Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary information

2D networks of metallo-capsules and other coordination polymers from a hexapodal ligand.

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1. NMR spectra

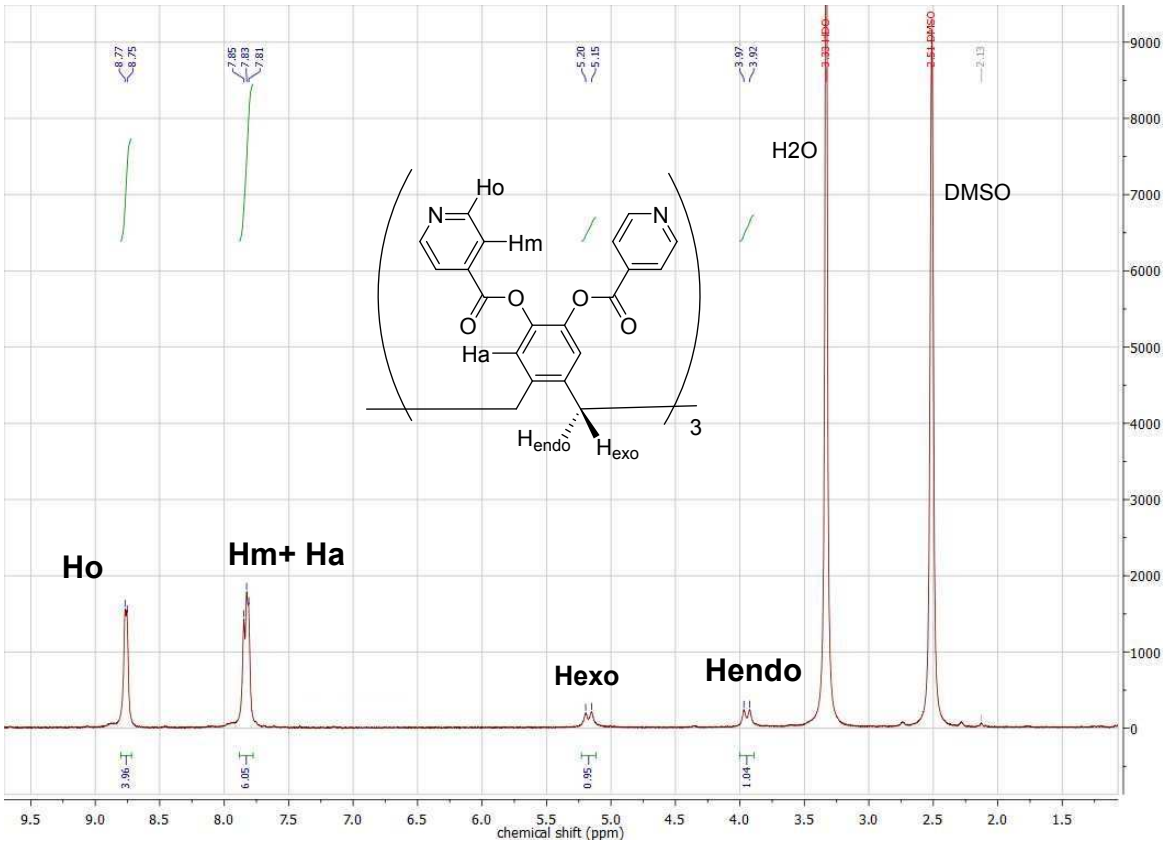


Figure S1. ^{1}H NMR spectrum (d_6-DMSO, 300 MHz) of ligand hexakis(isonicotinoyl)cyclotricatechylene, L1

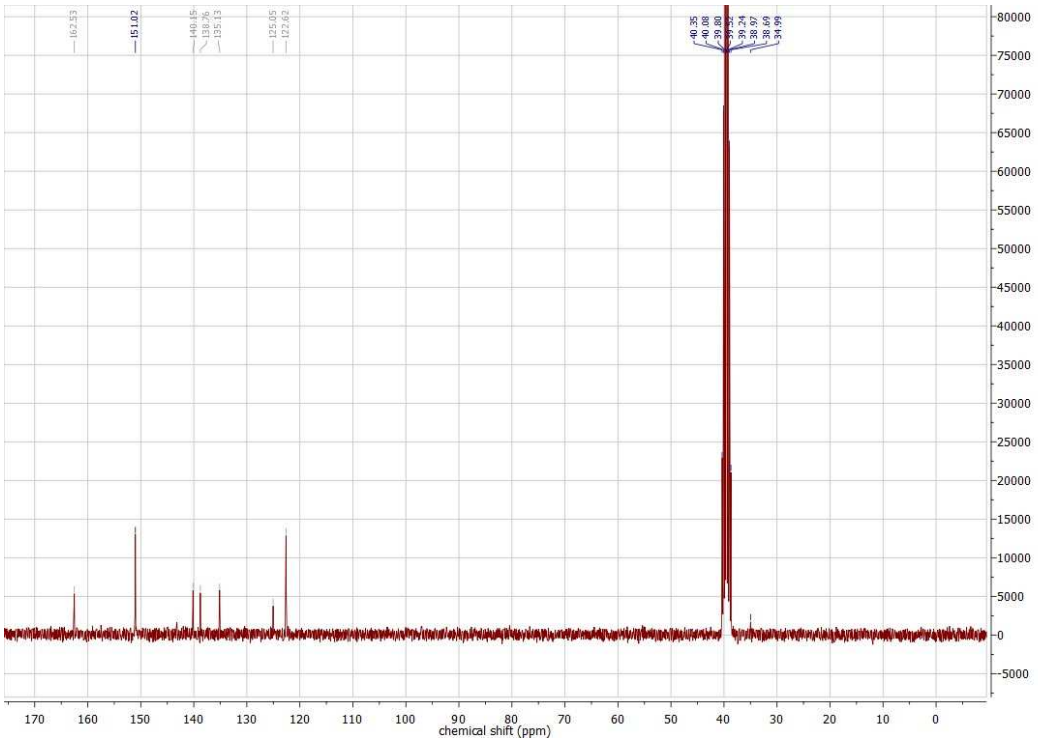


Figure S2. ^{13}C NMR spectrum (d_6-DMSO, 75 MHz) of L1.

2. Mass spectrometry

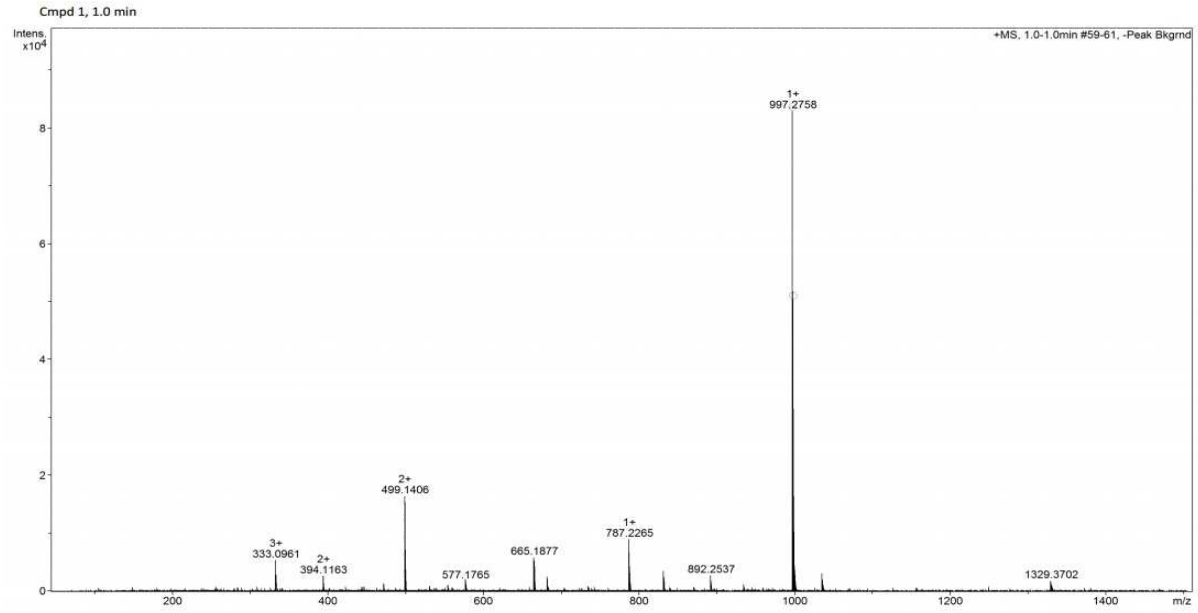


Figure S3. Mass spectrum of L1.

3. Infrared spectroscopy

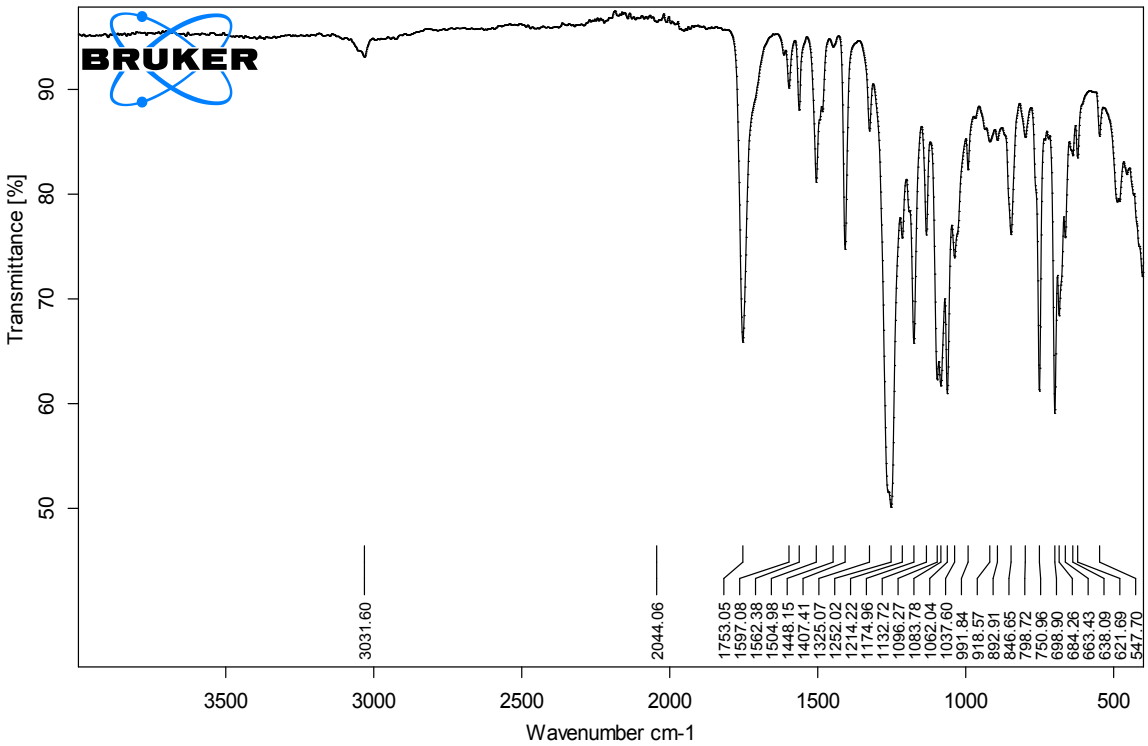


Figure S4. Infrared spectrum of L1.

