Electronic Supplementary Information

Chelation-driven fluorescence deactivation in three alkali earth metal MOFs containing 2,2'-dihydroxybiphenyl-4,4'-dicarboxylate

Damien Rankine,[a] Tony D. Keene,[ab] Christopher J. Sumby,[a*] and Christian J. Doonan[a*]

[a] School of Chemistry and Physics, The University of Adelaide, SA 5005, Australia.[b] Present address: School of Chemistry, University of Southampton, University Road, Southampton, SO17 1BJ, UK.
**Corresponding Author*

Contents

1. General Experimental

N,N'-Dimethylformamide (DMF) was dried twice consecutively over freshly activated 4Å molecular sieves and stored under N_2 atmosphere. The Campbell Microanalytical Laboratory at the University of Otago, Dunedin performed all elemental analyses. Thermogravimetric analysis (TGA) was performed on a Perkin−Elmer STA-6000 under a constant flow of N_2 (20L/min) at a temperature ramp rate of 5°C/min. Infrared (IR) spectra were recorded on a Perkin−Elmer Fourier Transform Infrared (FT−IR) spectrometer on a zinc−selenide crystal. N_2 adsorption isotherms at 77 K were recorded on a Micromeritics ASAP 2020 adsorption analyser. The Brunauer-Emmett-Teller (BET) method[1] was used for calculating surface area from N_2 isotherms at 77 K, and further validated using the method of Walton and Snurr.[2] Solid-state fluorescence emission spectra were collected on a Varian Cary Eclipse Fluorescence Spectrophotometer at an excitation wavelength of 240 nm. Samples were pressed onto a 1.0 x 1.0 mm quartz slide and oriented at approximately 135° to the incident excitation beam.

Ligand **H_4diol** was synthesised using literature procedures.[3-5]

2. Activation conditions

[Mg(H_2diol)(DMF)$_2$].DMF was activated by washing with 4 × 3 ml DMF and then soaked for 12 hours in 3 ml of DMF. Samples were then exchanged with 4 × 3 ml DCM and then soaked in fresh DCM for 2-3 hours. Excess liquid CH_2Cl_2 was extracted and the sample was dried briefly under a flow of N_2 before placing under dynamic vacuum overnight. Samples were then heated at 60 °C at 3 μbar for 4 hours prior to gas adsorption measurements.

3. Gas Adsorption Data

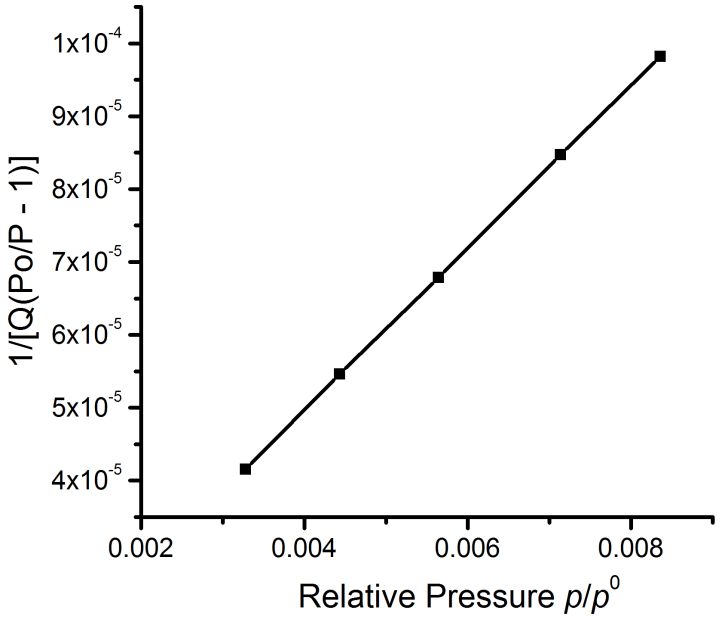

Figure S1. BET plot of [Mg(H_2diol)$(DMF)_2$] from N_2 isotherm at 77K.

	Mg(H_2diol)(DMF)
BET Surface Area	390.9406 ± 1.0363 m²/g
Slope	0.011130 ± 0.000030 g/cm³ STP
Y-Intercept	0.000005 ± 0.000000 g/cm³ STP
C	2146.925619
Qm	89.8054 cm³/g STP
Correlation Coefficient	0.9999895

Table S1. BET statistics from the N_2 isotherm collected at 77K.

