Electronic Supplementary Information for Dalton Transactions

A Catenated Imidazole-based Coordination Polymer Exhibiting Significant CO_2 Sorption at Low Pressure as a Single Crystal Transition

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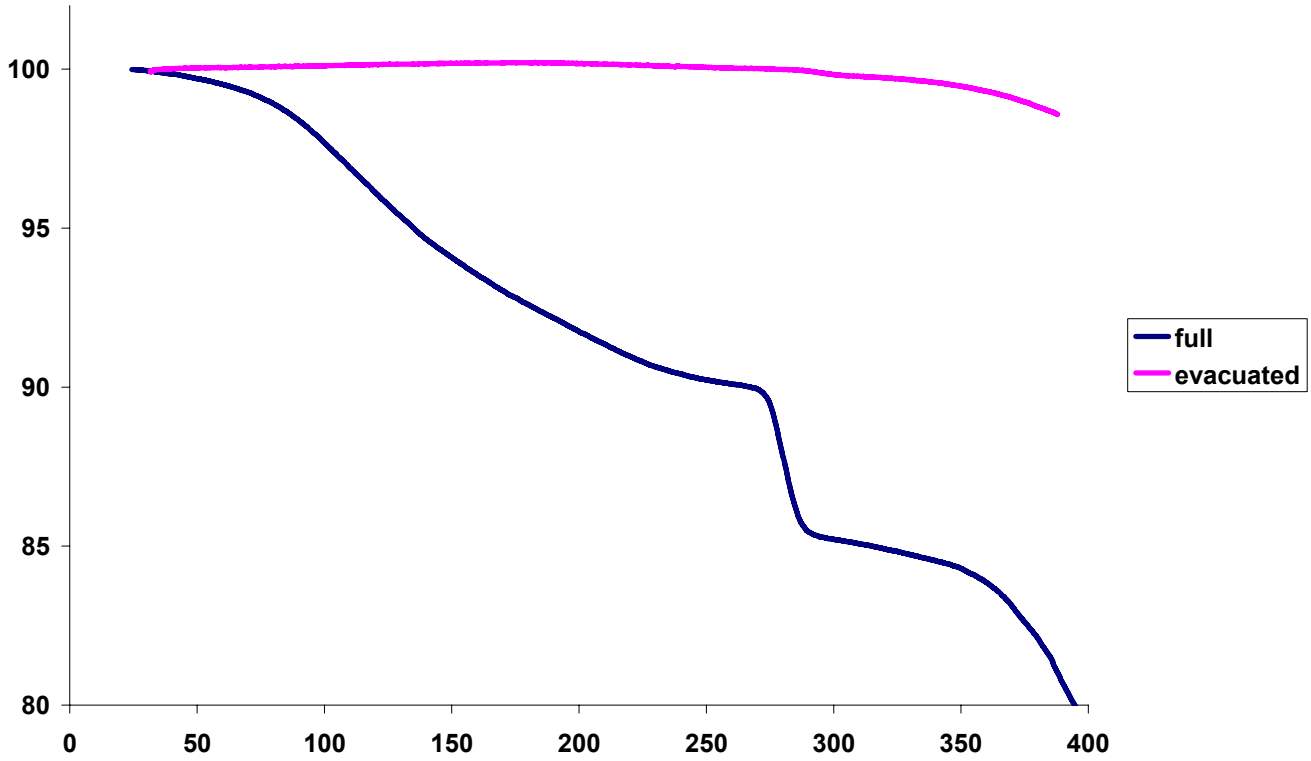

Figure S1: TGA curves for TIF 1.