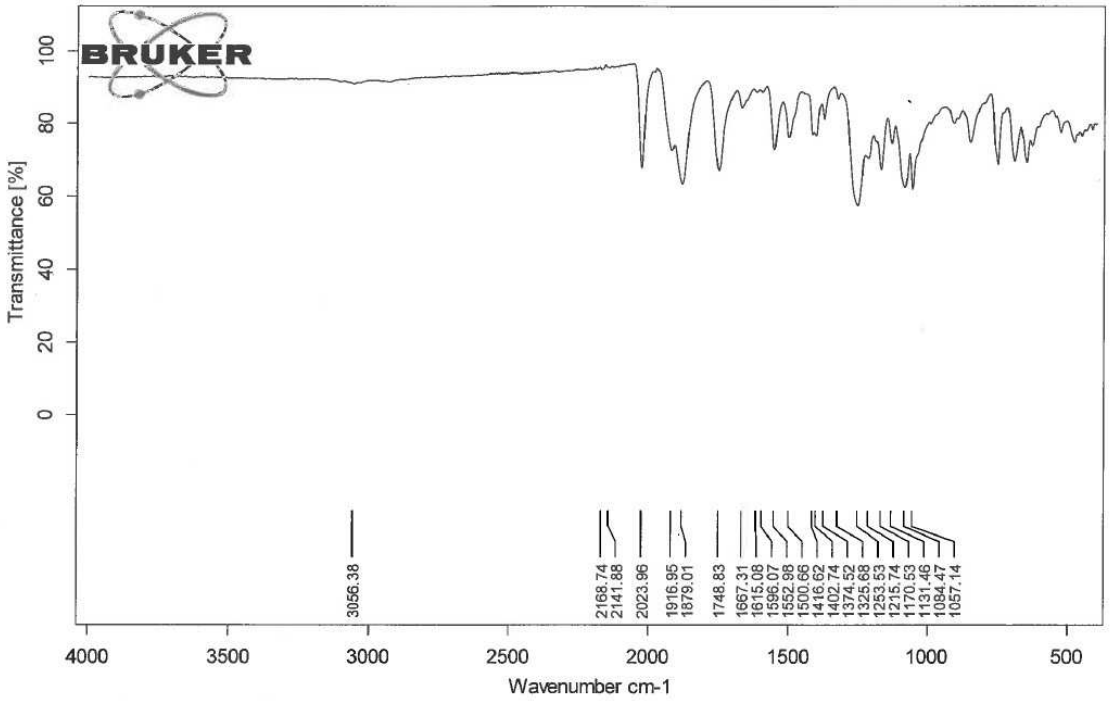


*Figure S5. Infrared spectrum of $[Re_3(L1)_2Br_3(CO)_3]\cdot n(CH_3NO_2)\cdot m(H_2O)$ **1**.*

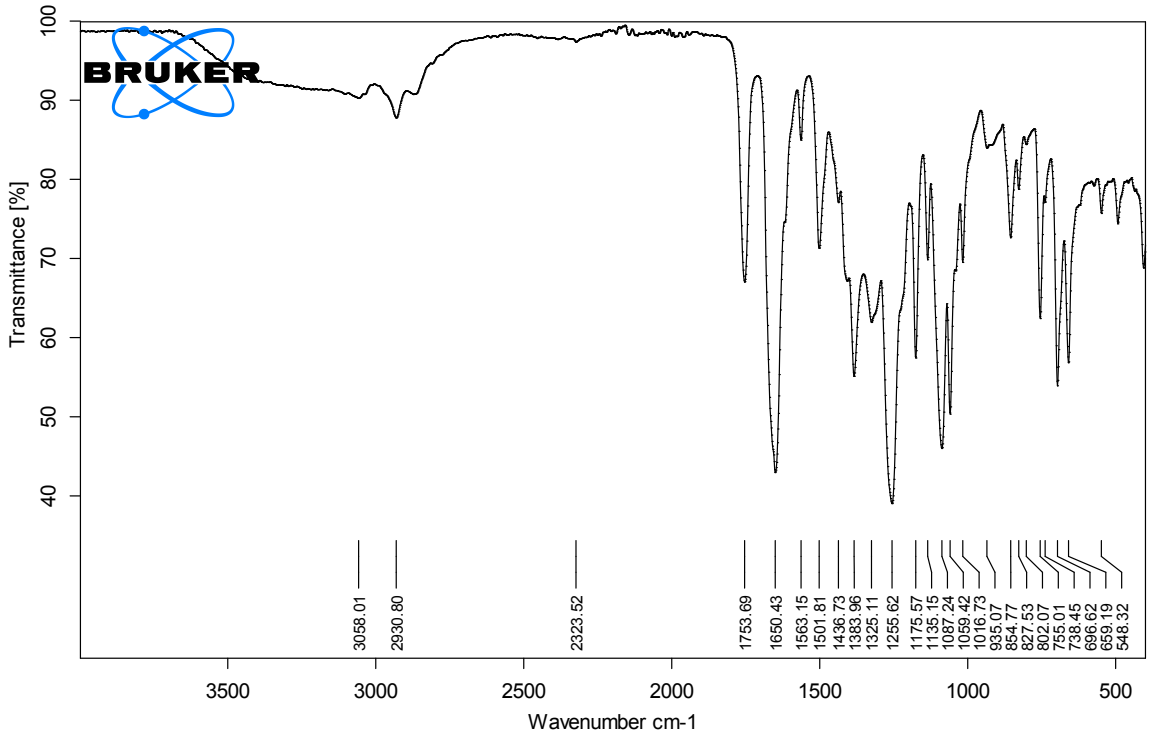


*Figure S6. Infrared spectrum of $[Co_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ **2a**.*

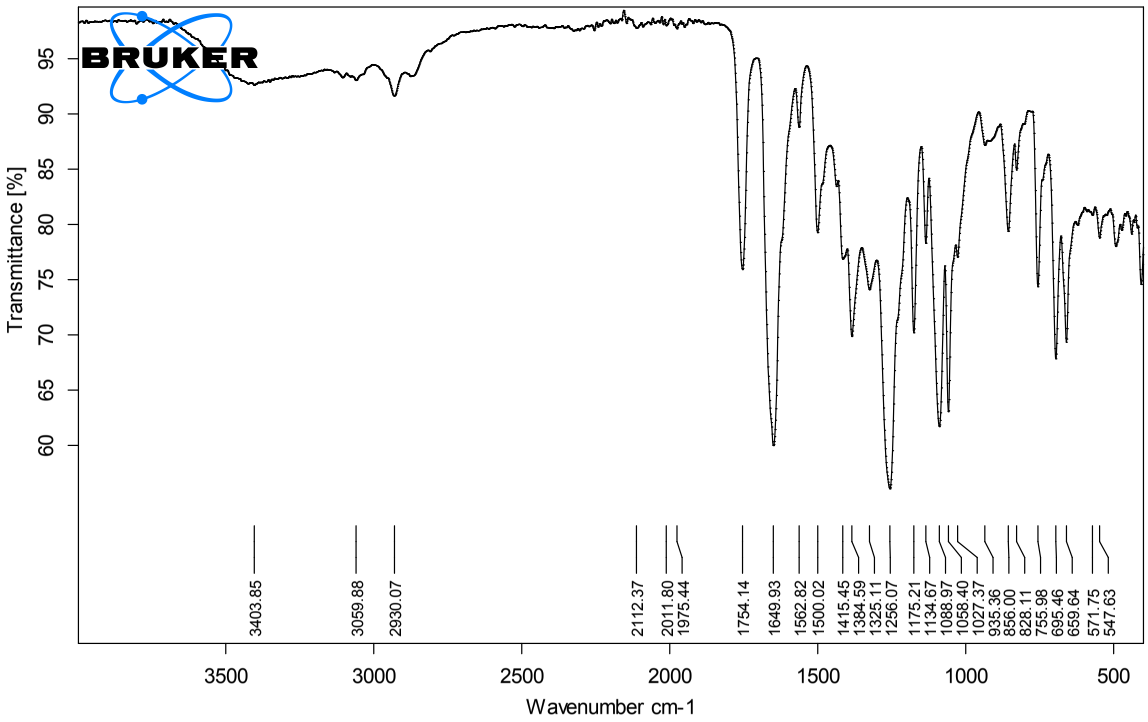


Figure S7. Infrared spectrum of $[Cu_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ ***2b****.*

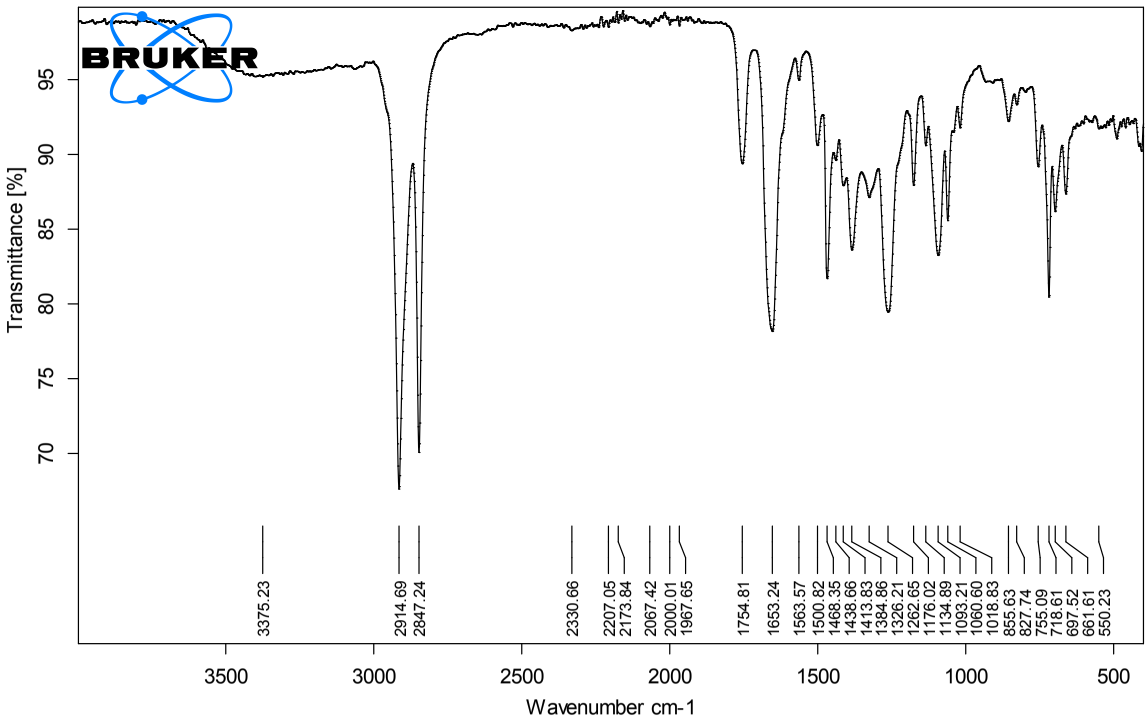


Figure S8. Infrared spectrum of $[Ni_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ ***2c****.*