4. Structural Characterisation

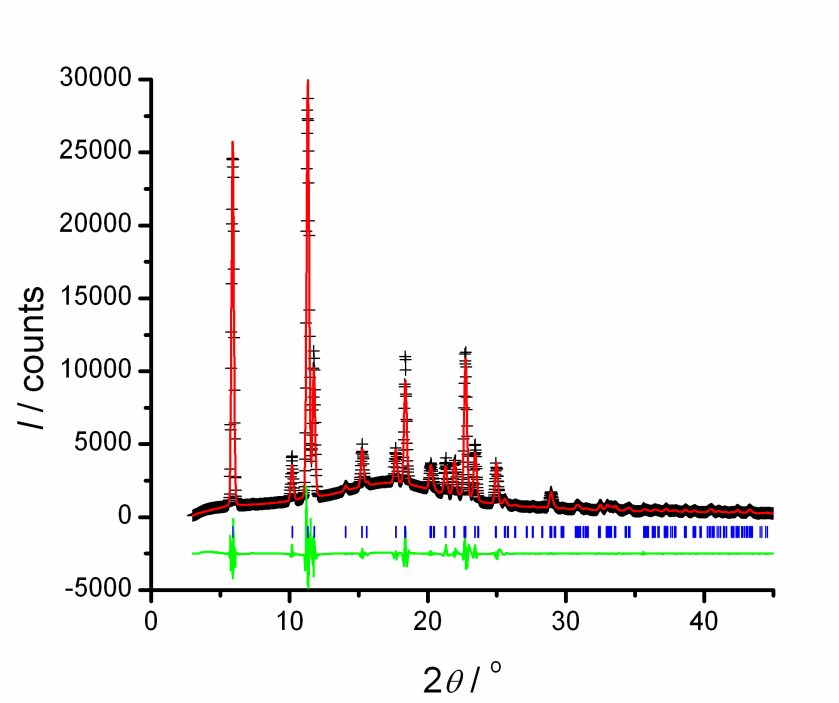

Figure S2. Le Bail refinement of [Mg(H_2diol)$(DMF)_2$].DMF showing the experimental pattern (crosses), model (red), peak positions (blue) and difference plot (green).

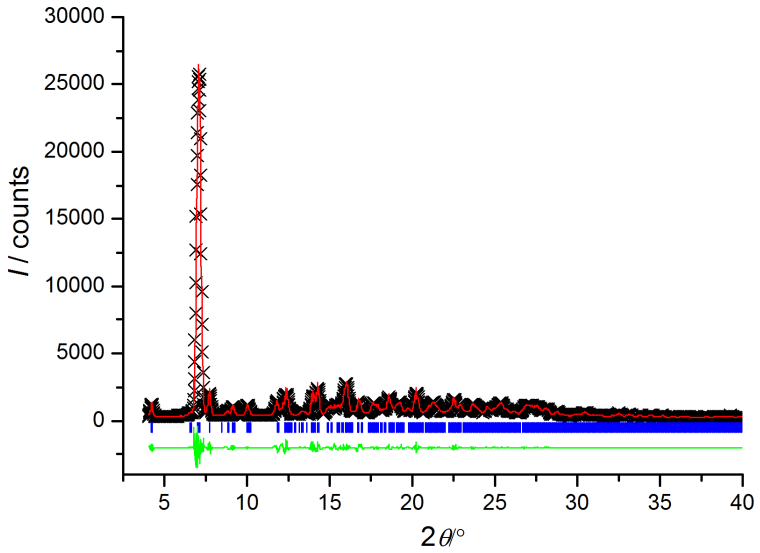

Figure S3. Le Bail refinement of [$Ca_{3.5}$(Hdiol)(H_2diol)$_2(DMF)_5$].1.2DMF showing the experimental pattern (crosses), model (red), peak positions (blue) and difference plot (green).

