Electronic Supplementary Information

Investigating the Solid State Hosting Abilities of Homo- and Heterovalent [Co_7] Metallocalix[6]arenes

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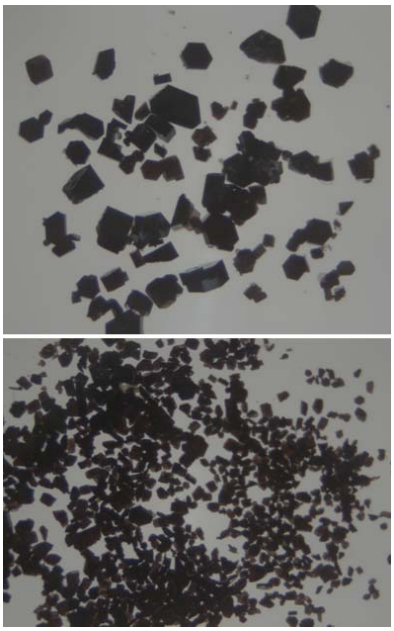

Fig. S1 Microscopic images of a sample of $[Co(II)_7(OH)_6(L_1)_6](NO_3)_2.2MeOH$ (**2**). This very sample was used for magnetic susceptibility measurements described in this work.

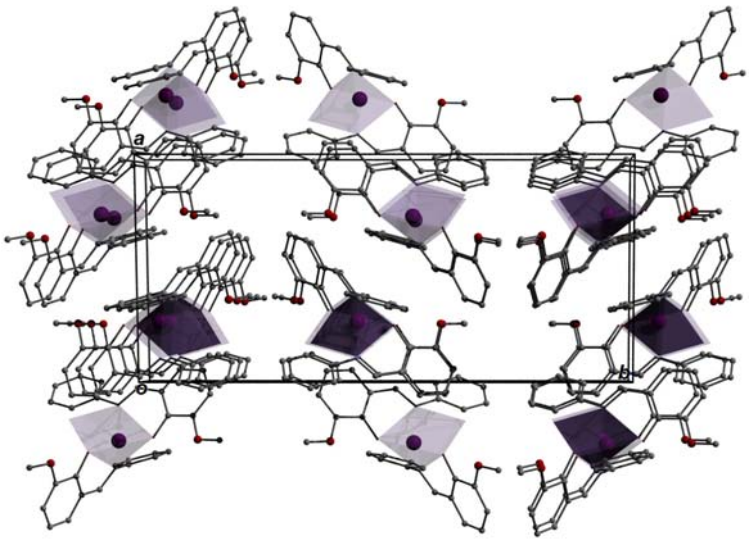

Fig. S2 Crystal packing shown in polyhedral form showing the 1D superimposable H-bonded chains of $[Co(II)(L_2)_2]$ (**5**) propagating along the *c* direction. H atom omitted for clarity.

