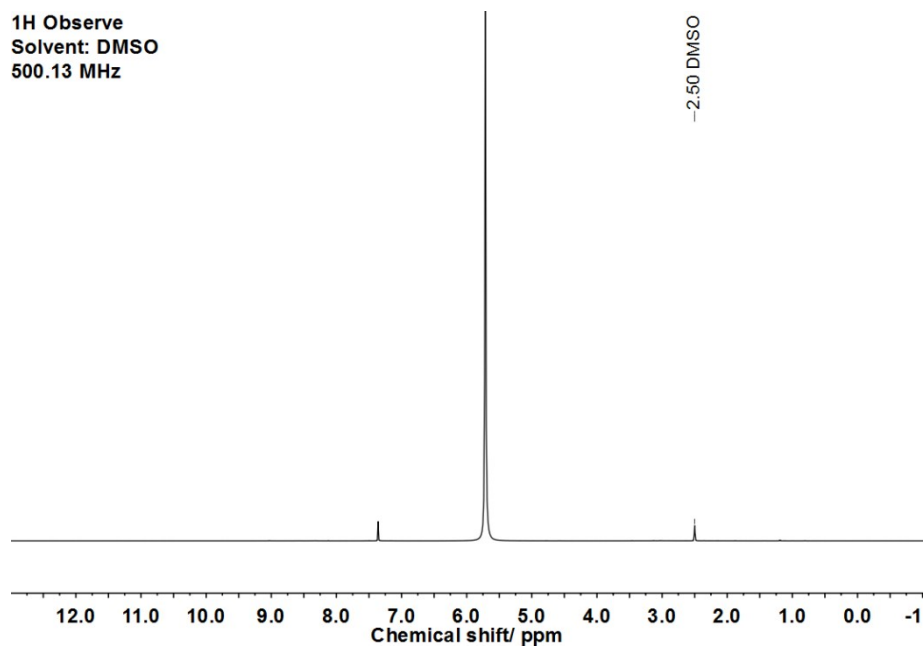


Figure S6. ^1H NMR spectrum of compound **2** from solvothermal preparation, dissolved (500 MHz, $\text{DMSO-}d_6$) δ 7.36 (s, 2H, CH), 5.71 (s, HCl).

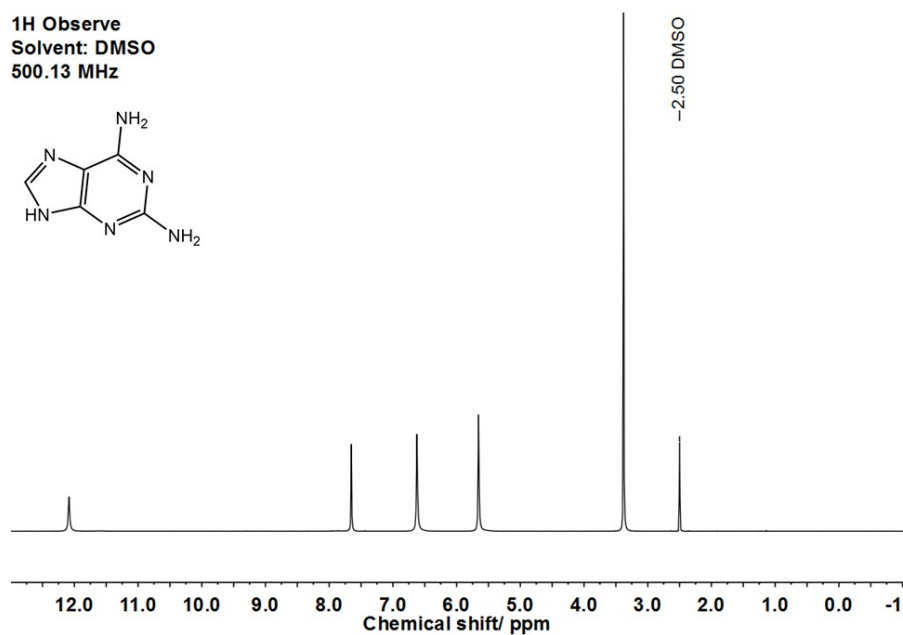


Figure S7. ^1H NMR spectrum of 2,6-diaminopurine (500 MHz, $\text{DMSO-}d_6$) δ 12.09 (s, 1H, NH), 7.65 (s, 1H, CH), 6.62 (s, 2H, NH_2), 5.66 (s, 2H, NH_2), 3.38 (s, H_2O).

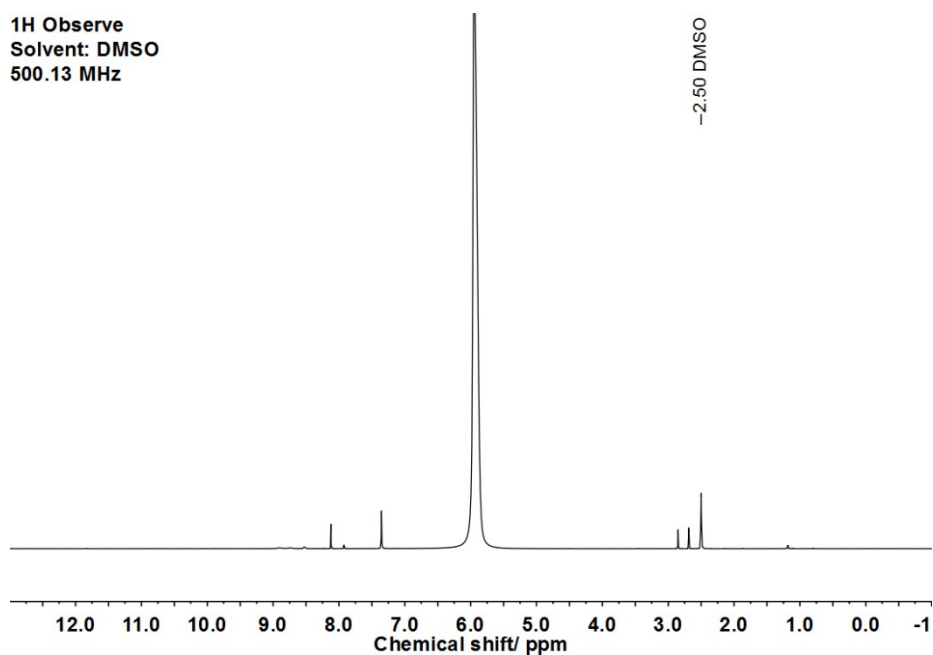


Figure S8. ^1H NMR spectrum of compound **3** from solvothermal preparation, dissolved (500 MHz, $\text{DMSO-}d_6$) δ 8.12 (s, DMF), 7.35 (s, 2H, CH), 5.95 (s, HCl), 2.85 (s, DMF), 2.96 (s, DMF).