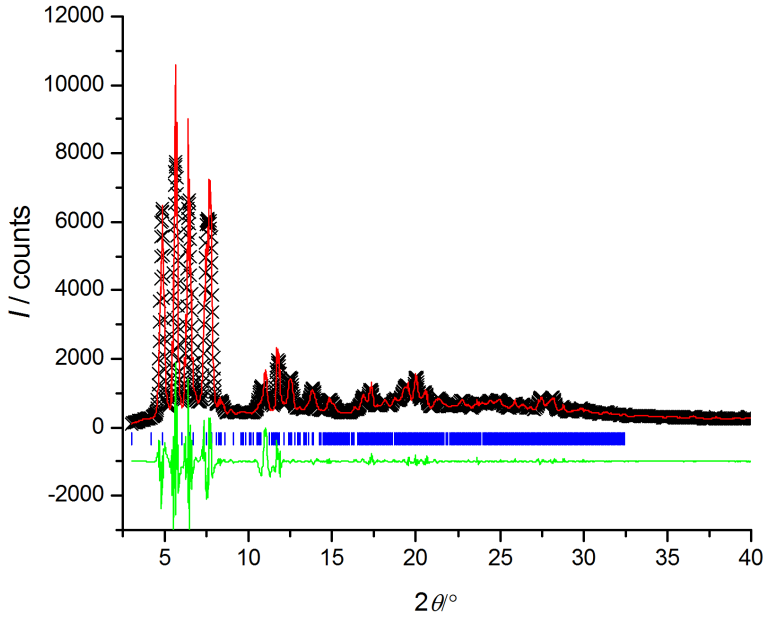

Figure S4. Le Bail refinement of $[Sr_3(H_2diol)_3(DMF)_5]$ showing the experimental pattern (crosses), model (red), peak positions (blue) and difference plot (green).

	$[Mg(H_2diol)(DMF)_2]$ .DMF	$[Ca_{3.5}(Hdiol)(H_2diol)_2(DMF)_5]$ .1.2DMF	$[Sr_3(H_2diol)_3(DMF)_5]$
Crystal System	h*P*	m*C*	o*P*
Space Group	$P3_121$	*C*2/c	*Pbcn*
a	17.4079	43.6529	29.221
b	17.4079	14.2076	18.3071
c	9.1873	26.4951	30.9435
α	90	90	90
β	90	106.868	90
γ	120	90	90
Volume ($Å^3$)	2784.07	15723.7	16550.84
R_1	4.175	4.568	8.351
R_{wp}	6.337	7.181	14.082
GooF	7.585	4.827	15.808

Table S2. Unit cell parameters calculated from Le Bail refinements of powder X-ray diffraction patterns.

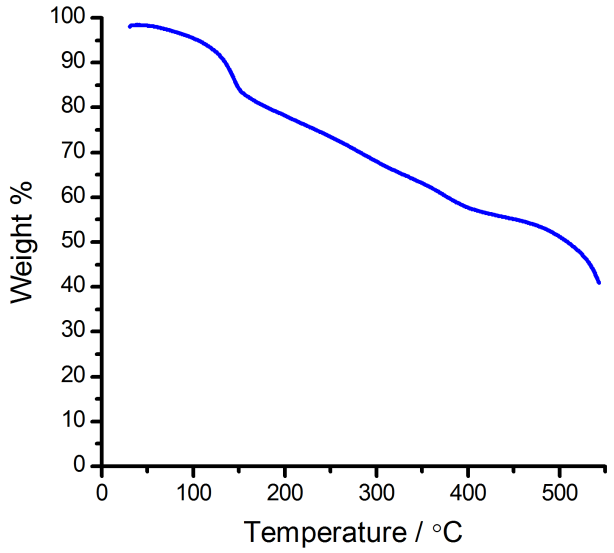

Figure S5. TGA plot for [Mg(H_2diol)$(DMF)_2$].DMF.

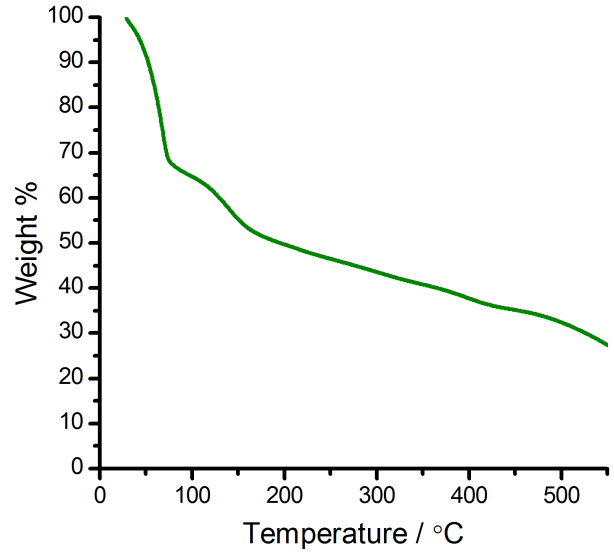

Figure S6. TGA plot for[$Ca_{3.5}$(Hdiol)(H_2diol)$_2(DMF)_5$].1.2DMF.