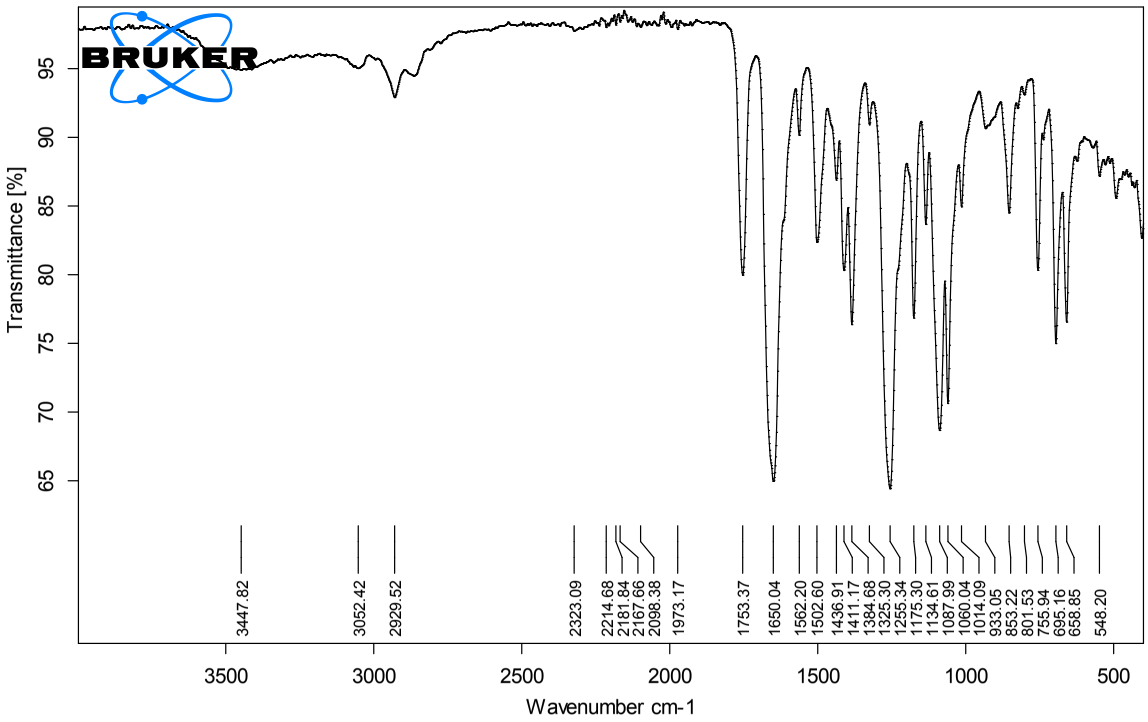


Figure S9. Infrared spectrum of $[Co_3Cl_6(L1)_2]\cdot n(DMF)$ ***3a***.

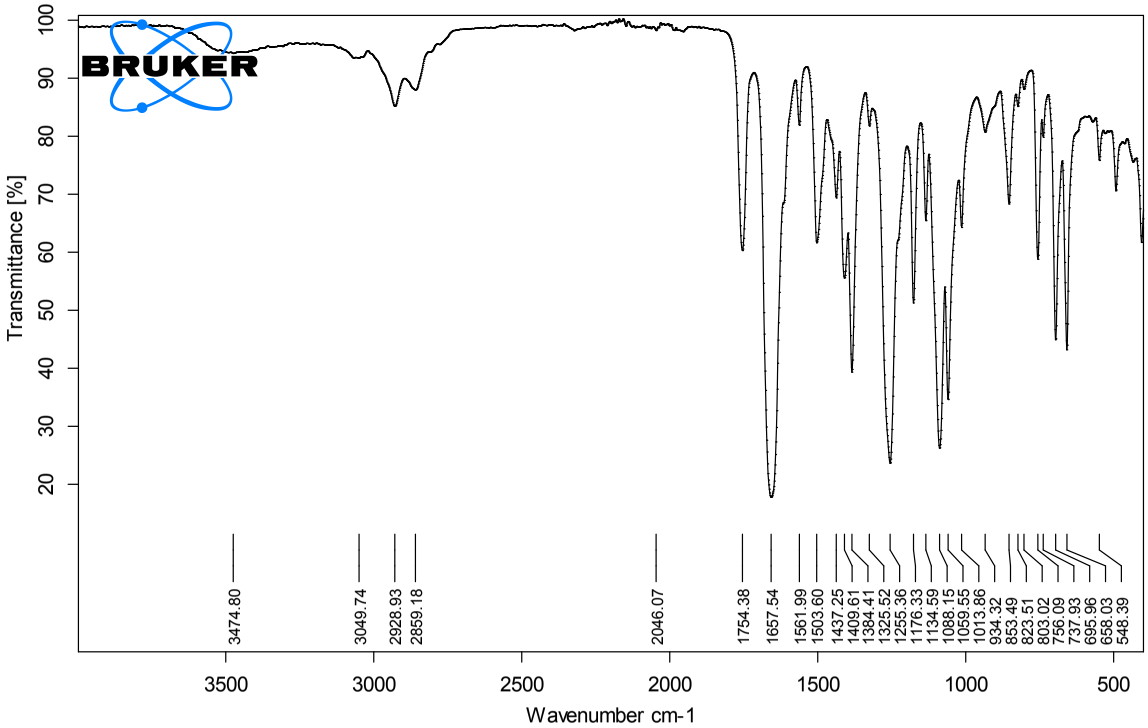


Figure S10. Infrared spectrum of $[Co_3Br_6(L1)_2]\cdot n(DMF)$ ***3b***.

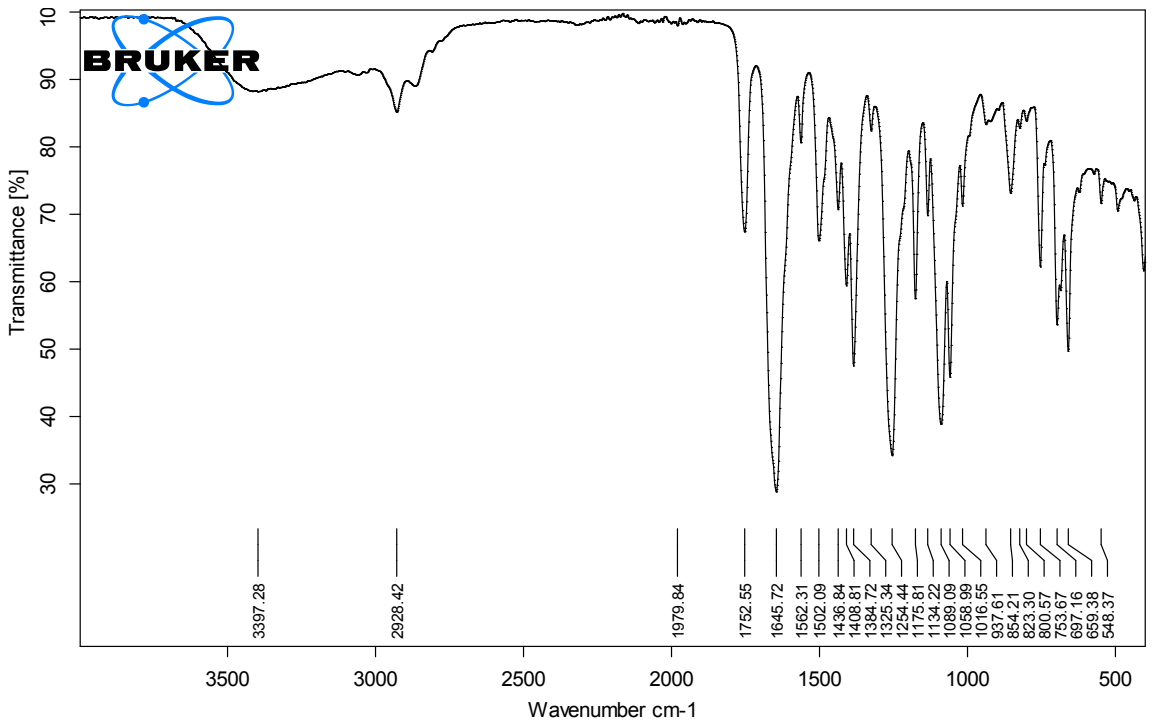


Figure S11. Infrared spectrum of $[Co_3I_{1.5}(H_2O)_{4.5}L1)_2]\cdot 4.5I\cdot m(DMF)$ ***4***.