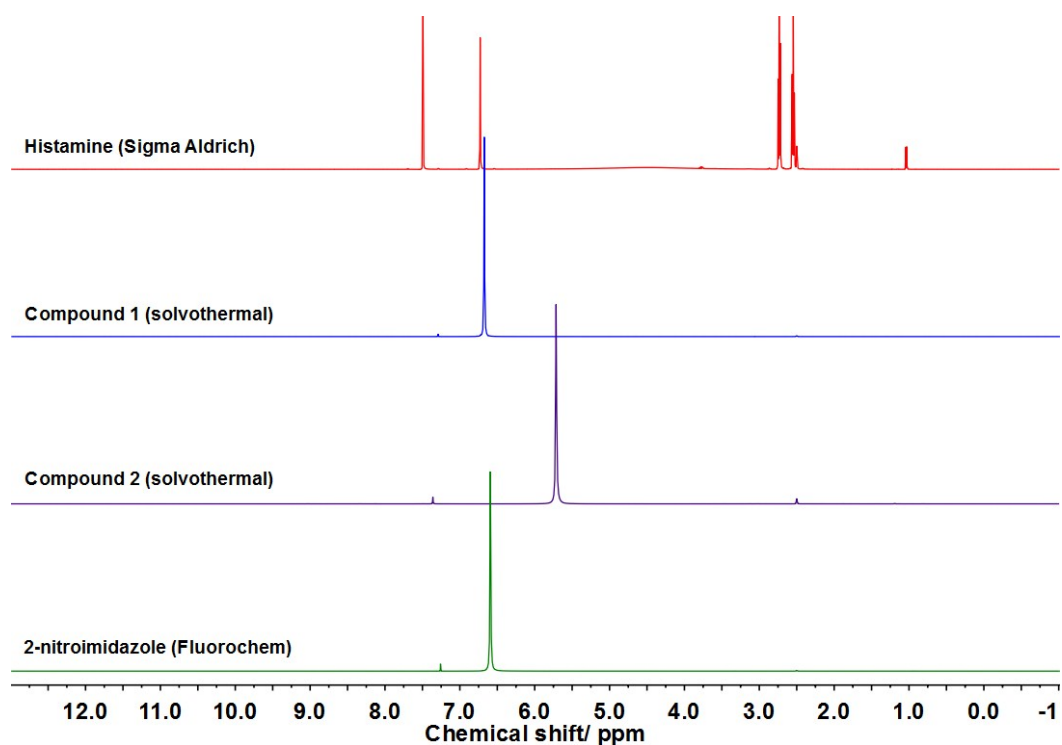


Figure S9. Stacked ^1H NMR of histamine (red) and dissolved compound **1** (blue), compound **2** (purple) and 2-nitroimidazole (green).

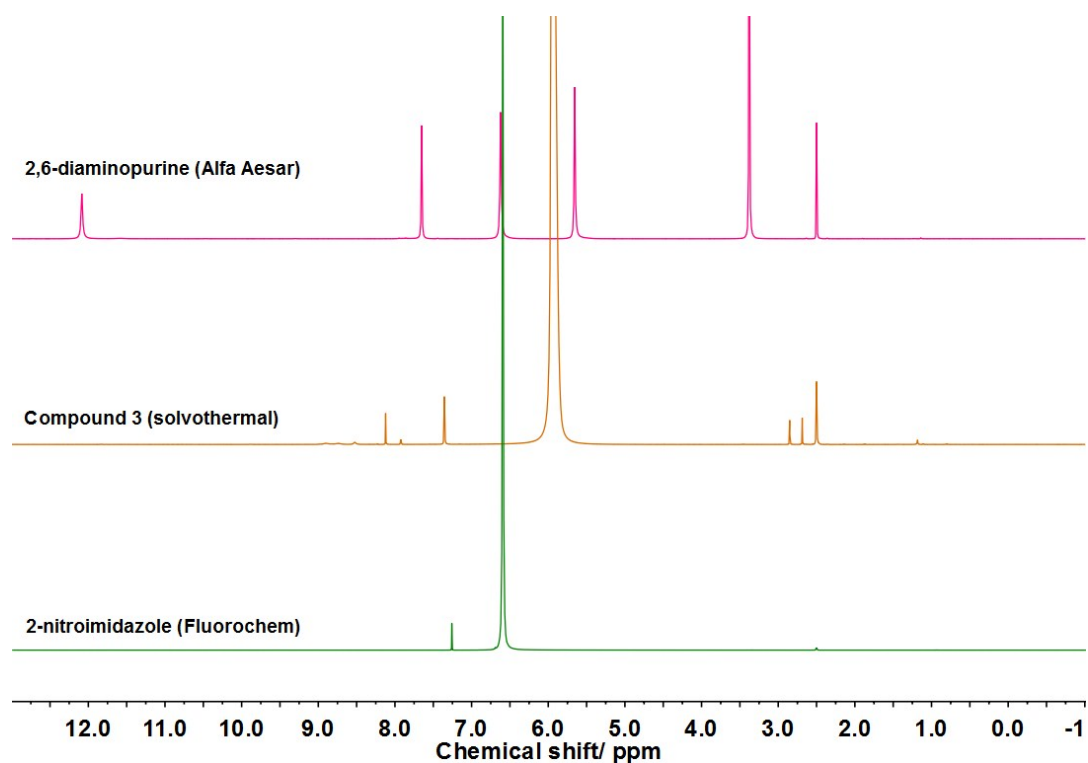


Figure S10. Stacked ¹H NMR of 2,6-diaminopurine (pink), dissolved compound **3** (orange) and 2-nitroimidazole (green).

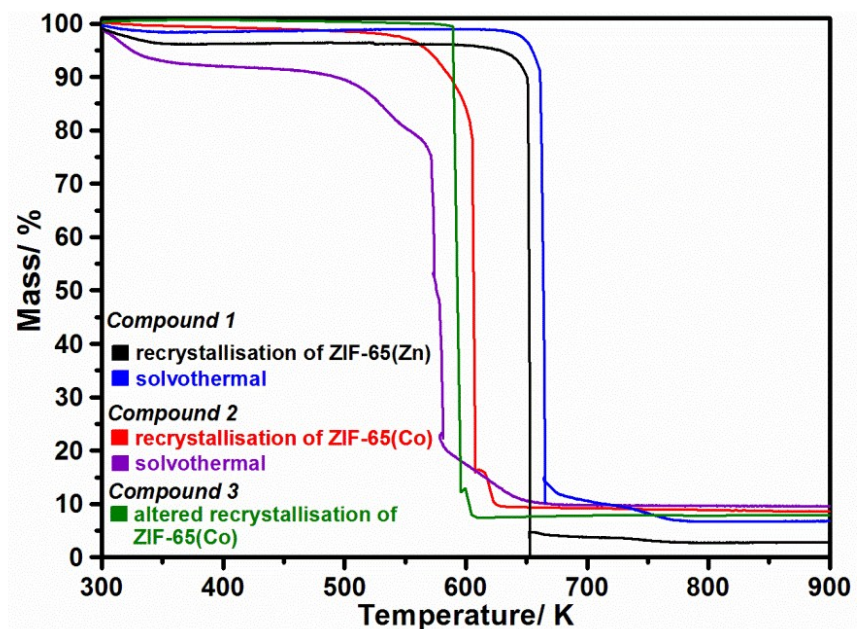


Figure S11. TGA (flowing air, ramp rate 5 °C min⁻¹) of as-prepared compound **1**, **2** and **3** from the described synthetic procedures.

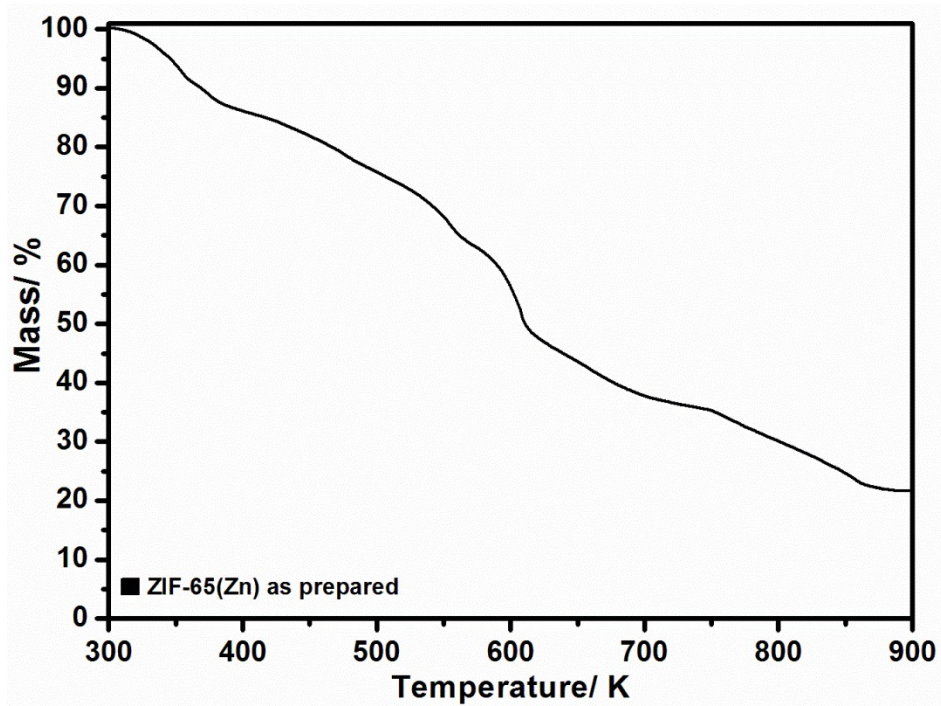


Figure S12. TGA (flowing air, ramp rate 5 °C min⁻¹) of as-prepared ZIF-65(Zn).