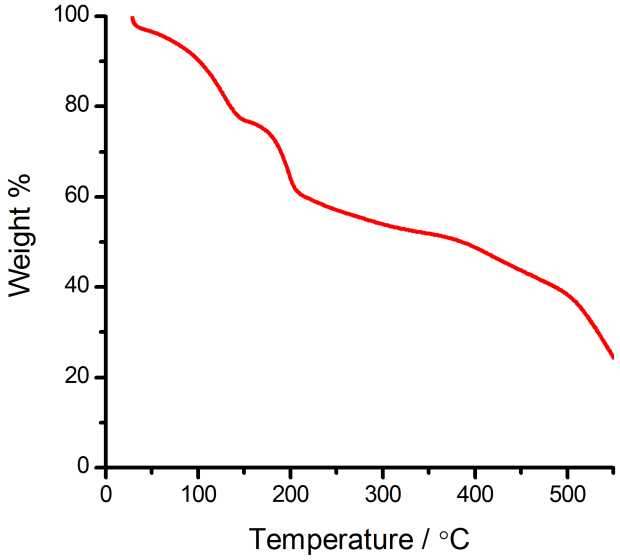

Figure S7. TGA plot for $[Sr_3(H_2diol)_3(DMF)_5]$.

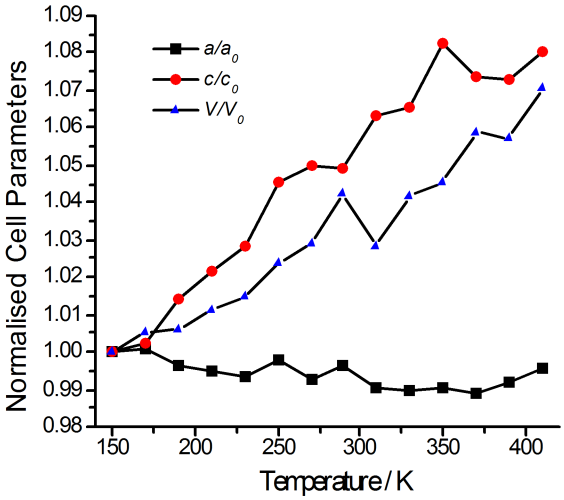

Figure S8. Variable-temperature X-ray diffraction data for $[Mg(H_2diol)(DMF)_2].DMF$.

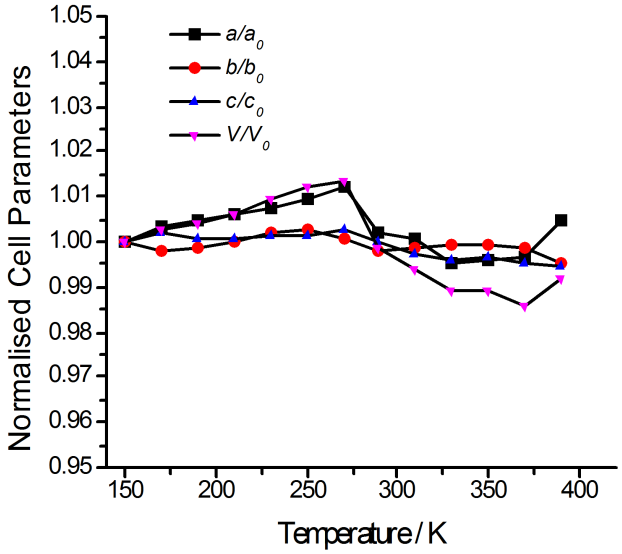

Figure S9. Variable-temperature X-ray diffraction data for $[Ca_{3.5}(Hdiol)(H_2diol)_2(DMF)_5].1.2DMF$.