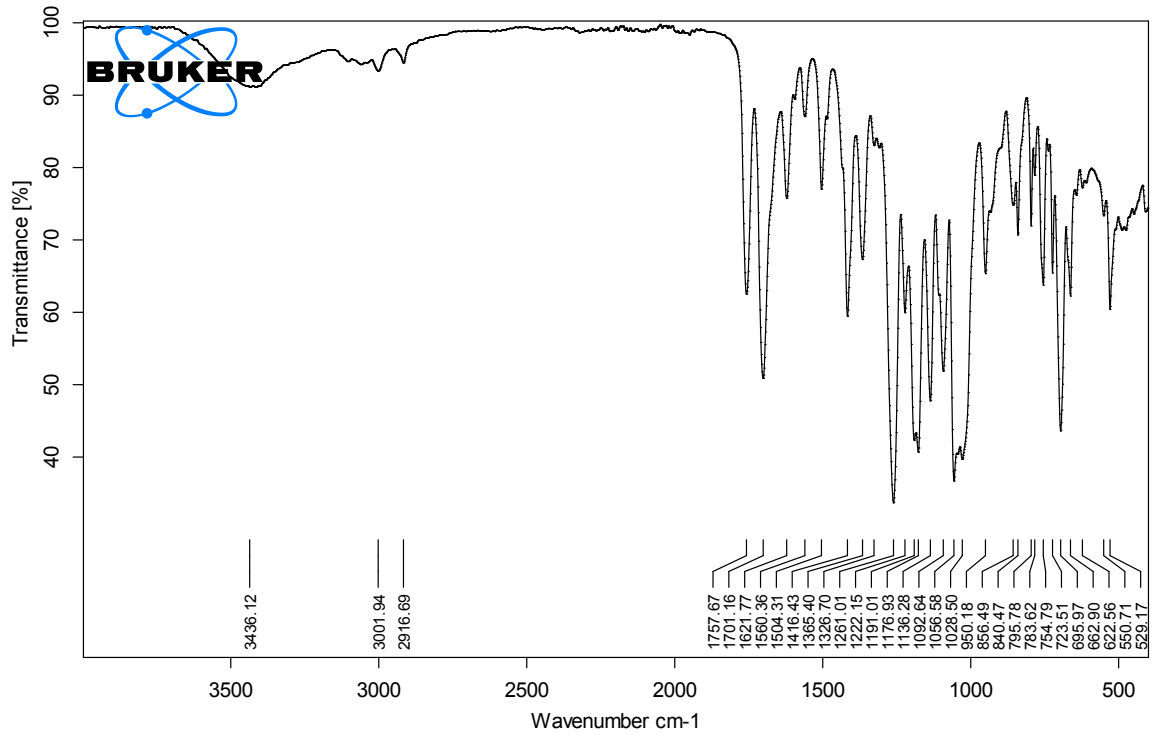


Figure S12. Infrared spectrum of $[Cu_2(L1)(TFA)_3(isonic)]\cdot n(DMF)$ ***5***, where tfa = trifluoroacetate and isonic = isonicotinate.

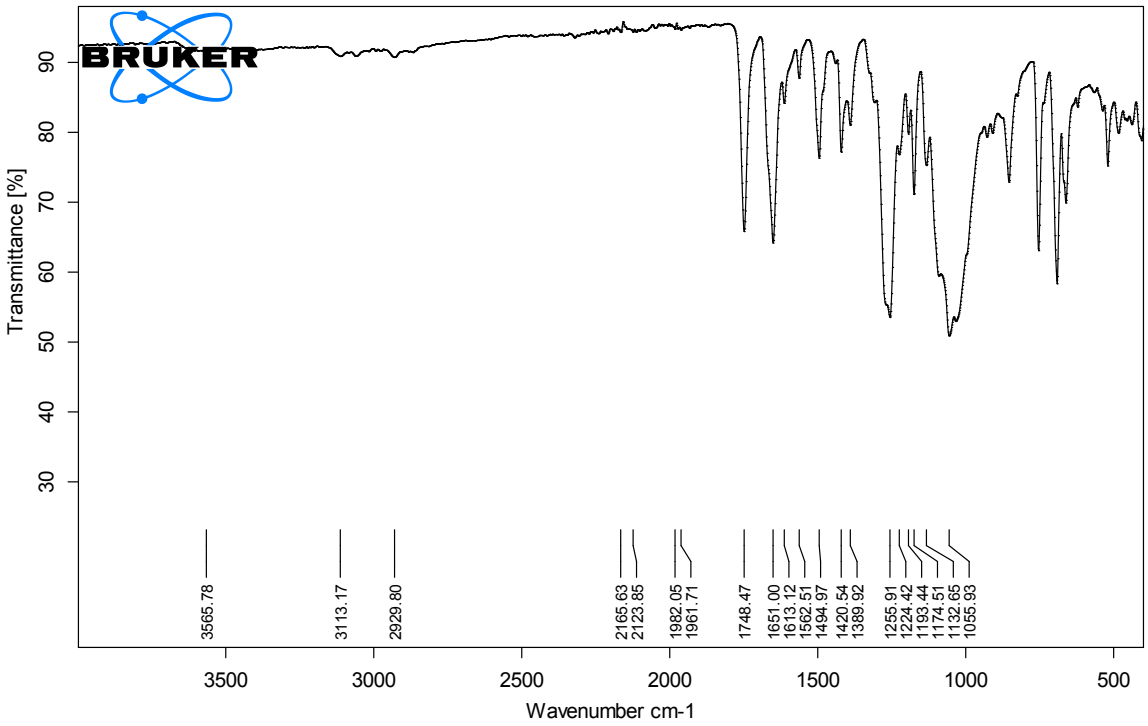


*Figure S13. Infrared spectrum of $[Ag_2(L1)(DMF)_2]\cdot 2BF_4\cdot 2(H_2O)\cdot 6(DMF)$ **6**.*

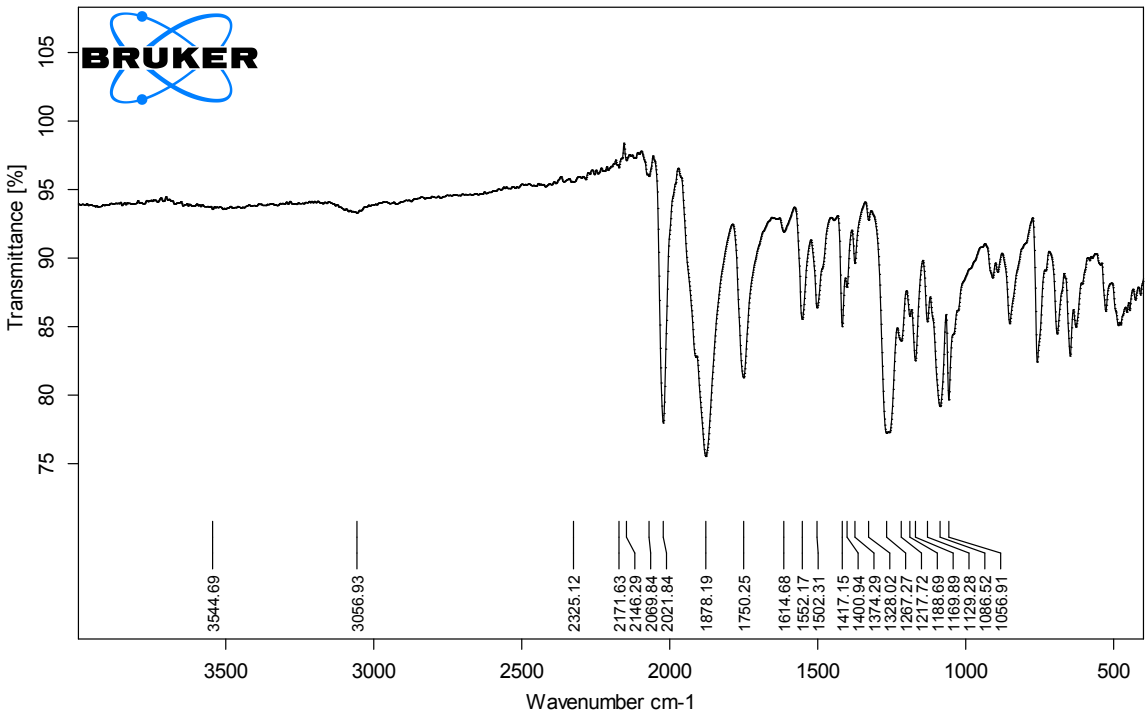
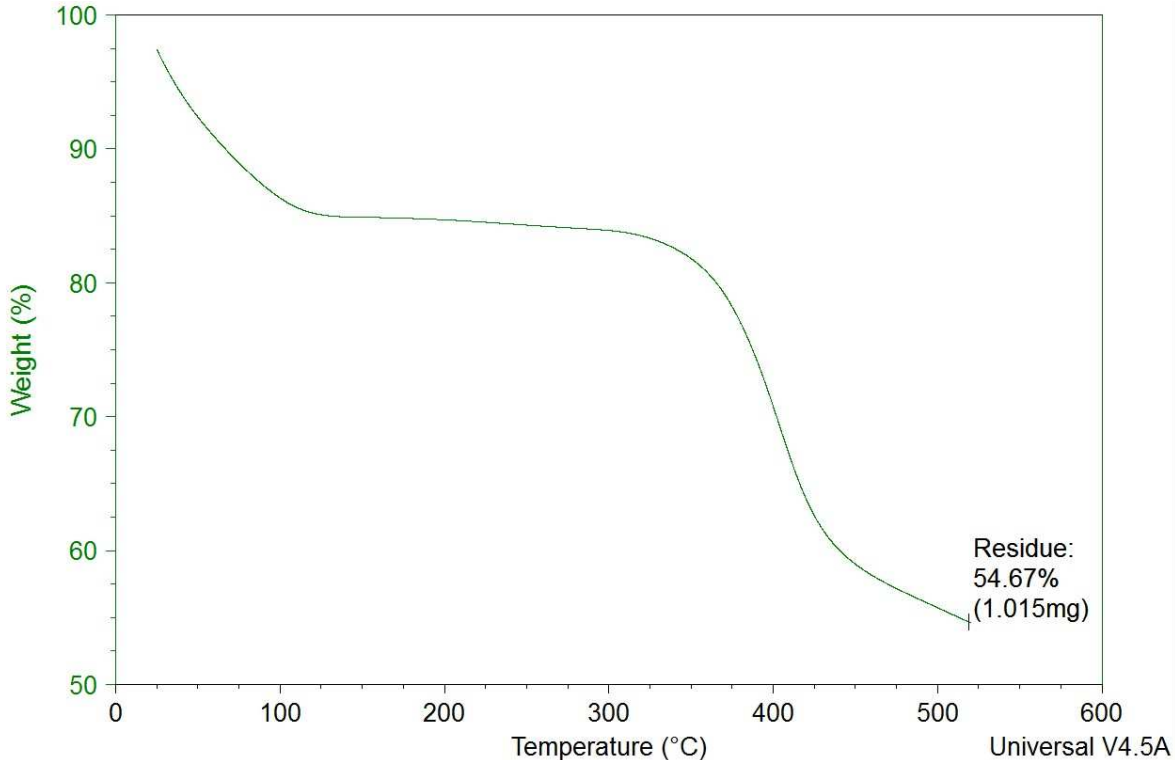