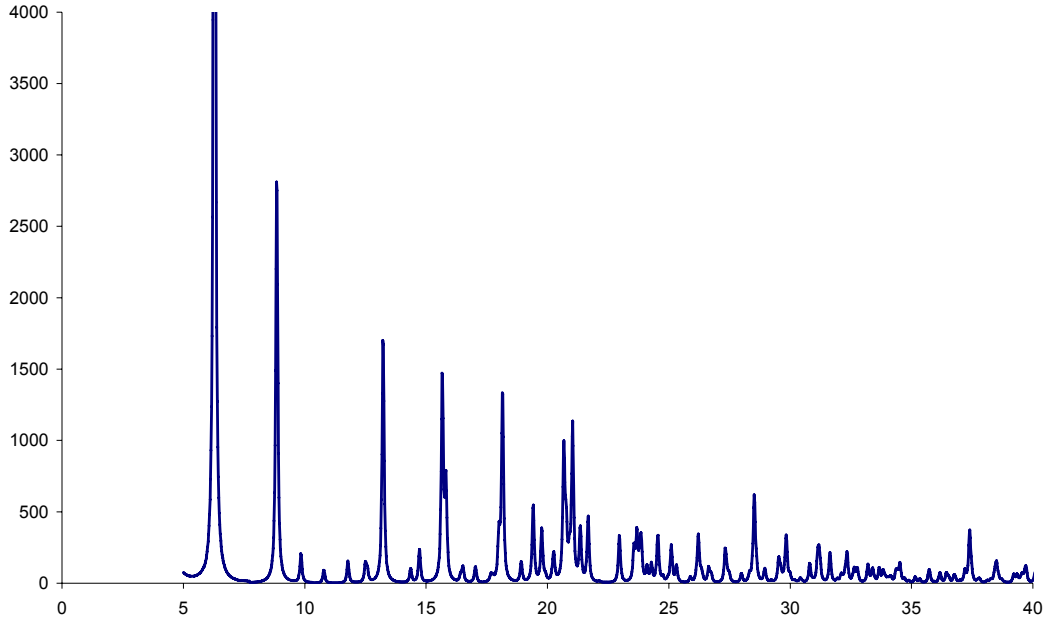

Figure S2: Calculated X-ray diffraction powder pattern of TIF 1 from X-ray crystal structure.

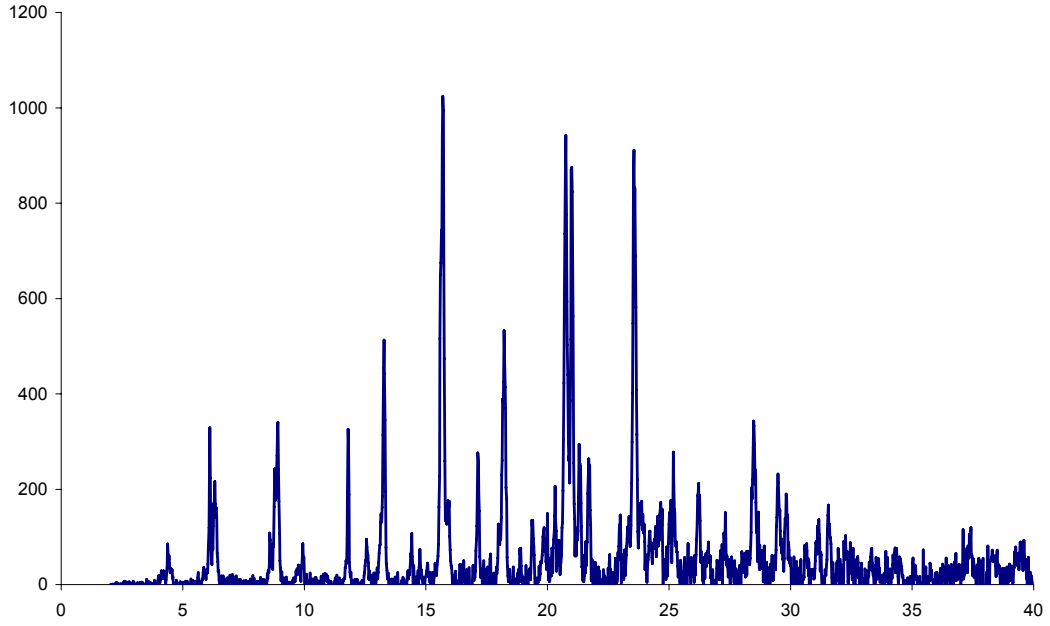

Figure S3: Experimental X-ray diffraction powder pattern of TIF 1 after grinding, washing with MeOH and subjecting to heating at 200 °C under vacuum for 2 days.