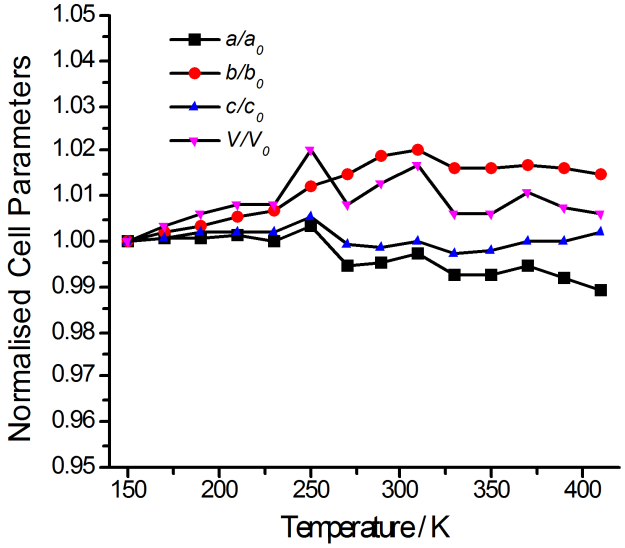

Figure S10. Variable-temperature X-ray diffraction data for $[Sr_3(H_2diol)_3(DMF)_5]$.

Laue Group	Temperature (K)	*a/b* (Å)	*c* (Å)	α/ β (°)	γ (°)	Volume (Å^3)
hP	150	17.43	8.39	90	120	2207.31
hP	170	17.45	8.41	90	120	2218.46
hP	190	17.36	8.51	90	120	2220.29
hP	210	17.34	8.57	90	120	2231.61
hP	230	17.32	8.63	90	120	2240.63
hP	250	17.39	8.63	90	120	2259.39
hP	270	17.3	8.77	90	120	2271.93
hP	290	17.36	8.81	90	120	2301.18
hP	310	17.26	8.8	90	120	2270.48
hP	330	17.25	8.92	90	120	2300.04
hP	350	17.26	8.94	90	120	2307.13
hP	370	17.24	9.08	90	120	2336.69
hP	390	17.29	9.01	90	120	2333.36
hP	410	17.3	9	90	120	2332.89

Table S3. Variable-temperature X-ray diffraction data and unit cell information for $[Mg(H_2diol)(DMF)_2].DMF$.

Laue Group	Temperature (K)	*a* (Å)	*b* (Å)	*c* (Å)	α/γ (°)	β (°)	Volume (Å^3)
mC	150	43.82	14.22	26.32	90	106.9	15693
mC	170	43.98	14.19	26.37	90	107	15740
mC	190	44.03	14.2	26.34	90	107	15753
mC	210	44.09	14.22	26.33	90	107.1	15784
mC	230	44.15	14.25	26.35	90	107.1	15843
mC	250	44.23	14.26	26.35	90	107.2	15881
mC	270	44.34	14.23	26.39	90	107.1	15908
mC	290	43.91	14.19	26.32	90	107.1	15675
mC	310	43.84	14.2	26.25	90	107.4	15596
mC	330	43.61	14.21	26.22	90	107.2	15519
mC	350	43.63	14.21	26.23	90	107.2	15525
mC	370	43.66	14.2	26.19	90	107.6	15471
mC	390	44.03	14.15	26.17	90	107.4	15566
mC	410	35.67	14.34	25.96	90	110	12482

Table S4. Variable-temperature X-ray diffraction data and unit cell information for $[Ca_{3.5}(Hdiol)(H_2diol)_2(DMF)_5].1.2DMF$.

Laue Group	Temperature (K)	*a*	*b*	*c*	α	γ	Volume (Å^3)	R_{int} (%)
oP	150	19.62	27.49	31.17	90	90	16814	4.43
oP	170	19.63	27.54	31.2	90	90	16868	4.52
oP	190	19.63	27.59	31.23	90	90	16916	4.65
oP	210	19.65	27.63	31.23	90	90	16951	4.3
oP	230	19.62	27.67	31.23	90	90	16952	4.36
oP	250	19.68	27.82	31.33	90	90	17152	7.72
oP	270	19.52	27.89	31.14	90	90	16945	8.26
oP	290	19.53	28.01	31.13	90	90	17025	7.45
oP	310	19.57	28.04	31.18	90	90	17103	8.32
oP	330	19.48	27.94	31.08	90	90	16912	8.52
oP	350	19.47	27.94	31.1	90	90	16920	8.72
oP	370	19.51	27.95	31.18	90	90	16998	27.69
oP	390	19.46	27.93	31.17	90	90	16940	8.57
oP	410	19.41	27.89	31.24	90	90	16914	8.51

Table S5. Variable-temperature X-ray diffraction data and unit cell information for $[Sr_3(H_2diol)_3(DMF)_5]$.