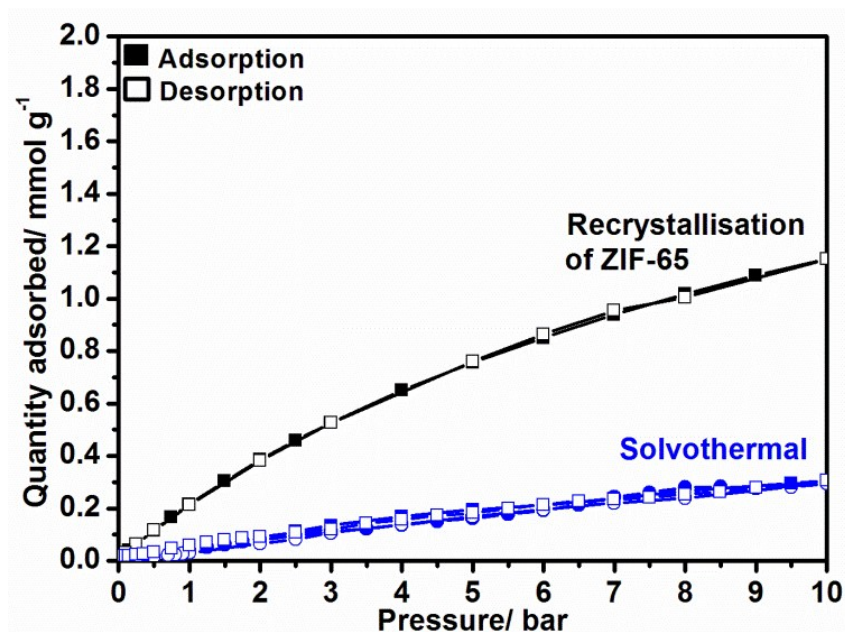
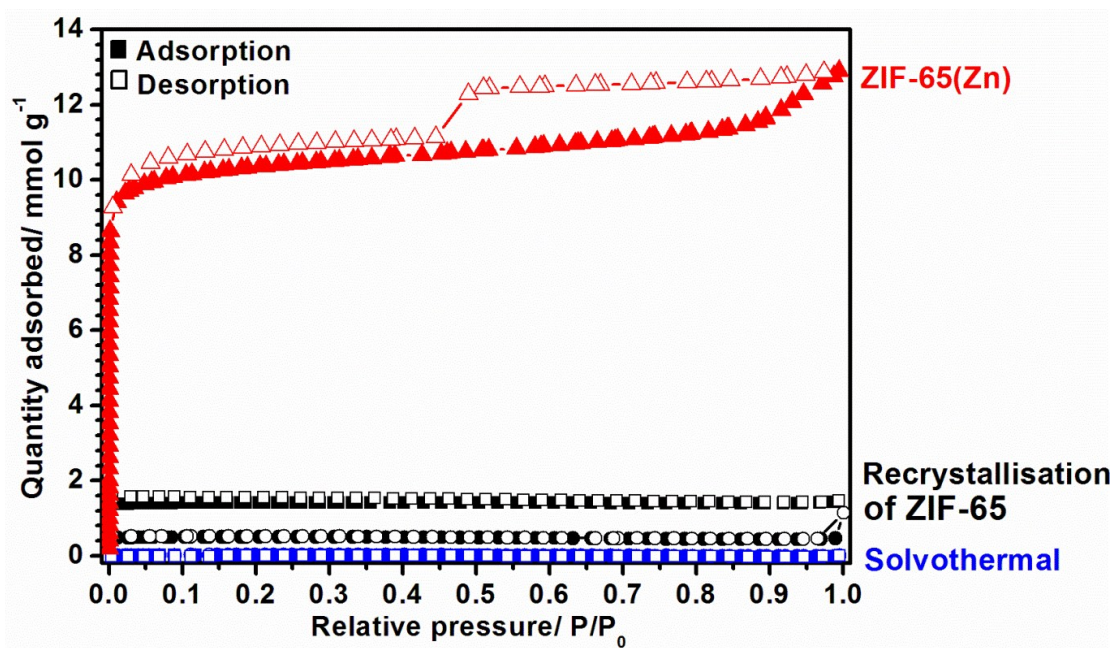


Figure S13. N₂ adsorption isotherms (-196 °C (top) and 25 °C (bottom)) for ZIF-65(Zn) (red) and compound 1 samples from the recrystallisation of ZIF-65(Zn) (black) and from direct solvothermal synthesis (blue). Activation conditions: 110 °C (circles), 140 °C (squares) and 200 °C (triangles) for 6 hours.

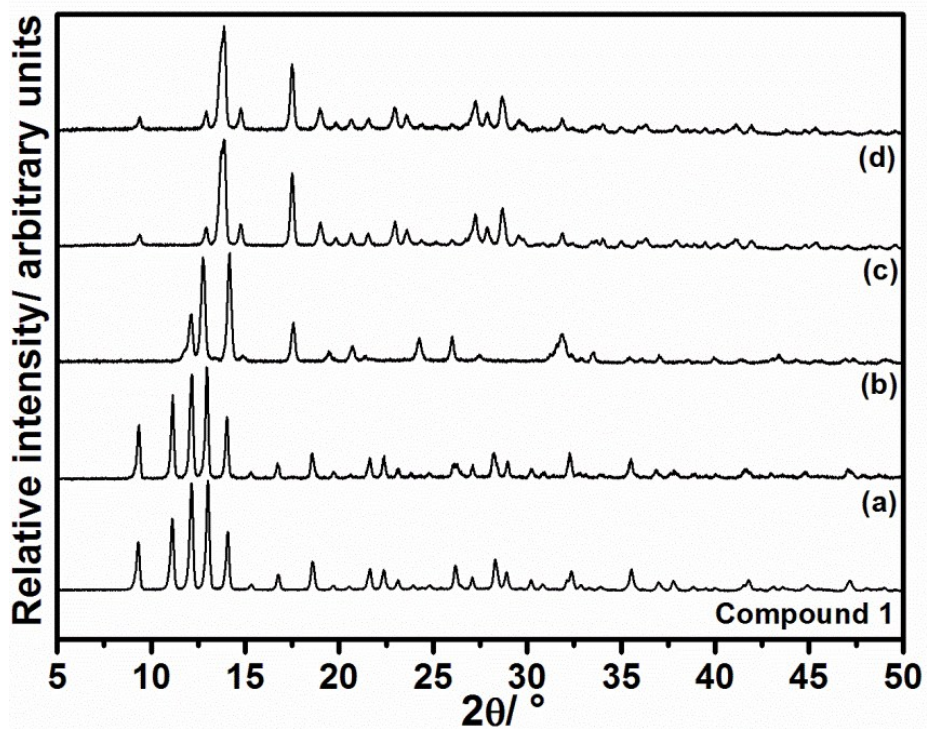


Figure S14. PXRD patterns of as-prepared compound **1** (bottom) and after various stability tests: (a) furnace heated (60 °C, 18 h, N_2+H_2O flow), (b) immersion in water (room temperature, 72 h), (c) water reflux (24 h) followed by (d) re-immersion in MeOH (room temperature 48 h).