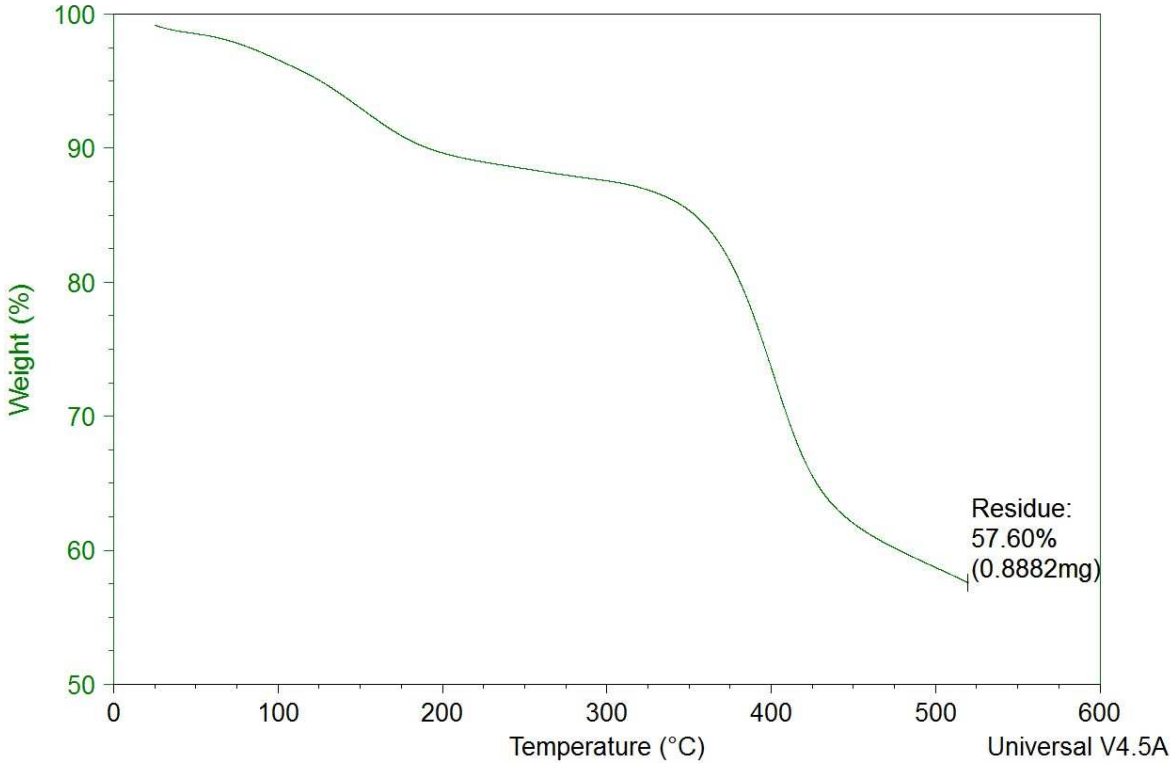
*Figure S14. Infrared spectrum of $[Re_3(L1)_2Br_3(CO)_3]\cdot n(CH_3NO_2)\cdot m(H_2O)$ **1** after I_2 up-take.*

4. Thermogravimetric Analysis

$[Re_3(L1)_2Br_3(CO)_3]\cdot n(CH_3NO_2)\cdot m(H_2O)$ 1



(a)



(b)

Figure S15. TGA of (a) $[Re_3(L1)_2Br_3(CO)_3]\cdot n(CH_3NO_2)\cdot m(H_2O)$ ***1***; and (b) *$Re_3(L1)_2Br_3(CO)_3]\cdot n(CH_3NO_2)\cdot m(H_2O)$* ***1*** *after I_2 up-take.*

$[Co_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ 2a

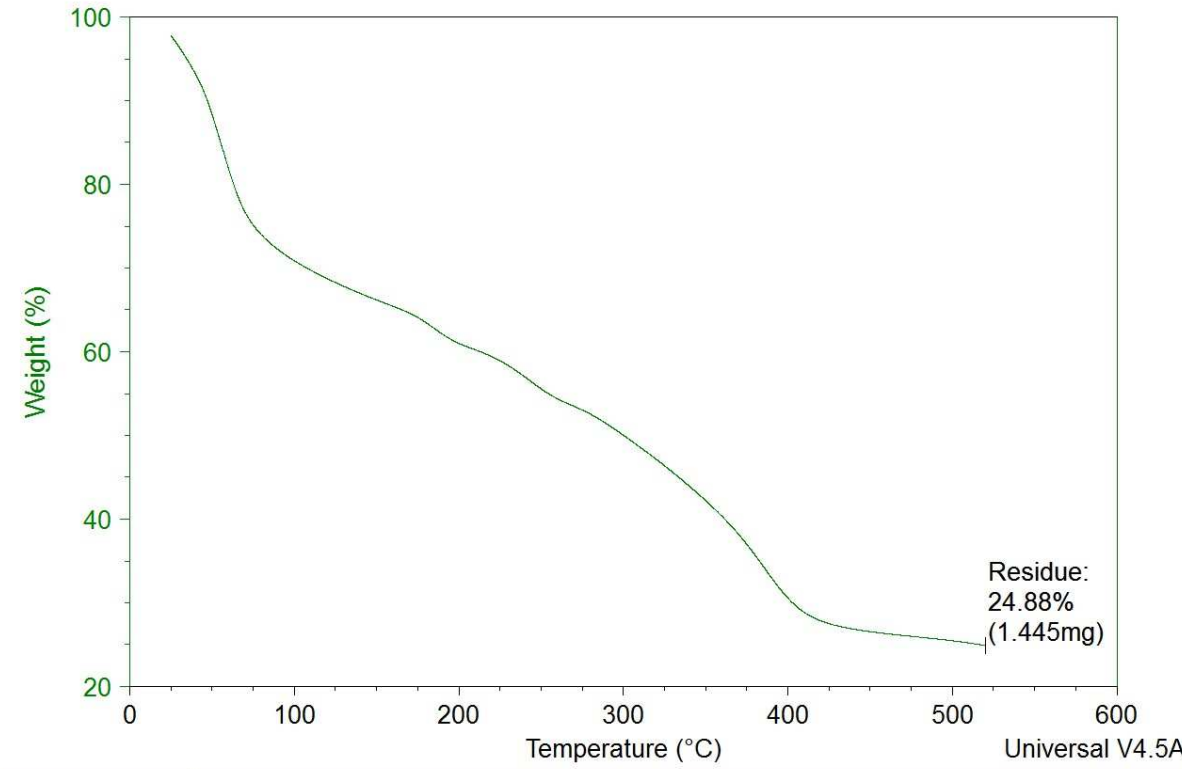


Figure S16. TGA of $[Co_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ ***2a***.

$[Ni_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ 2c

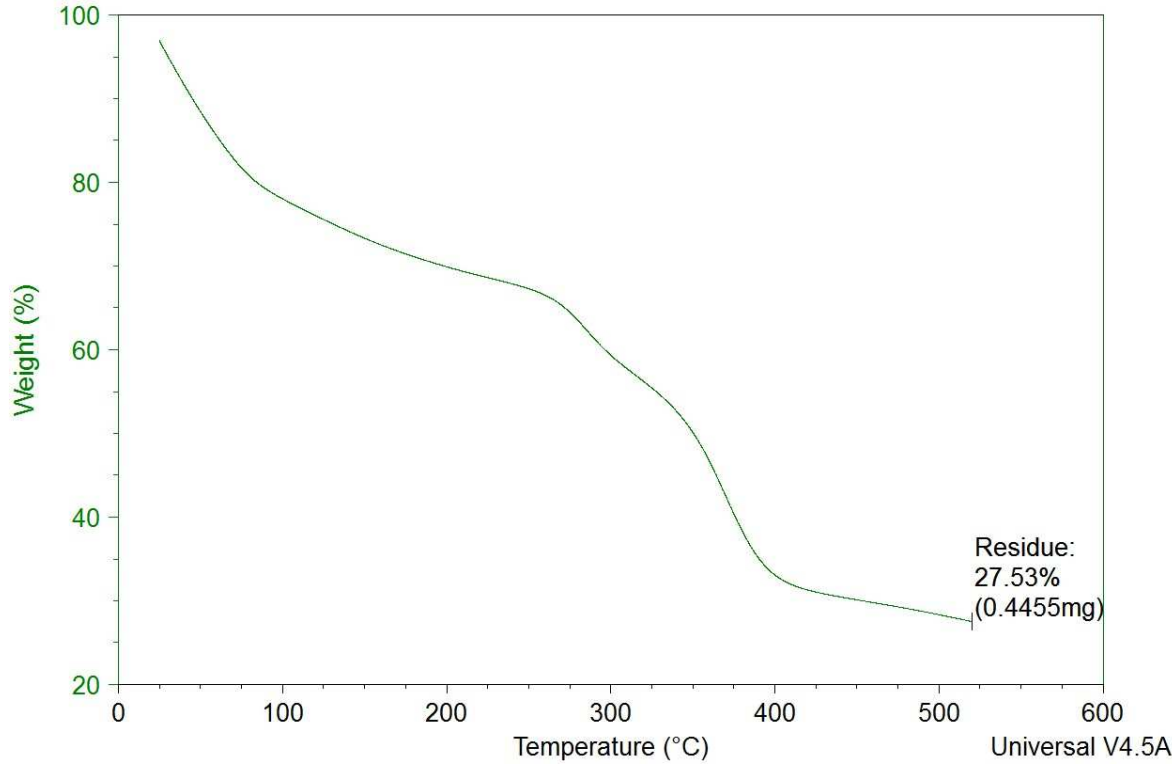


Figure S17. TGA of $[Ni_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ ***2c***.

$[Co_3Cl_6(L1)_2]$·n(DMF) 3a

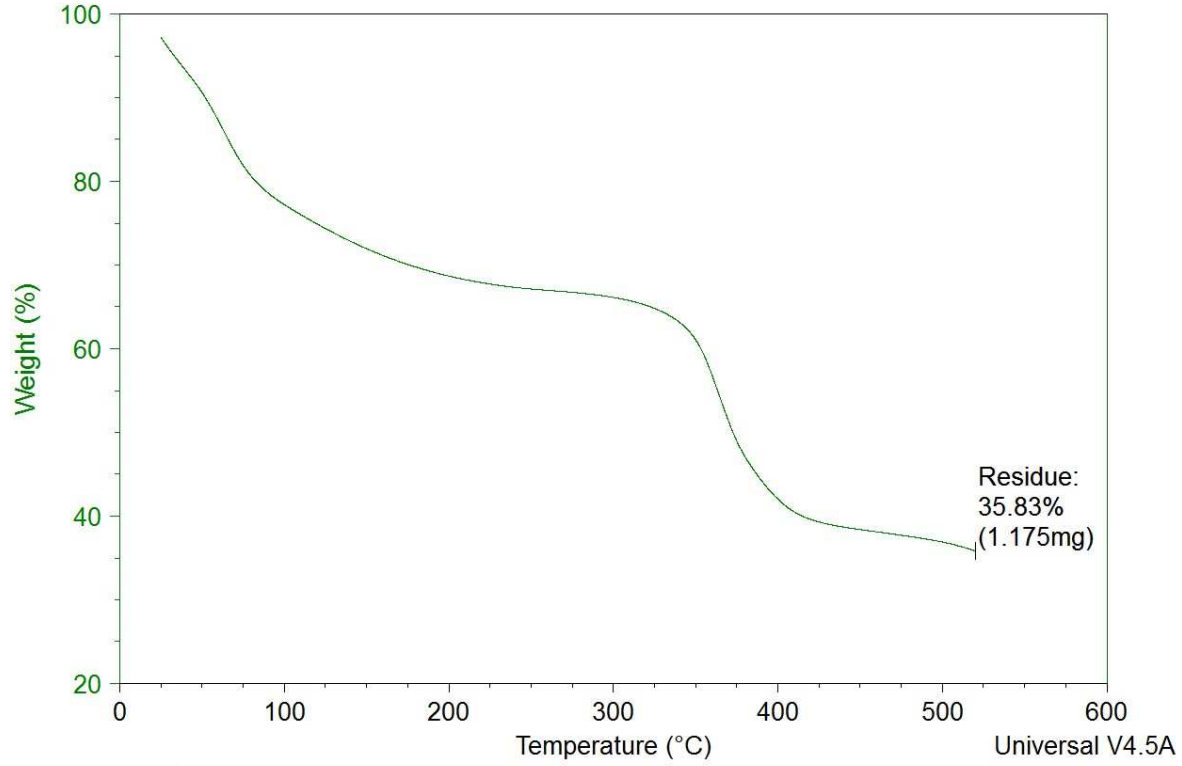


Figure S18. TGA of $[Co_3Cl_6(L1)_2]$·n(DMF) ***3a***.

