Electronic Supplementary Material (ESI) for *CrystEngComm*

Supporting materials

Unprecedented 3D polycatenation based on ribbons of rings found in two metallosupramolecular polymers whose open frameworks show reversible collapse upon de- and rehydration

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Materials, Methods, Syntheses and Characterizations

1-(4-carboxybenzyl)-4,4′-bipyridinium chloride was synthesized based on the nucleophilic substitution reaction of 4,4′-bipyridine and 4-(chloromethyl)benzoic acid. Other chemicals employed for synthesis were obtained commercially. Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. IR spectra were performed on a Spectrum One FT-IR spectrometer with KBr pellets in the range 4000–400 cm^{-1}. X-Ray powder diffraction (XRPD) data was obtained using a Rigaku DMAX 2500 powder diffractometer with Cu Kα radiation.

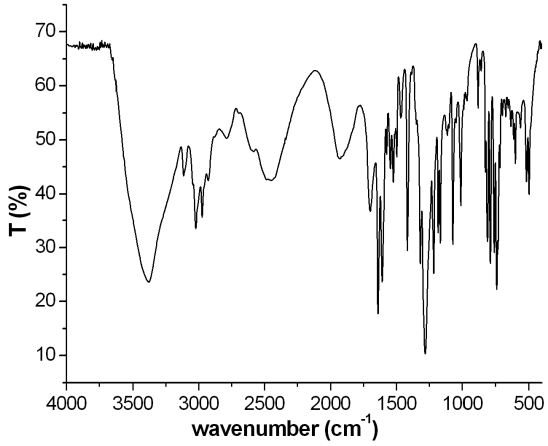

Fig. S1. IR spectrum of HBpybcCl salt.

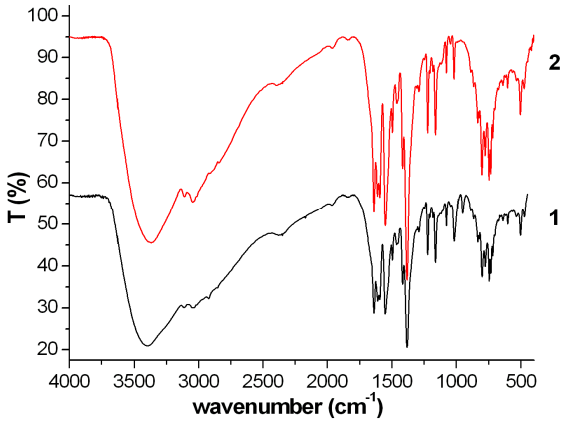

Fig. S2. IR spectra of **1** and **2**.

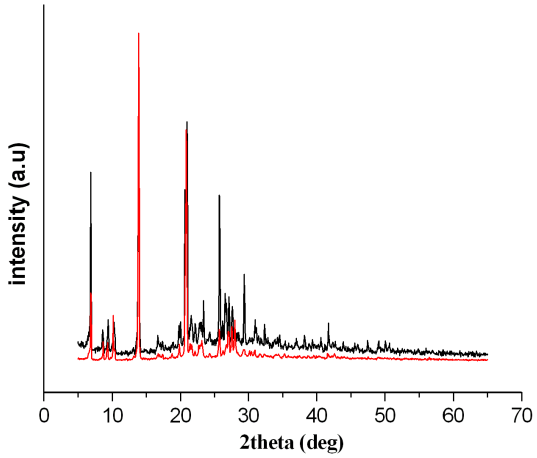

Fig. S3. Powder X-ray diffraction patterns of **1** and **2**.