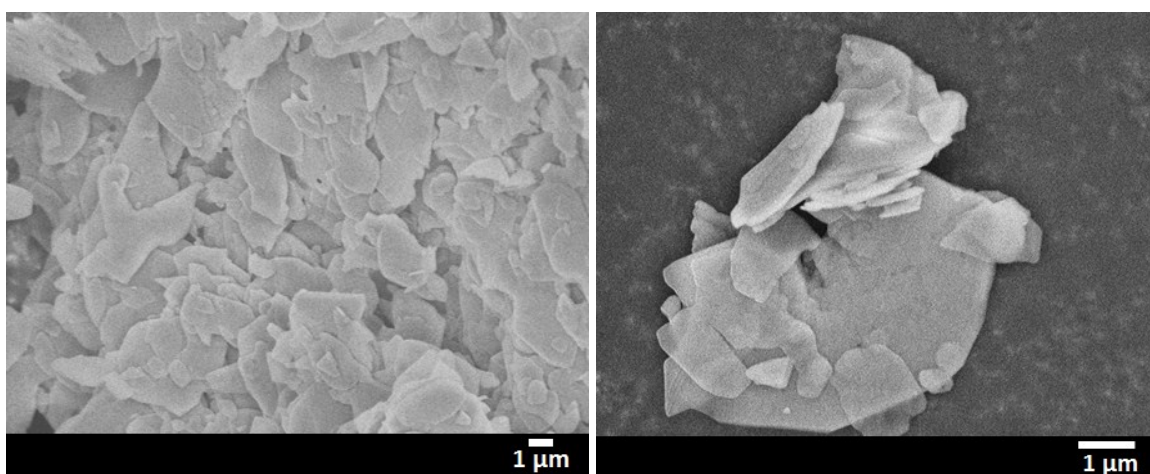


Figure S15. SEM images of compound **1** after refluxing in water (24 h).

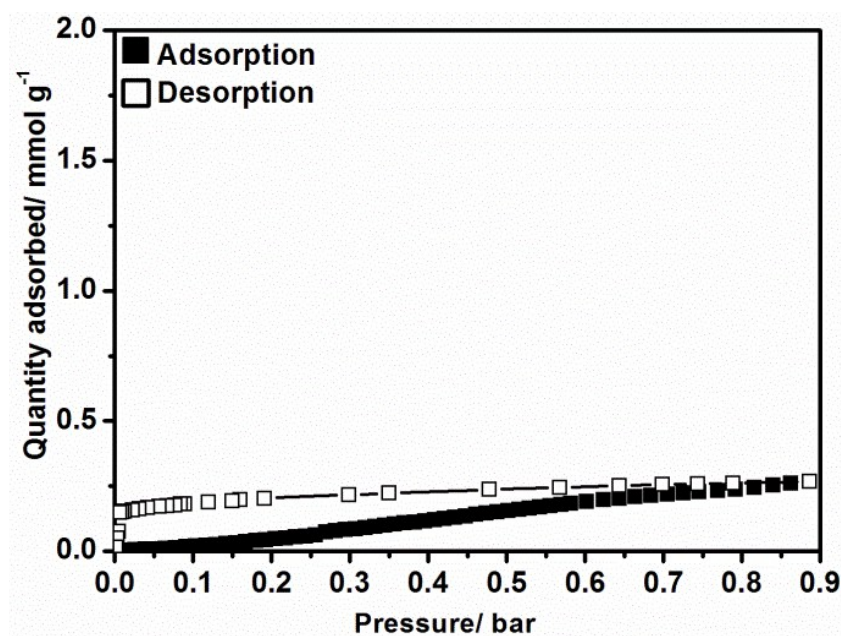
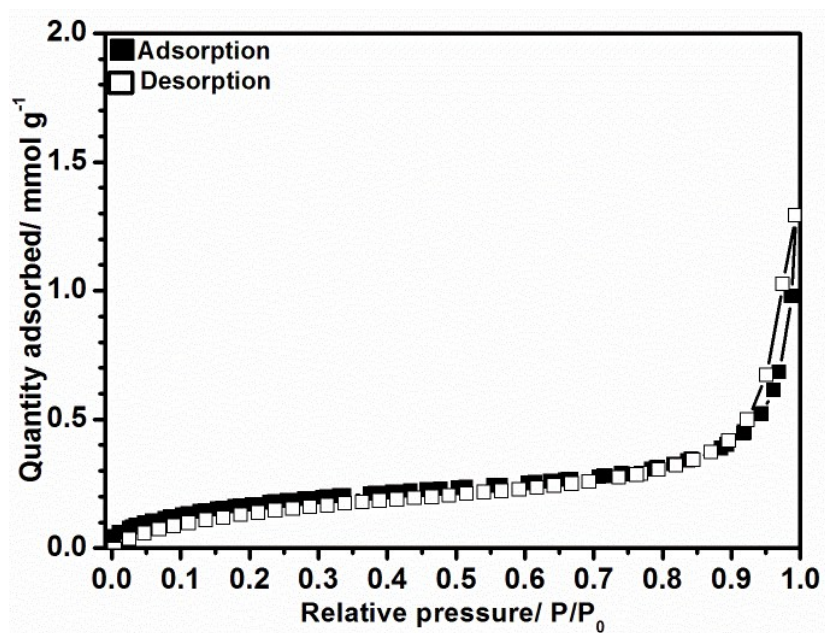


Figure S16. N₂ (-196 °C, top) and CO₂ (25 °C, bottom) isotherms of a dense phase achieved from refluxing compound **1** in water. Activation conditions: 140 °C for 6 hours.

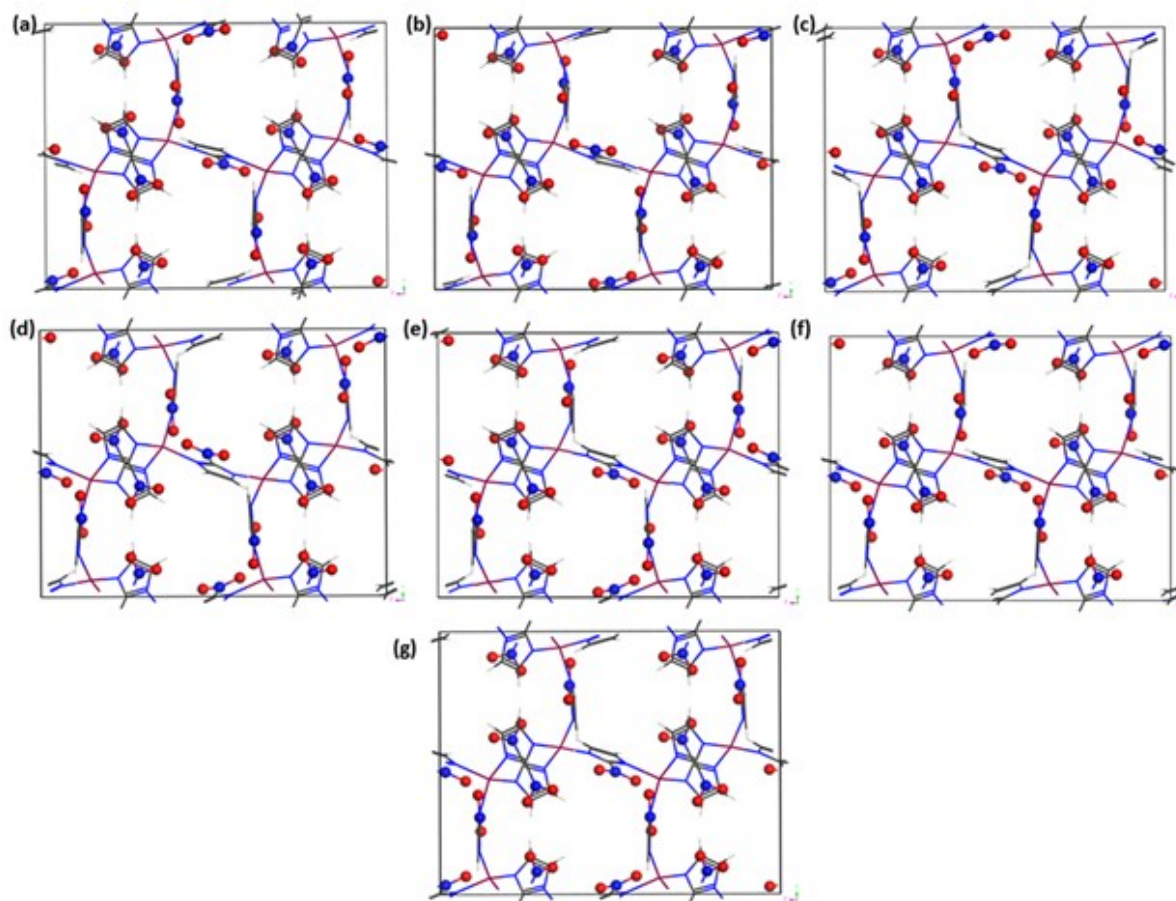


Figure S17. DFT-geometry optimized structures of the seven plausible models of compound **1** viewed along the *a* vector direction. Models: 1 (a), 2 (b), 3 (c), 4 (d), 5 (e), 6 (f) and 7 (g). Zn, orange; C, grey; O, red; N, blue; H, white.