$[Co_3Br_6(L1)_2]$·n(DMF) 3b

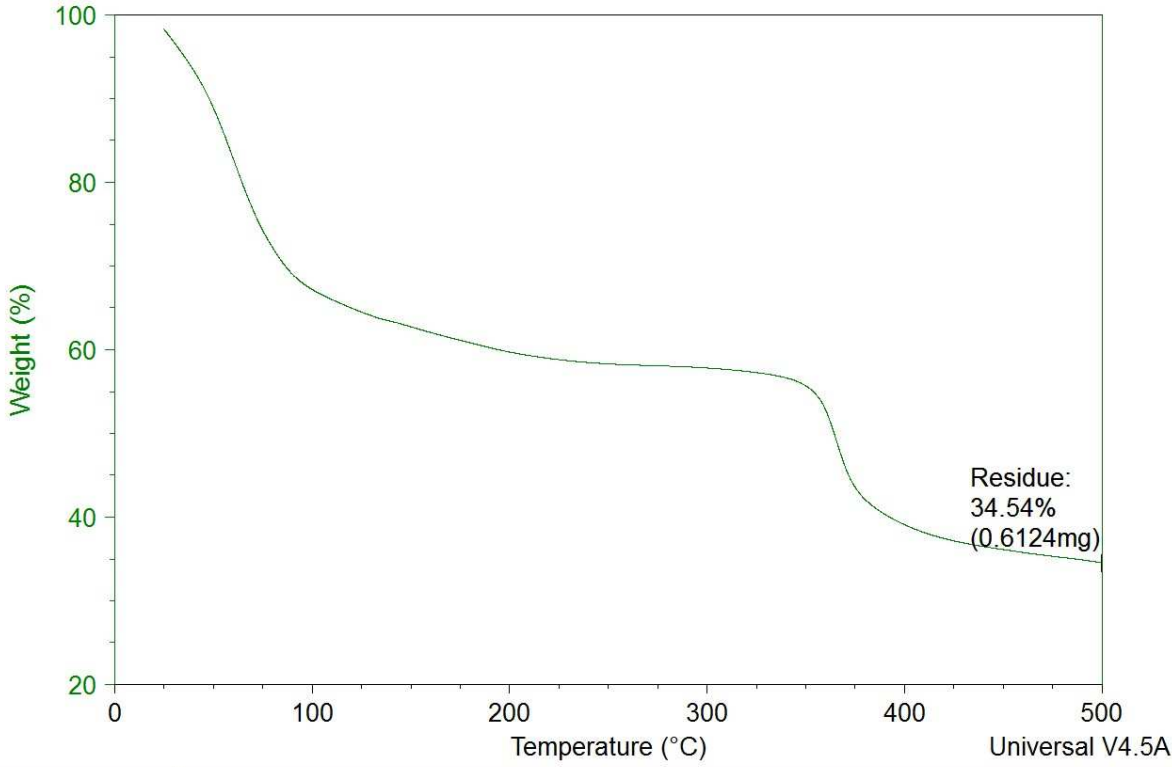


Figure S19. TGA of $[Co_3Br_6(L1)_2]$·n(DMF) ***3b***.

$[Co_3I_{1.5}(H_2O)_{4.5}L1)_2]\cdot 4.5I\cdot m(DMF)$ 4

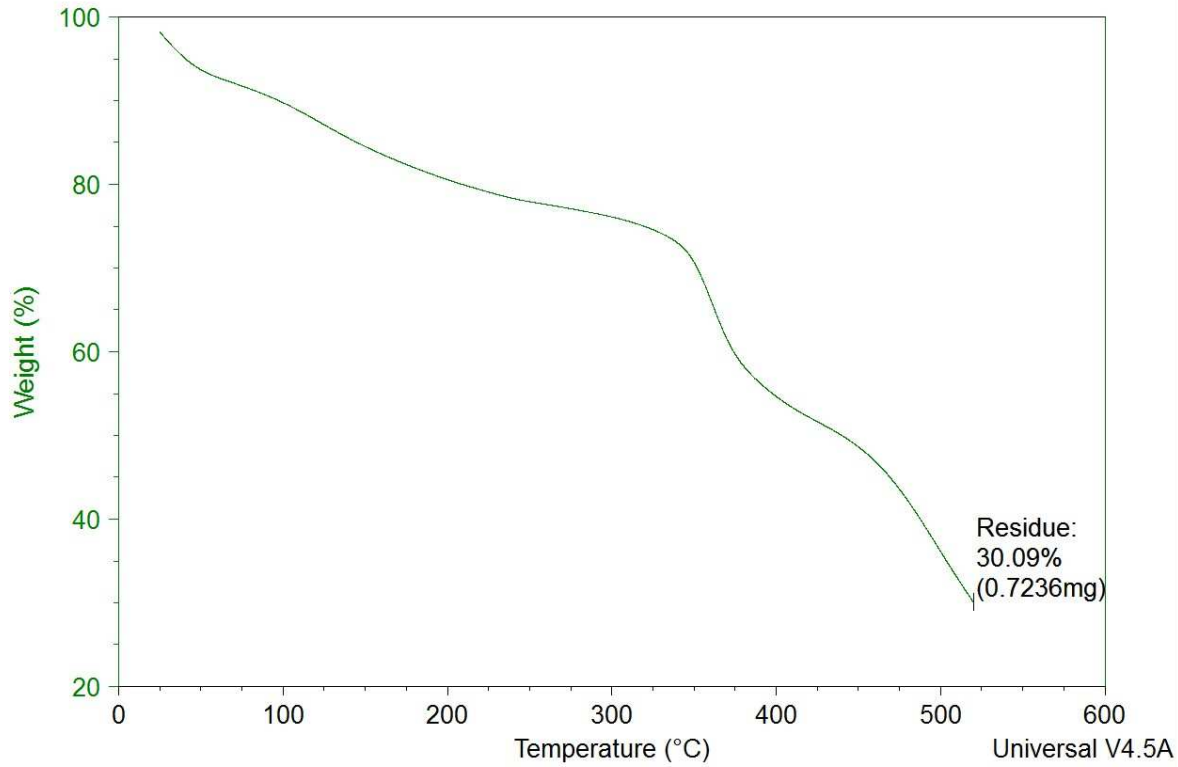


*Figure S20. TGA of $[Co_3I_{1.5}(H_2O)_{4.5}L1)_2]\cdot 4.5I\cdot m(DMF)$ **4**.*