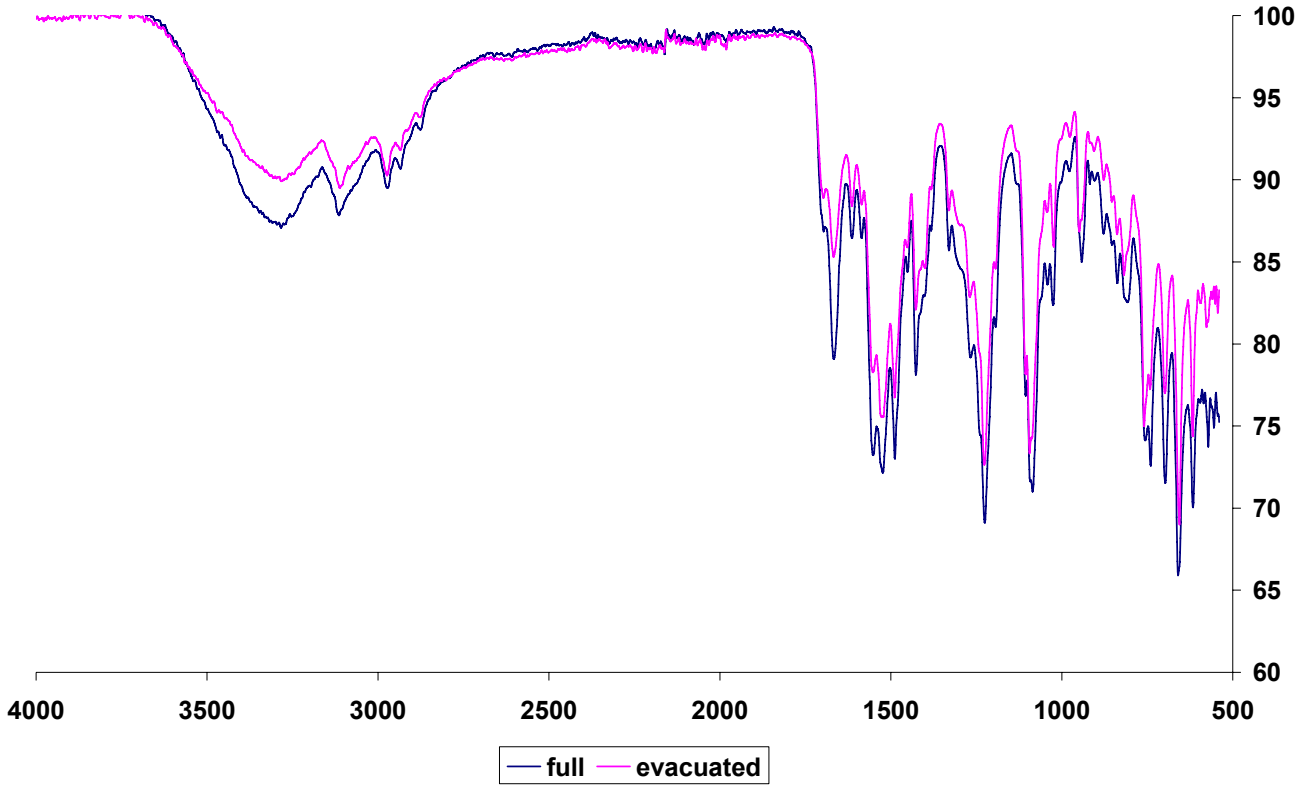

Figure S4: IR spectra of TIF 1.