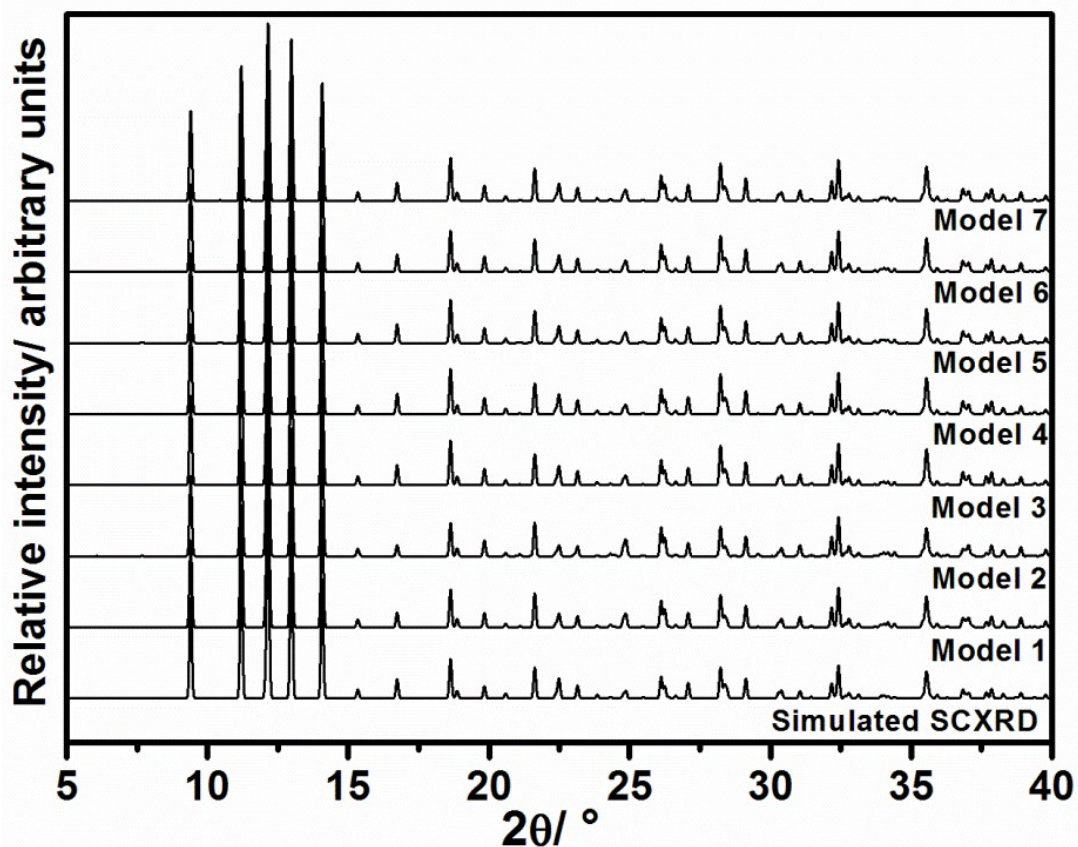


Figure S18. SCXRD of compound **1** compared to the calculated PXRD patterns for the seven DFT-geometry optimized structures of compound **1**.

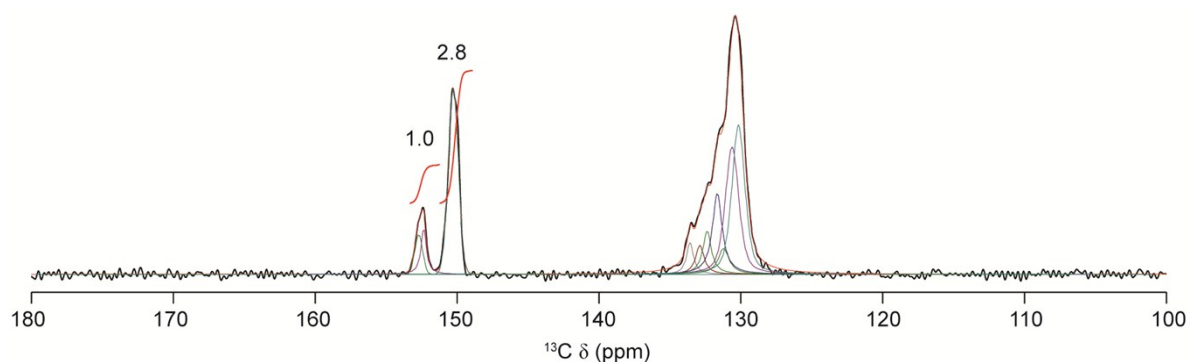


Figure S19. Fitting of the ^{13}C (9.4 T, 12.5 kHz MAS) CP MAS NMR spectrum of compound **1**, performed using dmfit, with the (integrated) intensity ratio of the two C–NO₂ resonances (1.0:2.8) shown.

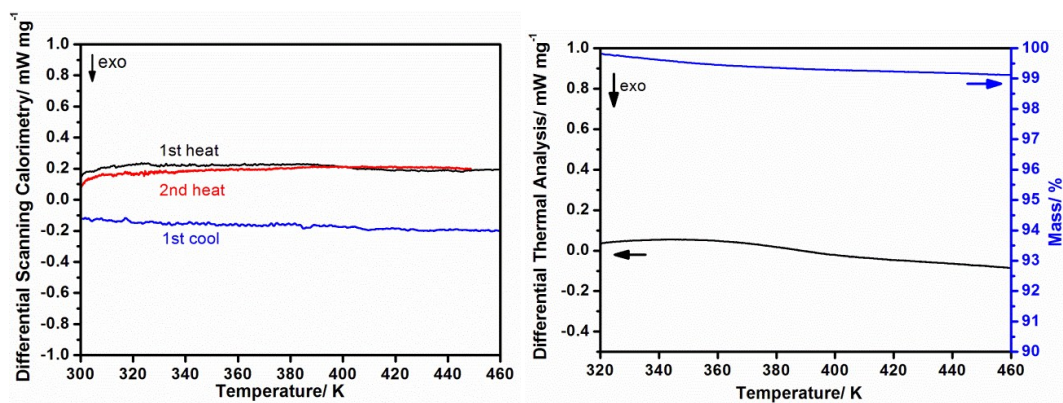


Figure S20. DSC (left) and DTA (right) of compound **1** (in flowing air).

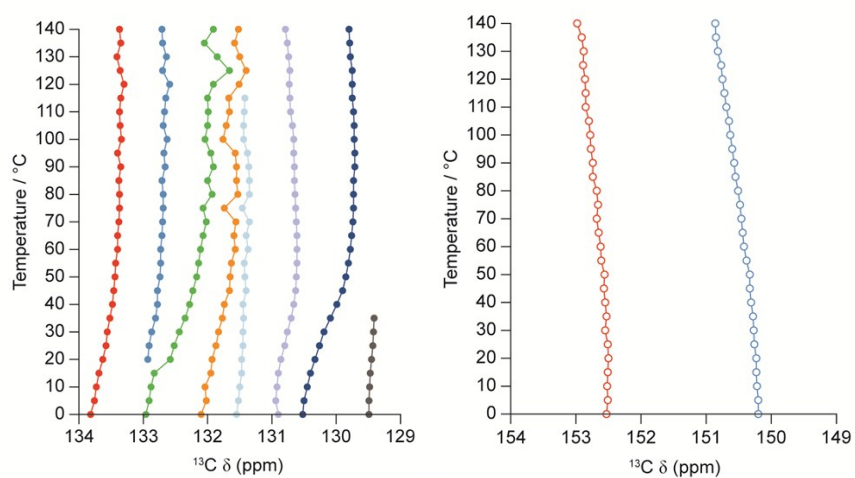


Figure S21. A plot of ^{13}C (9.4 T, 12.5 kHz MAS) chemical shift position as a function of temperature for CH (left) and C-NO₂ (right) species in compound **1**.