$[Cu_2(L1)(TFA)_3(isonic)]\cdot n(DMF)$ 5

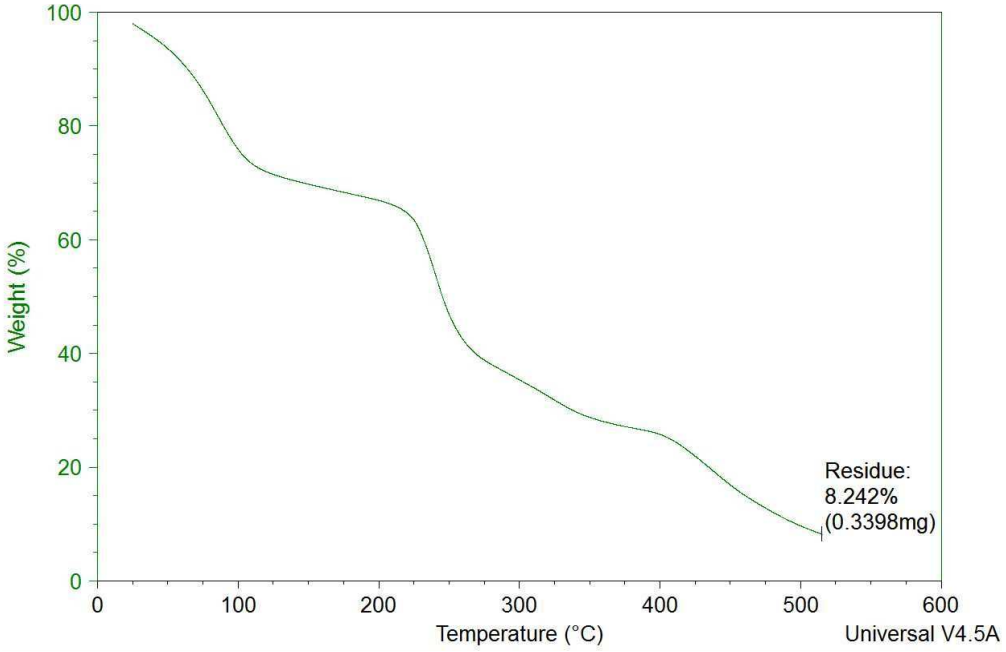


*Figure S21. TGA of $[Cu_2(L1)(TFA)_3(isonic)]\cdot n(DMF)$ **5**.*

$[Ag_2(L1)(DMF)_2]\cdot 2BF_4\cdot 2(H_2O)\cdot 6(DMF)$ 6

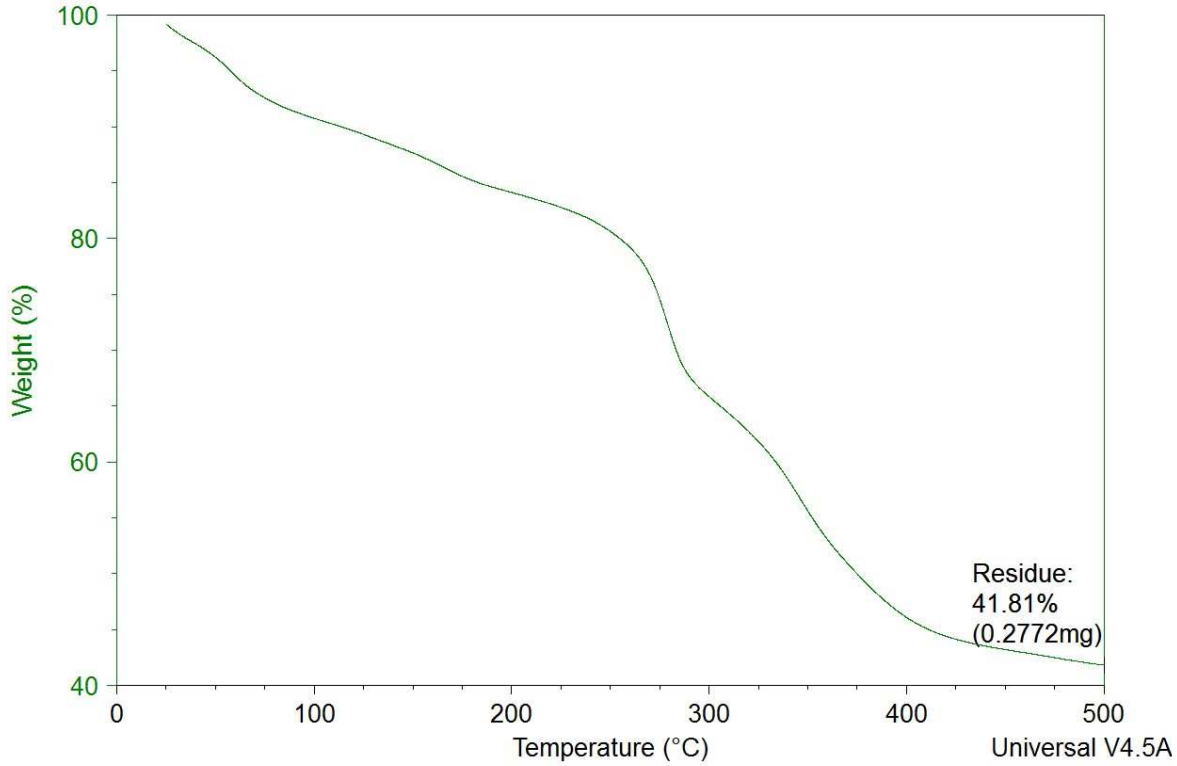


*Figure S22. TGA of $[Ag_2(L1)(DMF)_2]\cdot 2BF_4\cdot 2(H_2O)\cdot 6(DMF)$ **6**.*

5. Elemental analysis

CHN analysis

CHN analysis indicated high levels of solvation for materials **2-5** as expected, and satisfactory analyse cannot be established in some cases due to unknown levels of solvation (common for these types of materials) and small amounts of some amorphous powdered material. Presence of DMF and water are apparent from IR. Results obtained are given below (see main text for compound **1**, **4** and **6**).

Compound	**Calc (%) CHN for desolvated material***	**Calc (%) CHN for complex·n(DMF)·m(H_2O)**	**Found (%) CHN**
2a	C 51.64, H 3.20, N 9.51	n = 10, m = 20 C 46.20, H 5.23, N 10.48	C 44.39, H 2.65, N 10.88
2b	C 51.37, H 3.18, N 9.46	n = 10, m = 20 C 46.03, H 5.21, N 10.44	C 45.18, H 2.14, N 6.56
2c	C 51.65, H 3.20, N 9.52	n = 9, m = 15 C 47.31, H 4.99, N 10.57	C 47.68, H 4.37, N 9.51
3a	C 57.43, H 3.05, N 7.05	n = 10, m = 20 C 49.76, H 5.28, N 8.87	C 49.54, H 4.05, N 7.65
3b	C 51.67, H 2.74, N 6.34	n = 10, m = 20 C 46.21, H 4.91, N 8.24	C 46.84, H 3.36, N 6.66
5	C 52.26, H 2.54, N 6.19	n = 10, m = 15 C 45.96, H 5.46, N 9.21	C 45.60, H 4.00, N 8.35

* Lattice solvent excluded

SEM-EDX

SEM/EDX analysis data for compound 1 after I_2 up-take (Weight %).

Sample reference	Carbon	Oxygen	Aluminium	Bromine	Iodine	Rhenium
particle 1	24.24	15.51	2.77	5.15	16.44	35.89
particle 2	24.56	17.74	1.97	6.20	14.07	35.47
particle 3	27.39	20.04	2.31	4.73	10.80	34.73
* particle 4	30.32	16.04	0.68	3.15	27.84	21.98
particle 5	23.68	18.50	2.04	4.88	14.13	36.77
particle 6	24.86	17.81	1.40	7.33	11.44	37.17
particle 7	30.79	17.99	0.44	7.16	13.96	29.65
particle 8	35.10	18.24	2.07	5.70	10.10	28.79
many particles	36.36	18.32	2.65	7.86	10.23	24.58
Ground sample 1	39.10	20.76	0.76	6.72	8.45	24.21
Ground sample 2	39.46	20.60	1.17	5.80	7.77	25.20
Ground sample 3	39.41	21.20	1.41	4.78	9.05	24.14
Ground sample 4	41.14	20.93	0.80	6.37	8.02	22.57

* Outlier excluded from analyses.

6. Single crystal X-ray diffraction

6.1 Unit cell information for isostructural complexes

$[Ni_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ 2c

Unit cell parameters Monoclinic *a* = 35.0709(14), *b* = 20.2572(15), *c* = 33.454(3) Å. β = 110.482(7) °

6.2 Additional diagrams of single crystal structures

Hexakis(isonicotinoyl)cyclotricatechylene (L1)

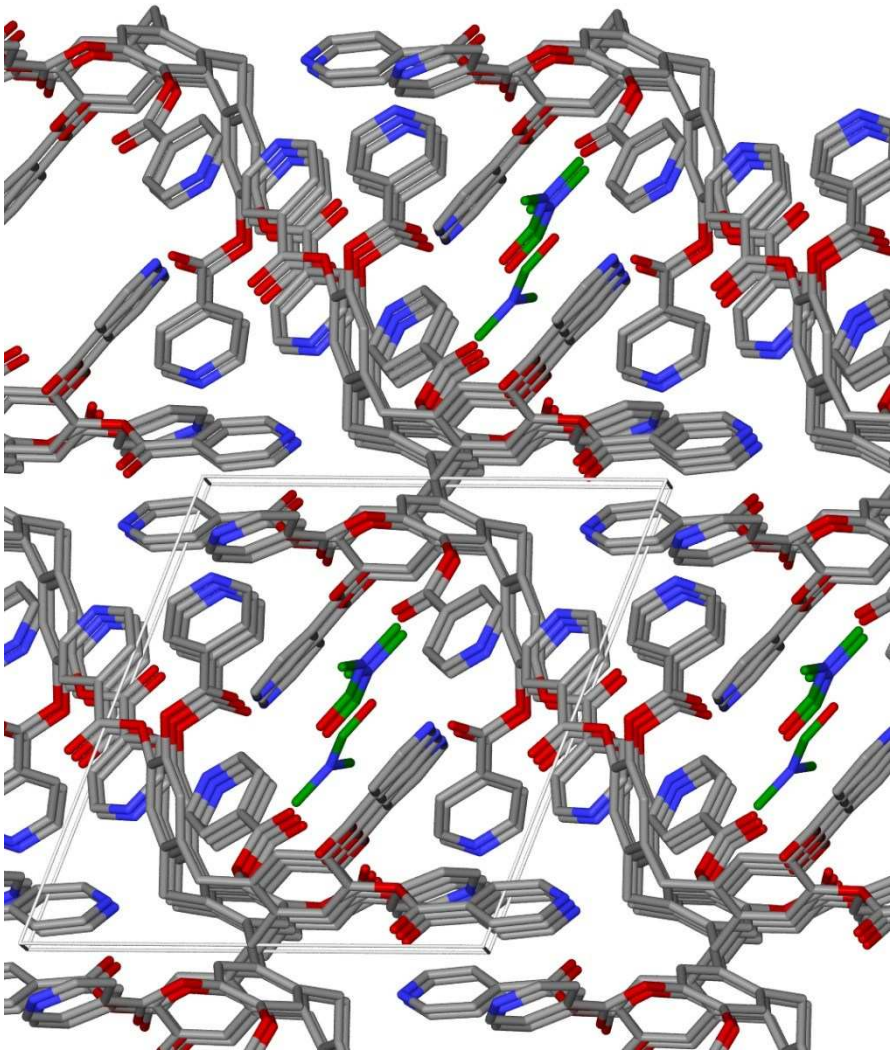


Figure S23: Packing diagram of L1·DMF viewed down b. Hydrogen atoms excluded for clarity and DMF shown in green.

$[Re_3(L1)_2Br_3(CO)_3]\cdot n(CH_3NO_2)\cdot m(H_2O)$ 1

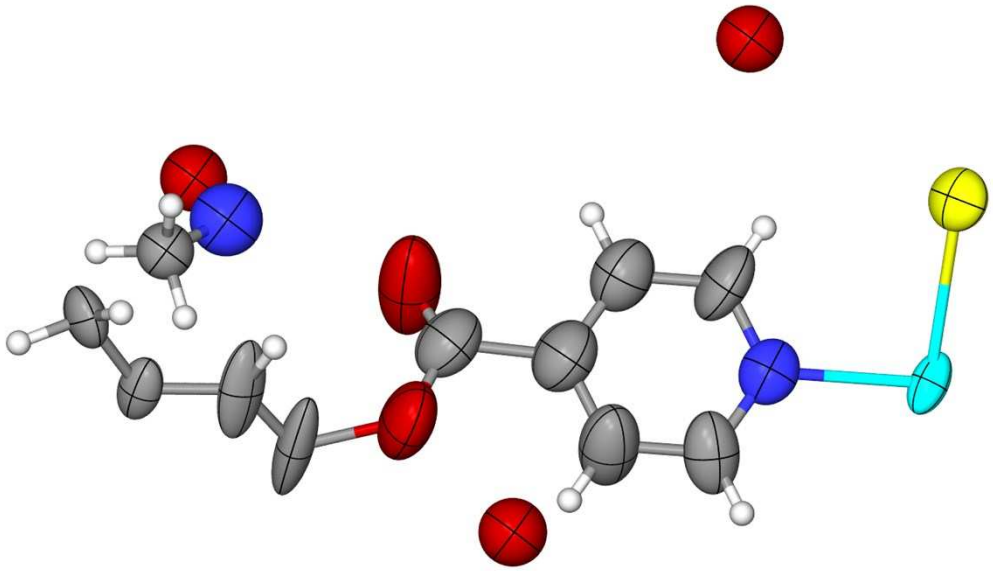


*Figure S24: Asymmetric unit of **1** with ellipsoids shown at 50% probability levels. Isotropic atoms are solvent CH_3NO_2 and partly occupied water positions.*