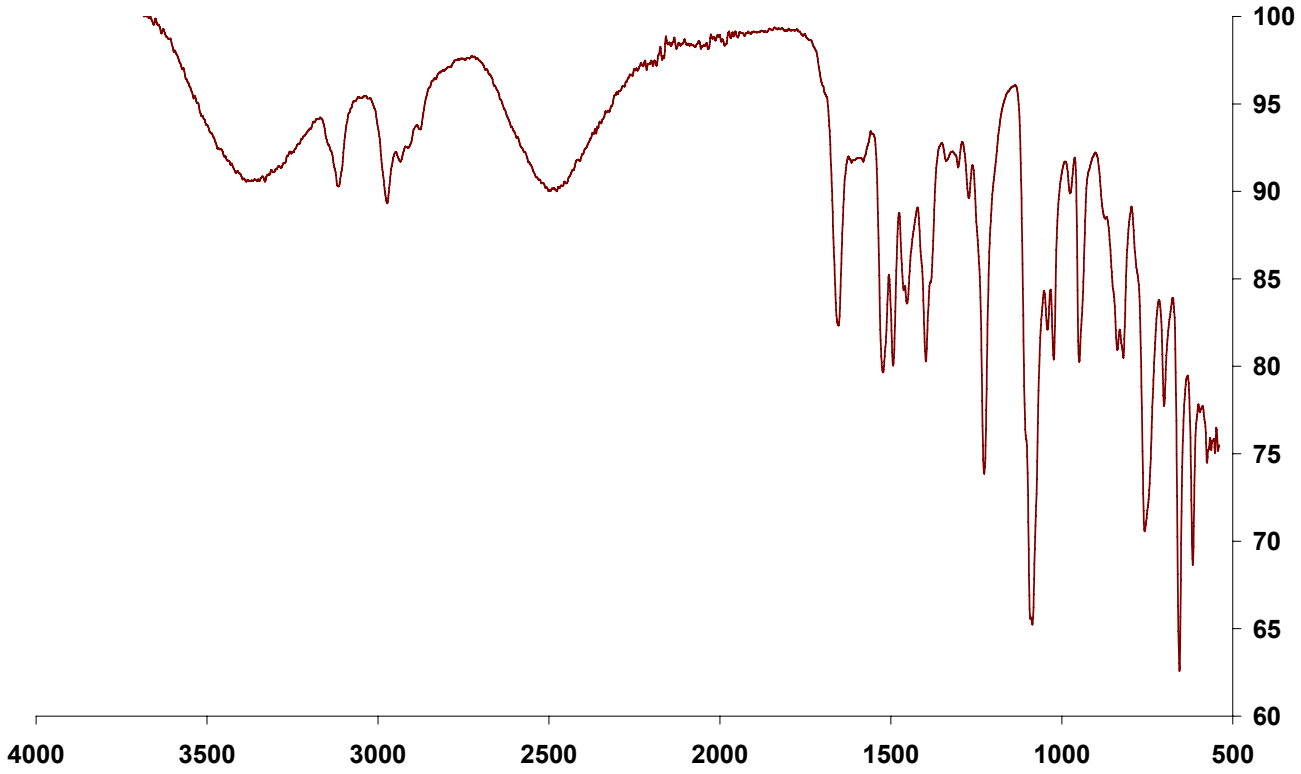

Figure S5: IR spectrum of TIF 1 following D_2O diffusion.

1,3,5-trimethylimidazole-2,4,6-triethylbenzene: To a degassed mixture of 1,3,5-tribromomethyl-2,4,6-triethylbenzene (4.5 g, 10.2 mmol) and imidazole (15.0 g, 220.0 mmol) was added dry MeOH (200 mL). The mixture was heated at reflux for 48 hours under nitrogen. The solvent was removed *in vacuo* resulting in yellow oil. Water (100 mL) was added to give a white precipitate, which was filtered and washed with water (2 x 50 mL). Colourless crystals were grown by slow cooling of a hot water solution. Yield: 2.48 g (60 %). ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.49 (s, 3H, N(CH)N), 6.94 (s, 3H, $N(CH)_2N$), 6.89 (s, 3H, $N(CH)_2N$), 5.25 (s, 6H, CH_2), 2.64 (q, $^{3}J_{H-H}$ = 7.4 Hz, 6H, CH_2), 0.80 (t, $^{3}J_{H-H}$ = 7.4 Hz, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, d_6-DMSO): δ 144.9 (N(CH)N), 136.6 (Ar), 128.4 ($N(CH)_2N$), 118.8 ($N(CH)_2N$), 44.0 (CH_2), 22.7 (CH_2), 15.1 (CH_3). Anal. Calcd. for $C_{24}H_{30}N_6{\cdot}2H_2O$: C, 65.73; H, 7.81; N, 19.16. Found: C, 66.08; H, 7.79; N, 18.73.

Synthesis of $[Co_3Cl_6(L')_2]$ (TIF 1). 1,3,5-Trimethylimidazole-2,4,6-triethylbenzene (0.50 g, 1.24 mmol) and $CoCl_2{\cdot}6H_2O$ (0.30 g, 1.26 mmol) in dimethylformamide (10 mL), ethane-1,2-diol (5 mL) and pyridine (5 mL) were added to a vial. After sonication for 10 minutes the mixture was heated at 140 °C in a sealed vial for 72 hours. The resulting royal blue crystals were filtered while hot and washed with chloroform. Yield: 0.42 g (84 % based on an empty host). Calcd. For $C_{48}H_{60}Cl_6Co_3N_{12}$: C, 48.26; H, 5.06; N, 14.07; Cl, 17.81 %. Found: C, 46.63; H, 5.58; N, 12.60; Cl, 12.47 %. Found after heating at 200 °C under vacuum for 2 days: C, 47.00; H, 4.95; N, 13.45; Cl, 15.65 %. There is residual guest species in the pores; calcd. for $C_{48}H_{60}Cl_6Co_3N_{12}{\cdot}2H_2O$: C, 46.84; H, 5.24; N, 13.66; Cl, 17.27 %.