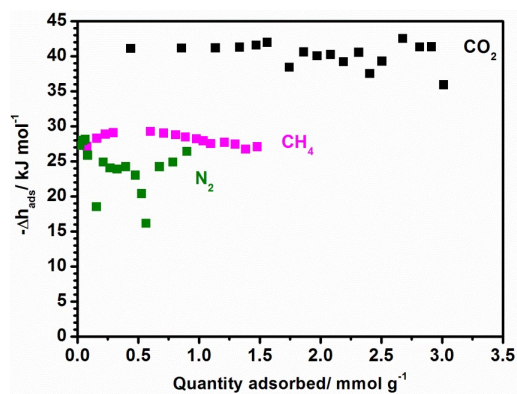


Figure S22. CO₂ (black), CH₄ (pink) and N₂ (green) adsorption enthalpies (0-10 bar, 30 °C) for compound **1** from the recrystallisation of ZIF-65(Zn).

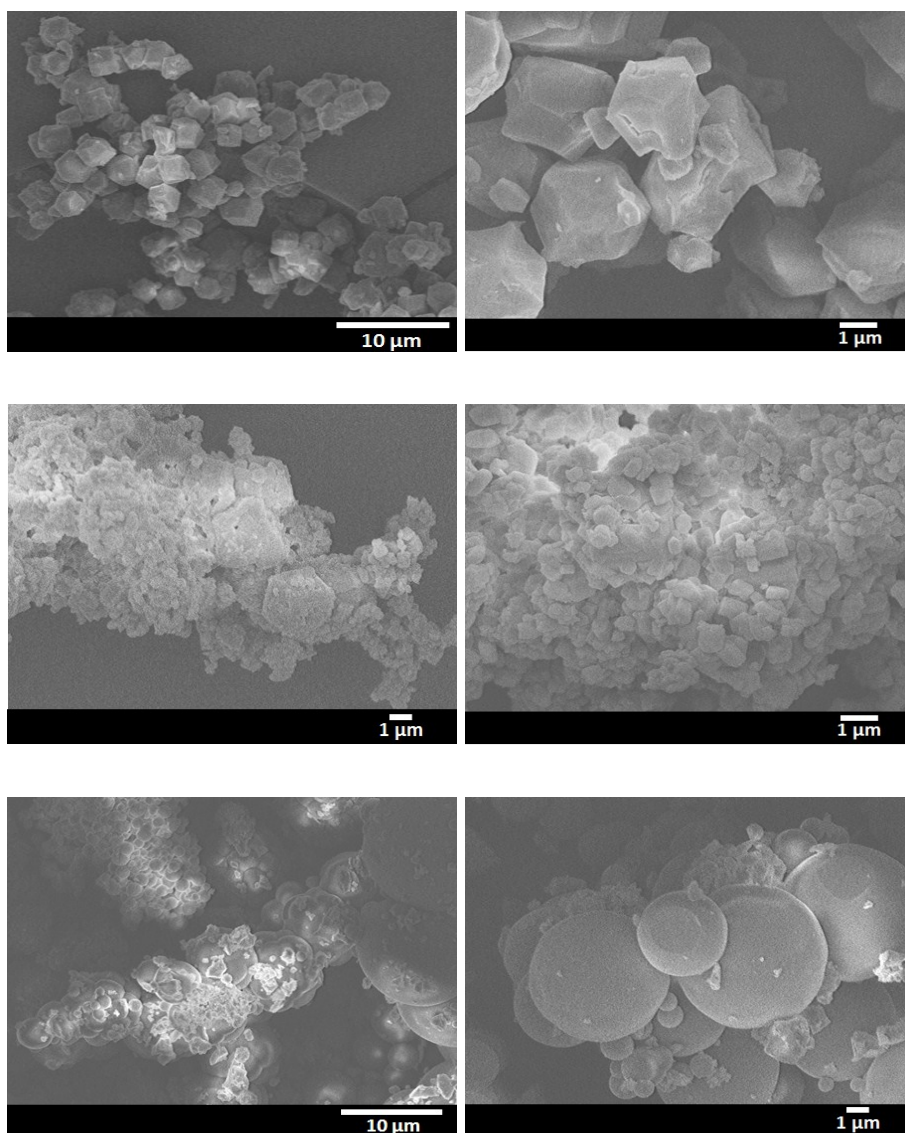


Figure S23. SEM images of as-prepared ZIF-65(Co) (top), compound **2** from the recrystallisation of ZIF-65(Co) (middle) and compound **2** from solvothermal synthesis (bottom).

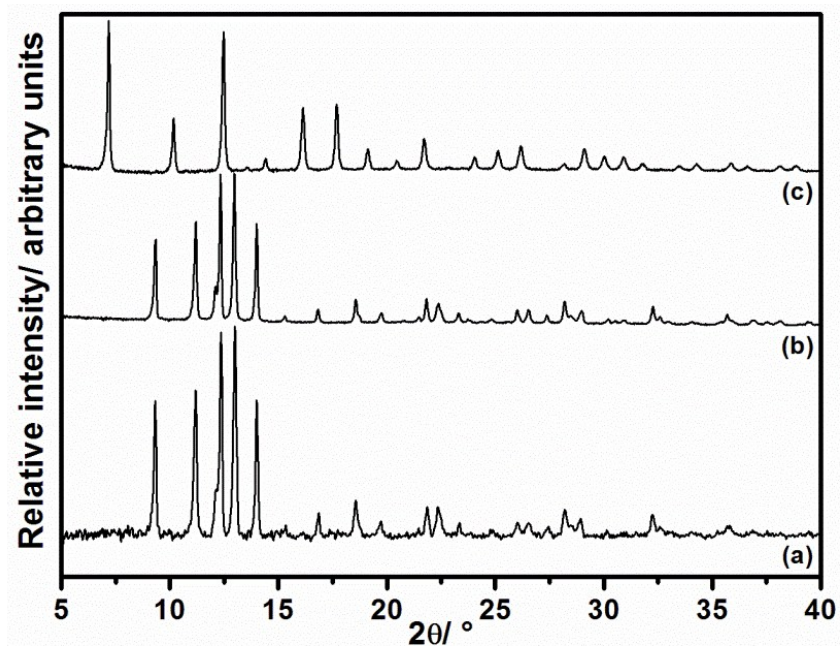


Figure S24. PXRD of compound **2** via (a) direct solvothermal synthesis and (b) recrystallization of ZIF-65(Co), and (c) of as prepared ZIF-65(Co).