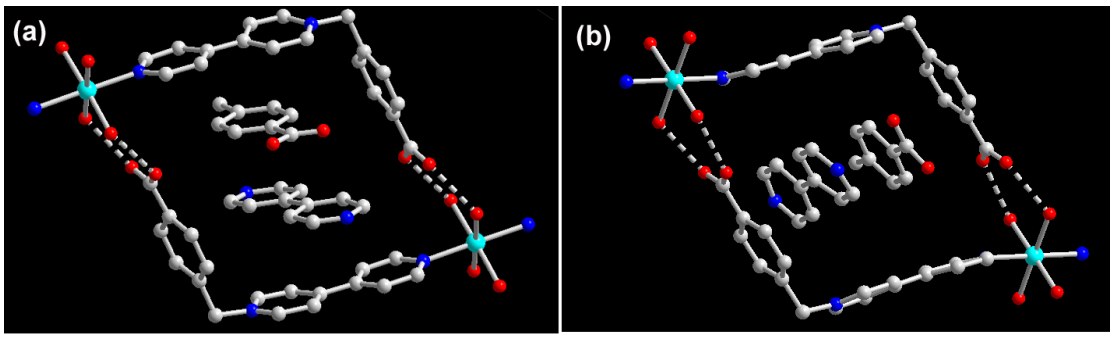

Fig. S4. Two different interpenetrating ways: bipyridinium and benzyl carboxylate groups are sandwiched between and orthogonally oriented with respect to two bipyridinm units within the rings of ribbons A (a), or two benzyl carboxylate units within the rings of ribbons B (b).

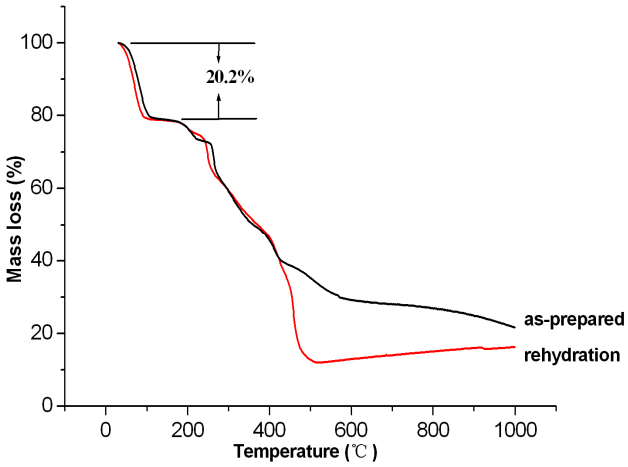

Fig. S5. TGA plots of complex **1** as the prepared material and after rehydration.

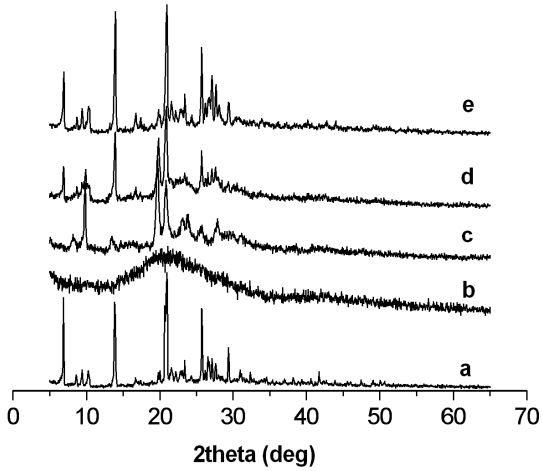

Fig. S6. Powder X-ray diffraction patterns of **1** measured at room temperature (from bottom to top) as the prepared material (1a), after dehydration (1b) and after rehydration in moist air for ten minutes (1c), 3 hours (1d) and 3 days (1e).

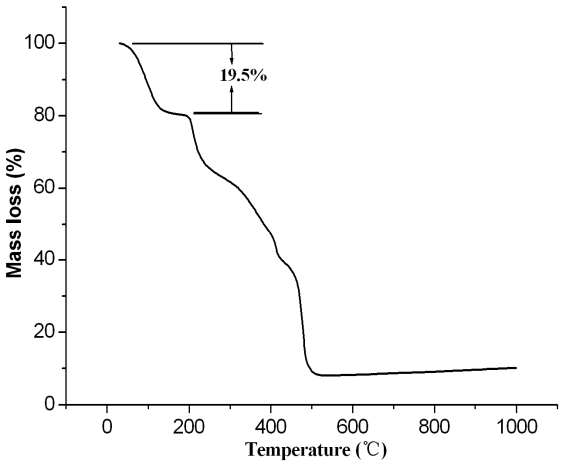

Fig. S7. TGA plots of complex **2**.