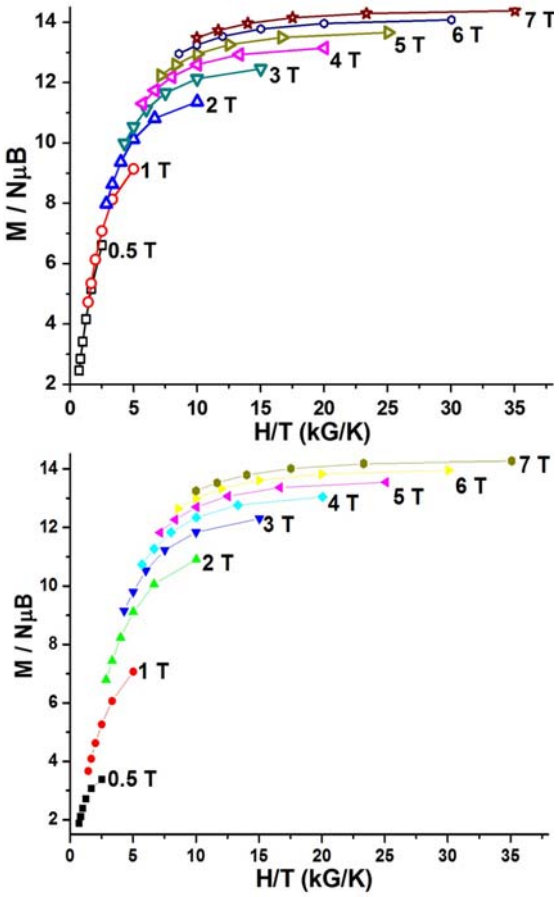

Fig. S3 Plots of Reduced magnetisation (M /NμB)) vs. Field (H /T) obtained from complexes **2** (top) and **4** (bottom), measured in the 2-7 K temperature range.

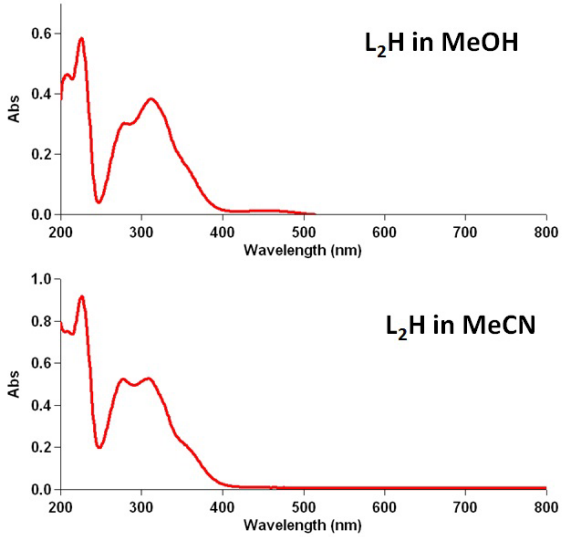

Fig. S4 UV-vis spectra obtained from MeOH (top) and MeCN (bottom) solutions of L_2H. For UV-vis data on L_1H see L. F. Jones et al., *Dalton Trans.*, 2010, 39, 4809–4816.

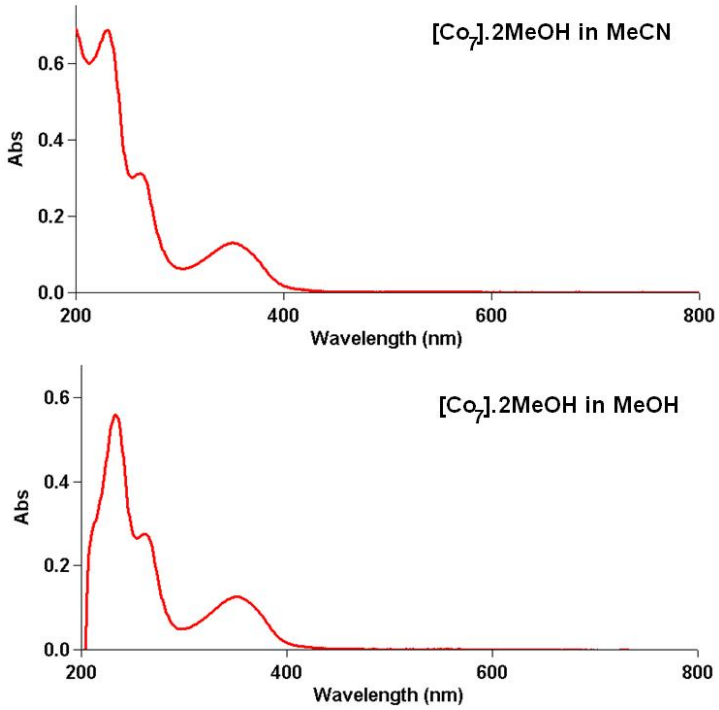

Fig. S5 UV-vis spectra obtained from MeCN (top) and MeOH (bottom) solutions of $[Co_7(OH)_6(L_1)_6](NO_3)_2.2MeOH$ (**2**).