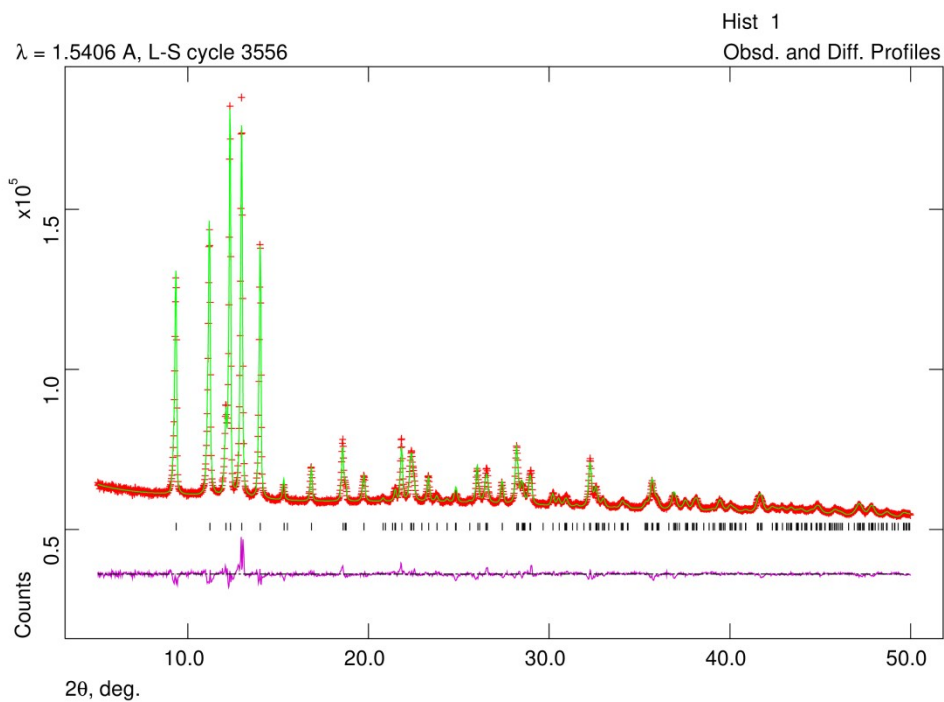


Figure S25. Difference plot (purple) between experimental PXRD profile of compound **2** from the recrystallisation of ZIF-65(Co) (red) and simulated PXRD (green).

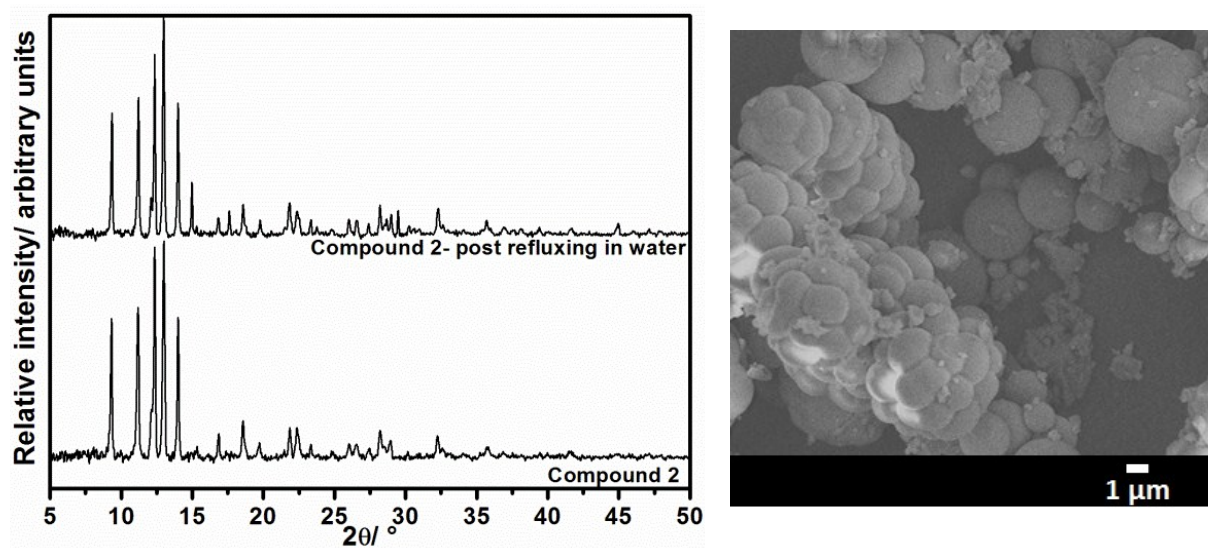


Figure S26. PXRD patterns (left) of as-prepared compound **2** from solvothermal synthesis and the same sample after refluxing in water (8 hours). SEM image (right) of compound **2** particles after refluxing in water.

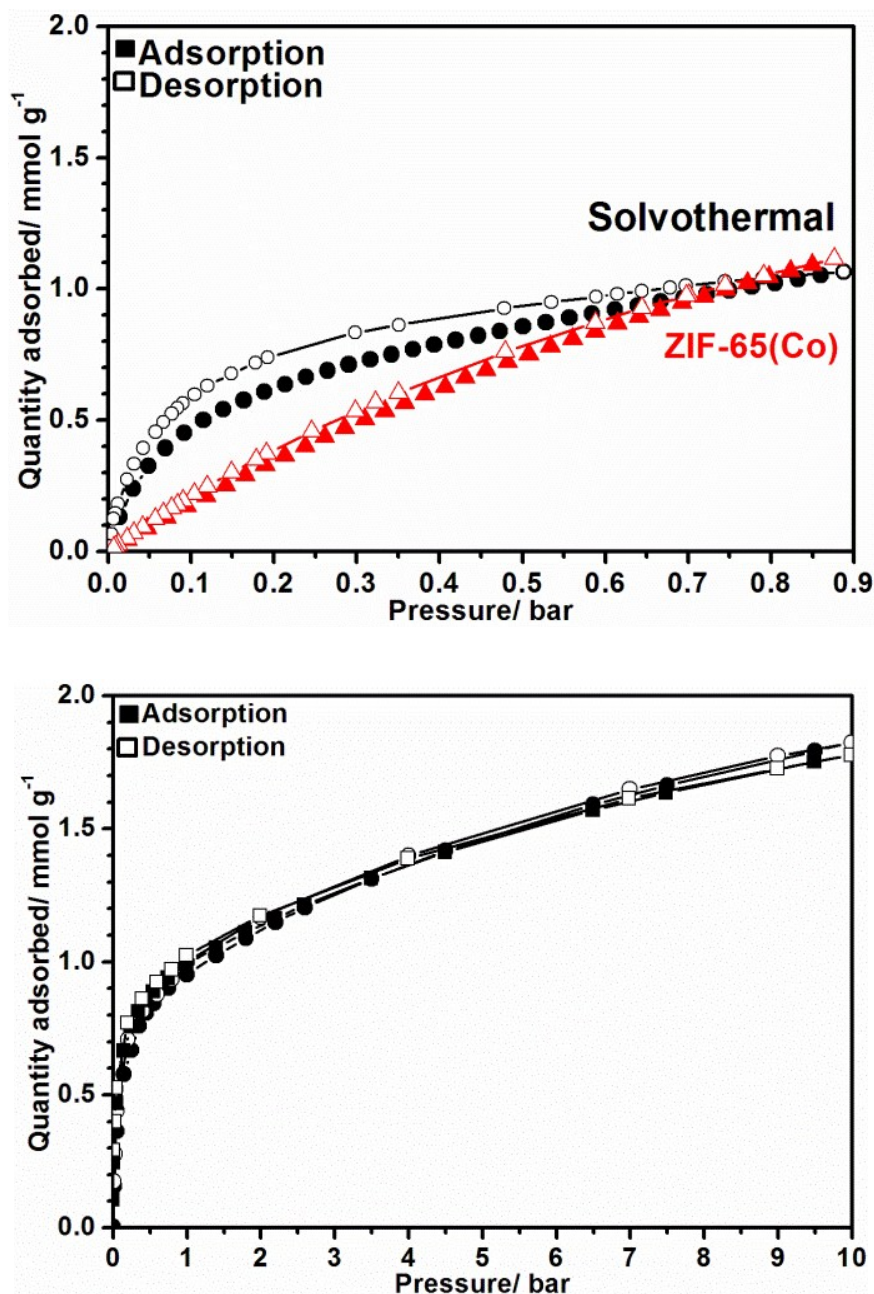


Figure S27. (Above) Low pressure CO₂ single gas adsorption isotherms (298 K, 1 bar, top) for ZIF-65(Co) and compound **2** from direct solvothermal synthesis. (Below) High pressure isotherm for compound **2** from direct synthesis (298 K, 10 bar, bottom) Activation conditions: 110 °C (circles), 150 °C (squares) and 200 °C (triangles) for 6 h.