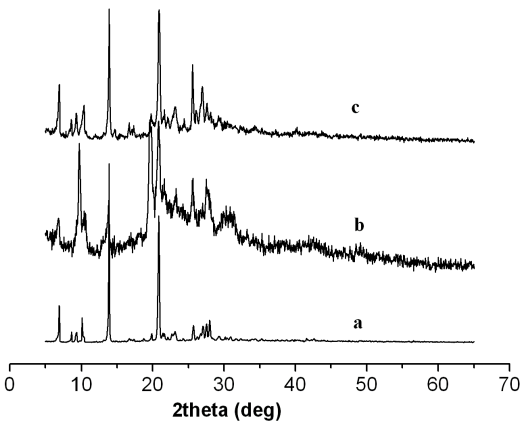

Fig. S8. Powder X-ray diffraction patterns of **2** measured at room temperature (from bottom to top) as the prepared material (2a), after rehydration in the ambient laboratory air for 3 days (2b) and 7 days (2c).

Table S1. Selected bond lengths (Å) and angles (deg) for **1**.

Bond Lengths			
Co1-N1	2.186(4)	Co2-N5	2.162(4)
Co1-N3	2.153(4)	Co2-N7	2.167(4)
Co1-O1W	2.071(4)	Co2-O5W	2.097(4)
Co1-O2W	2.083(4)	Co2-O6W	2.068(4)
Co1-O3W	2.080(4)	Co2-O7W	2.078(4)
Co1-O4W	2.095(4)	Co2-O8W	2.086(5)
Bond Angles			
N1-Co1-N3	179.3(2)	N5-Co2-N7	179.38(18)
O1W-Co1-O3W	178.76(17)	O6W-Co2-O8W	178.78(19)
O1W-Co1-O2W	90.51(17)	O6W-Co2-O7W	92.17(18)
O3W-Co1-O2W	89.04(17)	O8W-Co2-O7W	87.91(18)
O1W-Co1-O4W	90.70(18)	O6W-Co2-O5W	87.37(18)
O2W-Co1-O4W	178.08(17)	O7W-Co2-O5W	179.5(2)
O3W-Co1-O4W	89.72(16)	O8W-Co2-O5W	92.55(19)
O1W-Co1-N1	87.26(17)	O5W-Co2-N5	88.19(16)
O2W-Co1-N1	87.55(16)	O6W-Co2-N5	89.63(16)
O3W-Co1-N1	91.57(16)	O7W-Co2-N5	92.09(16)
O4W-Co1-N1	91.02(16)	O8W-Co2-N5	91.59(17)
O1W-Co1-N3	92.29(16)	O5W-Co2-N7	92.43(16)
O2W-Co1-N3	93.01(17)	O6W-Co2-N7	90.45(16)
O3W-Co1-N3	88.89(16)	O7W-Co2-N7	87.29(16)
O4W-Co1-N3	88.44(15)	O8W-Co2-N7	88.34(18)

Table S2. Hydrogen-bonding parameters in **1**.

D	**A**	**Symmetry code**	**d(D…A) (Å)**
O1W	O4	0.5+x, -0.5+y, z	2.627(7)
O2W	O3	0.5+x, -0.5+y, z	2.674(7)
O3W	O2	-0.5+x, 0.5+y, z	2.642(6)
O4W	O1	-0.5+x, 0.5+y, z	2.670(6)
O5W	O7	0.5+x, 0.5+y, z	2.656(8)
O6W	O8	0.5+x, 0.5+y, z	2.627(8)
O7W	O6	-0.5+x, -0.5+y, z	2.614(7)
O8W	O5	-0.5+x, -0.5+y, z	2.648(9)