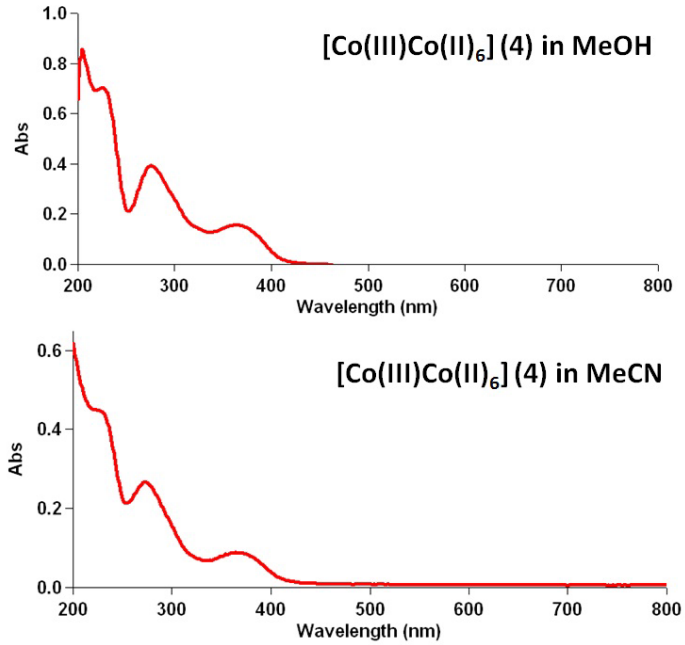

Fig. S6 UV-vis spectra obtained from MeOH (top) and MeCN (bottom) solutions of $[(NO_3)_2{\subset}Co(III)Co(II)_6(OH)_6(L_2)_6](NO_3).3MeCN$ (**4**).