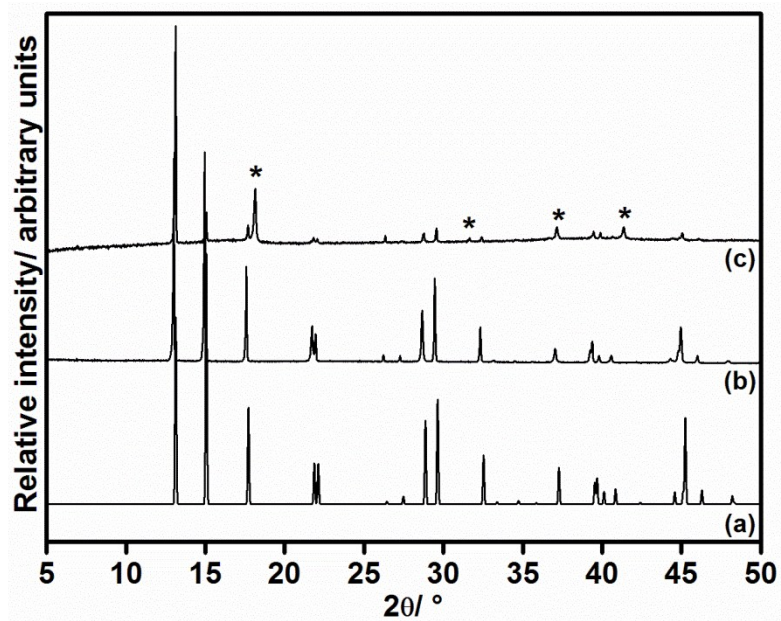


Figure S28. PXRD patterns of compound **3** prepared via two different synthetic routes: (b) recrystallization of ZIF-65(Co) and (c) direct solvothermal synthesis (* Teflon insert), compared to (a) the simulated PXRD from single crystal XRD data of compound **3**

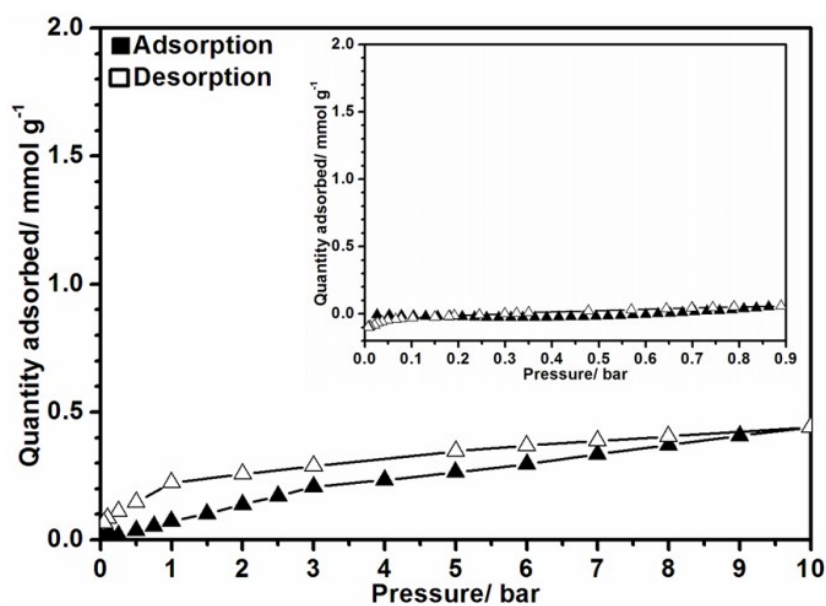
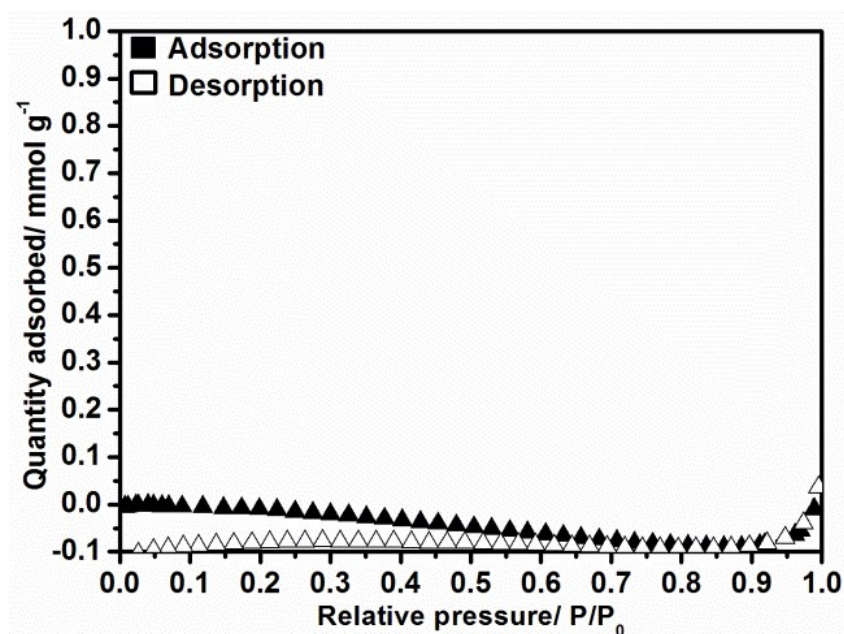


Figure S29. N₂ adsorption isotherm (298 K, top) for compound **3**. High pressure CO₂ single gas adsorption isotherms (298 K, 10 bar, bottom) for compound **3** from recrystallisation of ZIF-65(Co) and inset the low pressure isotherm (298 K, 1 bar). Activation conditions: 120 °C for 6 h.

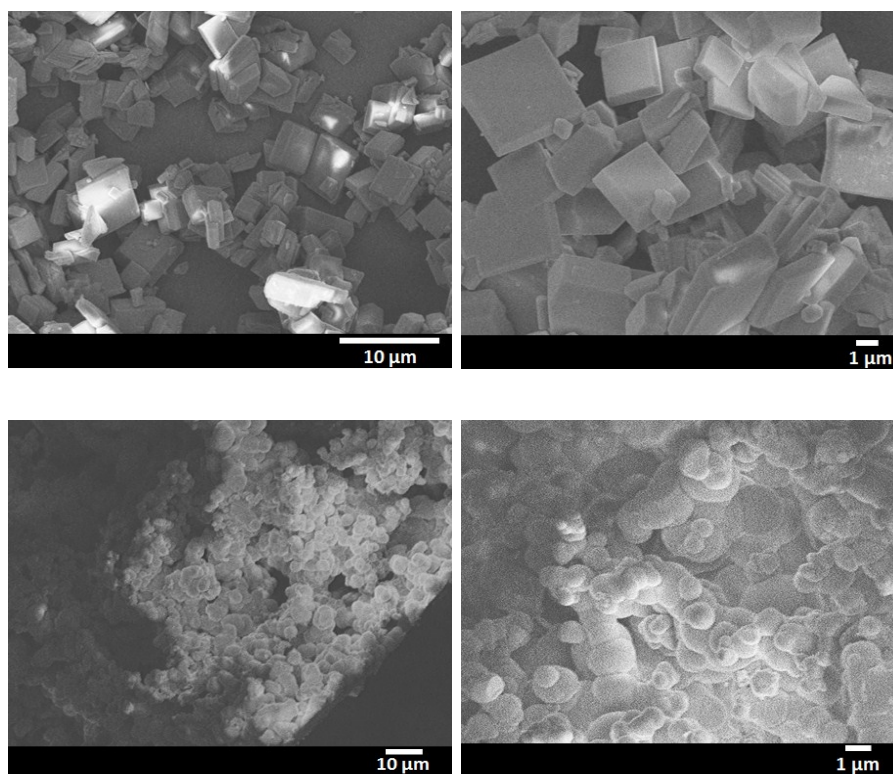


Figure S30. SEM images of compound **3** from the recrystallisation of ZIF-65(Co) (top) and from solvothermal synthesis (bottom).

Table S1. Gas adsorption parameters for compound **1**. Adsorbed quantities (30 °C, 1 bar), Henry's law constants (K_H), enthalpies of adsorption ($(-\Delta h_{ads})$), 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	$(-\Delta h_{ads})$/ 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			
CH ₄	0.45	0.7	26.0	75	17	10
N ₂	0.21	0.2	18.5			