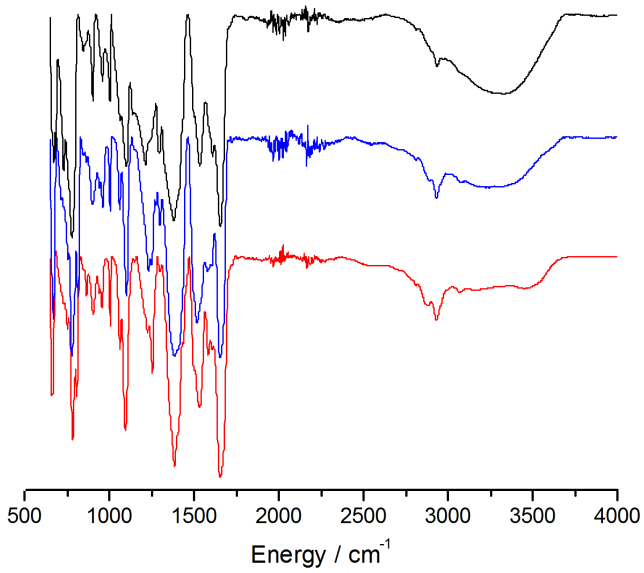

Figure S11. Infrared transmission spectra of $[Mg(H_2diol)(DMF)_2]$.DMF (black), $[Sr_3(H_2diol)_3(DMF)_5]$ (blue) and $[Ca_{3.5}(Hdiol)(H_2diol)_2(DMF)_5]$.1.2DMF (red).

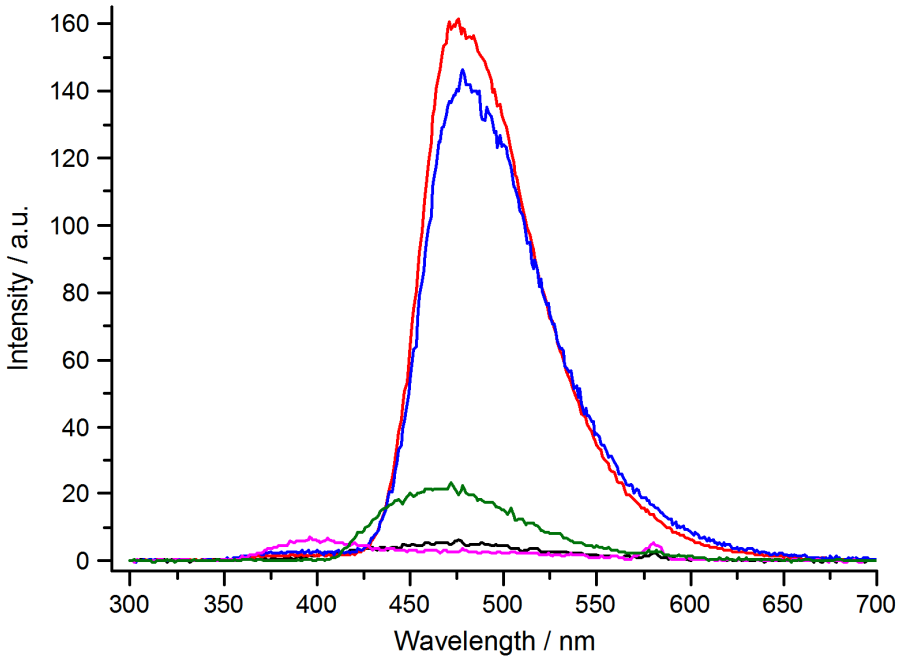

Figure S12. Fluorescence emission spectra (λ_{exc} = 260nm) of H_4diol dissolved in DMF (red), DMSO (blue), 1:2:0.5 10 M NaOH/THF/MeOH (green), MeOH (pink) and 0.1 M NaOH (black).

5. References

1. S. Brunauer, P. H. Emmett, E. Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.
2. K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, 2007, **129**, 8552.
3. T. D. Keene, D. Rankine, J. D. Evans, P. D. Southon, C. J. Kepert, J. B. Aitken, C. J. Sumby and C. J. Doonan, *Dalton Trans.*, 2013, **42**, 7871.
4. D. Rankine, A. Avellaneda, M. R. Hill, C. J. Doonan and C. J. Sumby, *Chem. Commun.*, 2012, **48**, 10328.
5. M. A. Rizzacasa and M. V. Sargent, *Aust. J. Chem.*, 1988, **41**, 1087.