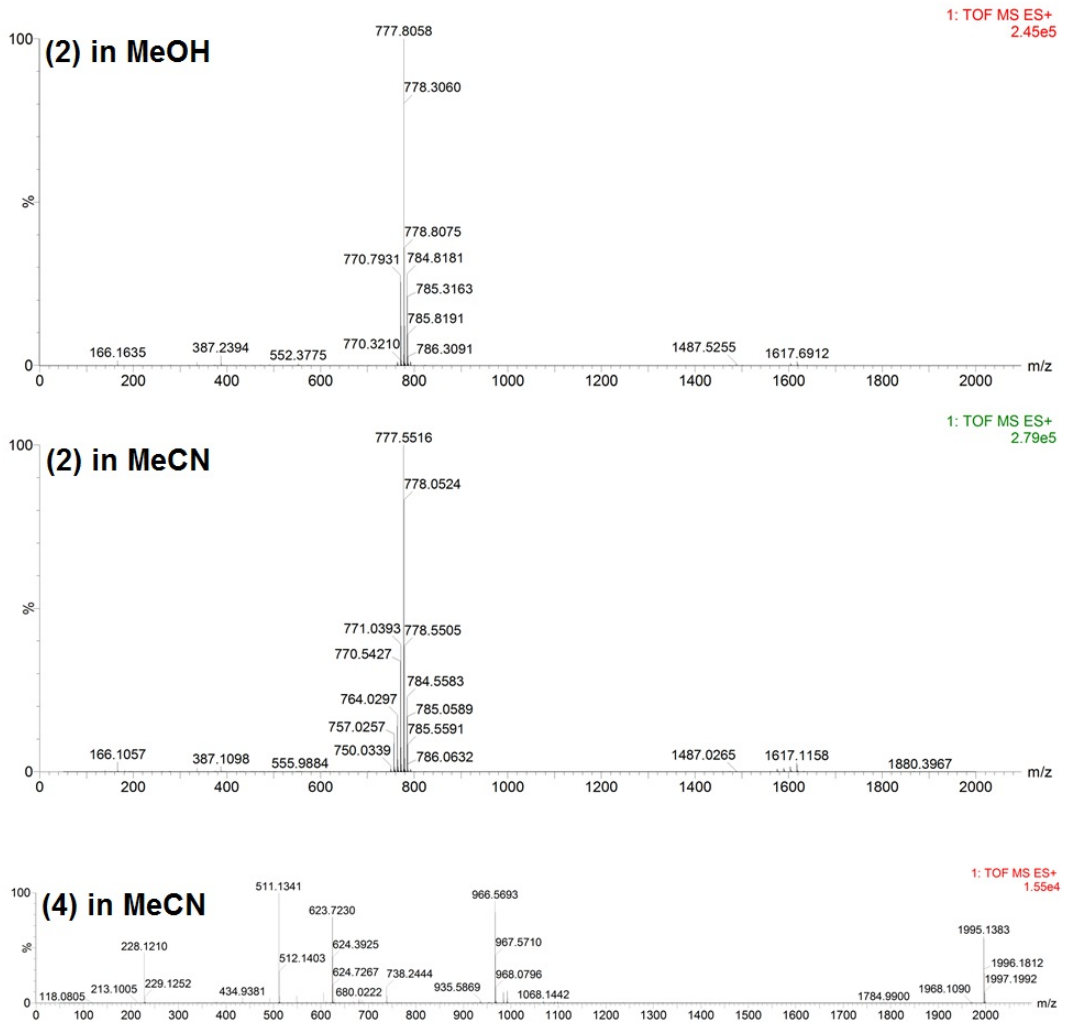

Fig. S7: ESI-MS spectra obtained from MeOH and MeCN samples of **2** and **4**. Peak assignments are discussed in the main text.

Table S1 Crystal data obtained from **5** and **6** (carried out at 296.9 and 150 K respectively).

	5	**6**
Formula	$C_{28}H_{24}N_2O_4Co_1$	$C_{54}H_{54}B_1Br_6F_4N_6O_{12}Co_2Na_1$
Formula Weight	511.42	1686.15
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2/c
a / Å	11.6622(8)	24.774(5)
b / Å	23.9507(13)	15.542(3)
c / Å	9.2521(6)	15.416(3)
α, β, γ (°)	90,109.596(7), 90	90, 93.61(3), 90
V / Å^3	2434.6(3)	5924(2)
Z	4	4
D_c (g cm^{-3})	1.395	1.891
μ (mm^{-1})	0.742	4.693
Reflections	4448	5423
Unique reflections	3291	4199
GOF on F^2	1.139	1.039
R_{int}	0.0341	0.0298
R1 [I>2σ(I)]	0.0544	0.0302
wR2 (all data)	0.1250	0.0713
Restraints, Parameters	0, 318	0, 395

Table S2: BVS calculations on complexes **1**, **2, 4** and **6**.

Complex	Atom label and BVS result
(1)	**Co1 (central)**
	1.98
	Co2 (outer ring)
	2.05
(2)	**Co1 (central)**
	1.92
	Co2 (outer ring)
	2.01
(4)	**Co1 (central)**
	3.37
	Co2 (outer ring) 2.06
	Co3 (outer ring)
	1.99
	Co4 (outer ring)
	1.98
(6)	**Co1**
	3.3

X-ray diffraction details on the collection of 1-6

The structures of **1-6** were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source**.** Each data reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)[1] and refined by full matrix least squares using SHELXL-97.[2] SHELX operations were automated using the OSCAIL software package.[3] All hydrogen atoms were placed in calculated positions. The non hydrogen atoms were refined anisotropic except for the disordered guest MeOH molecules in complex **2** which were left isotropic. DFIX and restraints were required on the disordered MeOH guest solvent molecules in **2** as a result of high isotropic thermal parameters upon refinement.

1. G. M. Sheldrick, *Acta. Crystallogr., Sect. A: Found. Crystallogr.,* 1990, **A46**, 467.
2. G. M. Sheldrick, SHELXL-97, A computer programme for crystal structure determination, University of Gottingen, 1997.
3. P. McArdle, P. Daly and D. Cunningham, *J. Appl. Crystallogr*., 2002, **35**, 378.