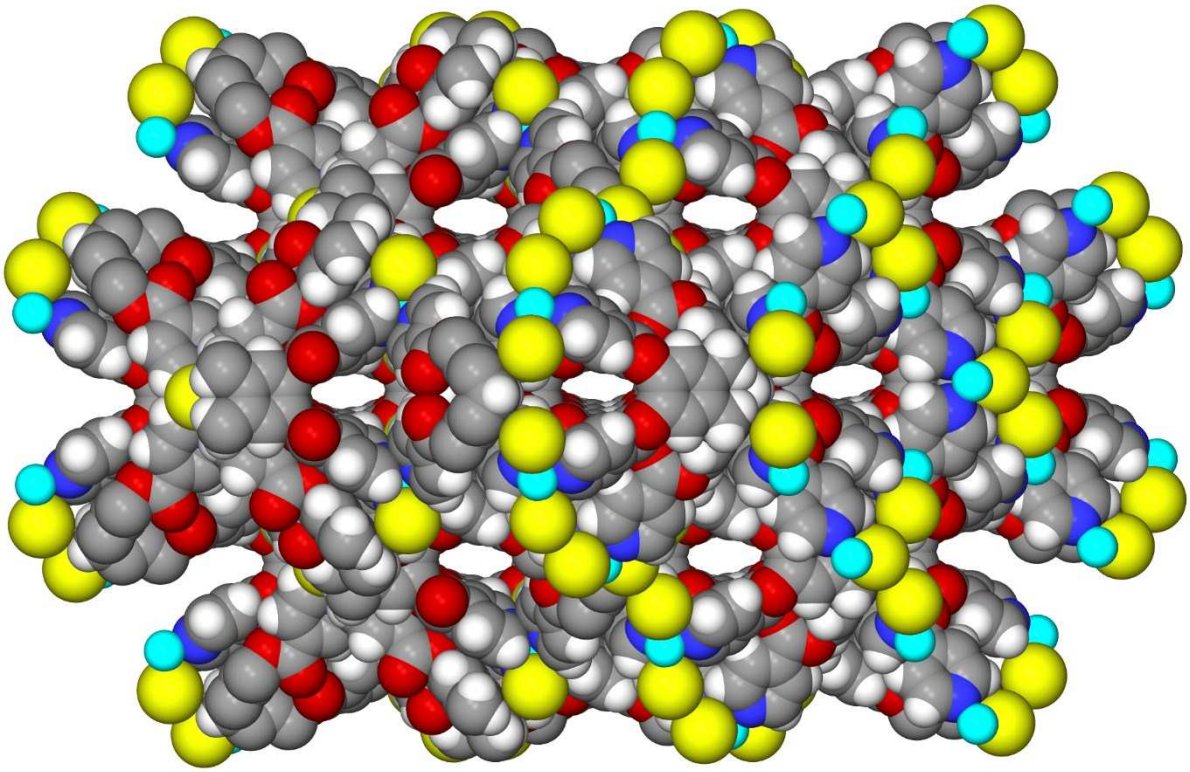


*Figure S25: Packing diagram of **1b** in space-filing mode showing channels in structure.*

$[Co_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ 2a

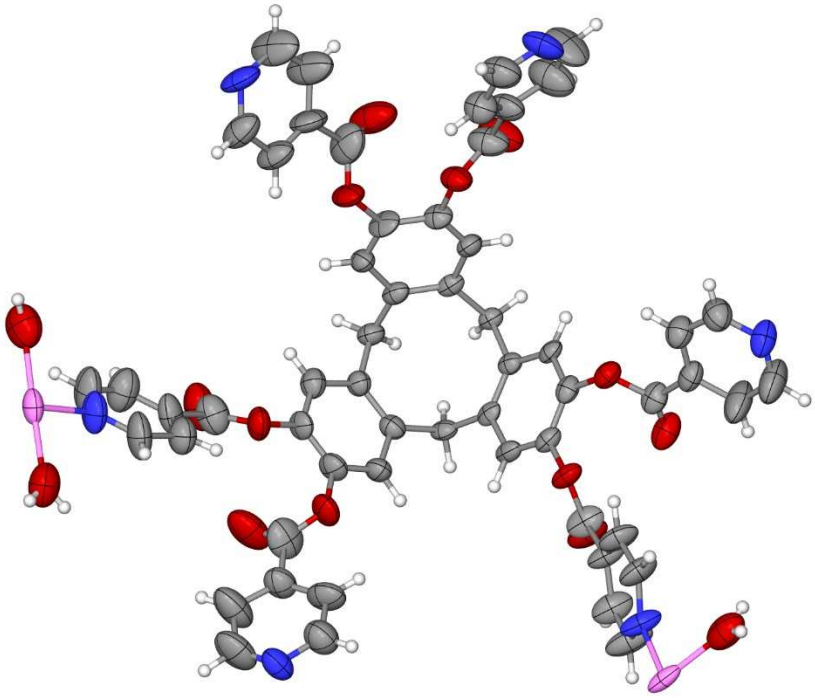


*Figure S26: Asymmetric unit of **2a** with ellipsoids shown at 50% probability levels.*

$[Cu_3(H_2O)_6(L1)_2]\cdot 6(NO_3)\cdot n(DMF)$ 2b

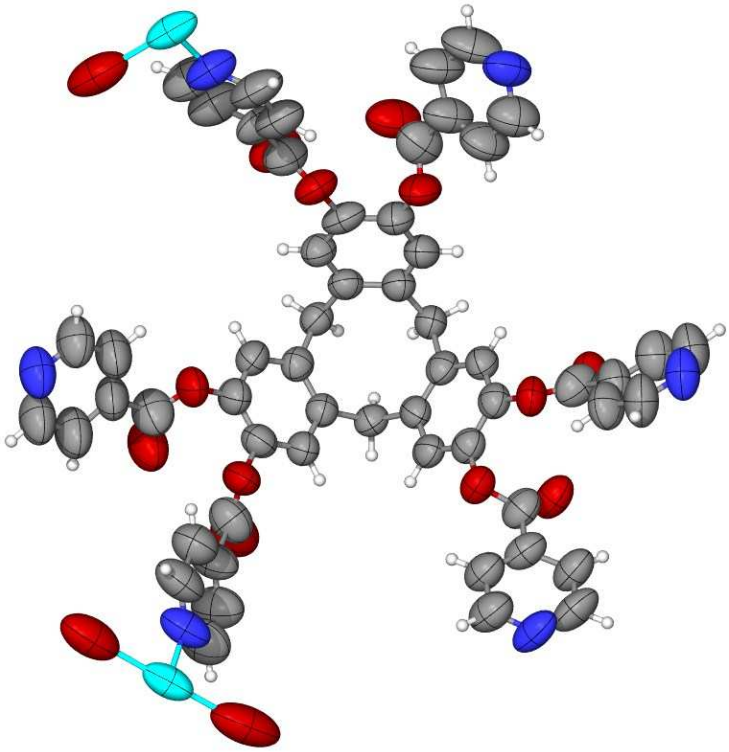


*Figure S27: Asymmetric unit of **2b** with ellipsoids shown at 50% probability levels.*

$[Co_3Cl_6(L1)_2]\cdot n(DMF)$ 3a

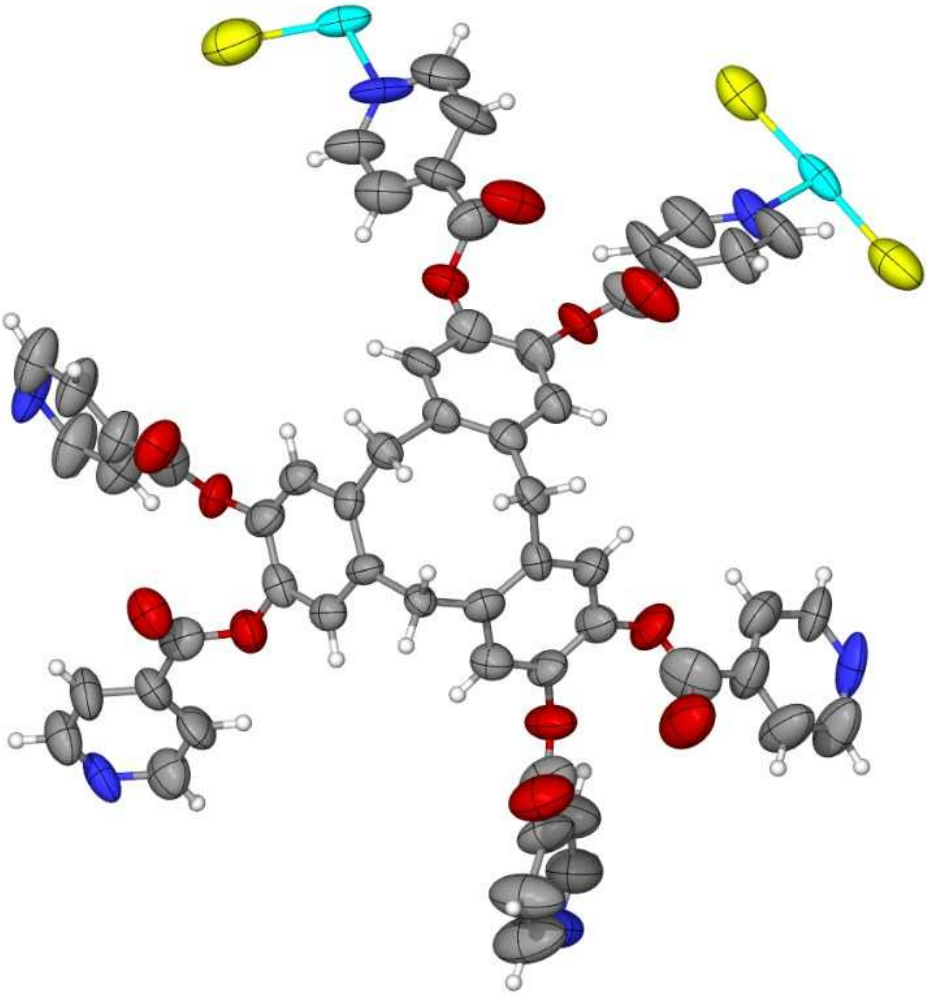


*Figure S28: Asymmetric unit of **3a** with ellipsoids shown at 50% probability levels.*

$[Co_3Br_6(L1)_2]\cdot n(DMF)$ 3b

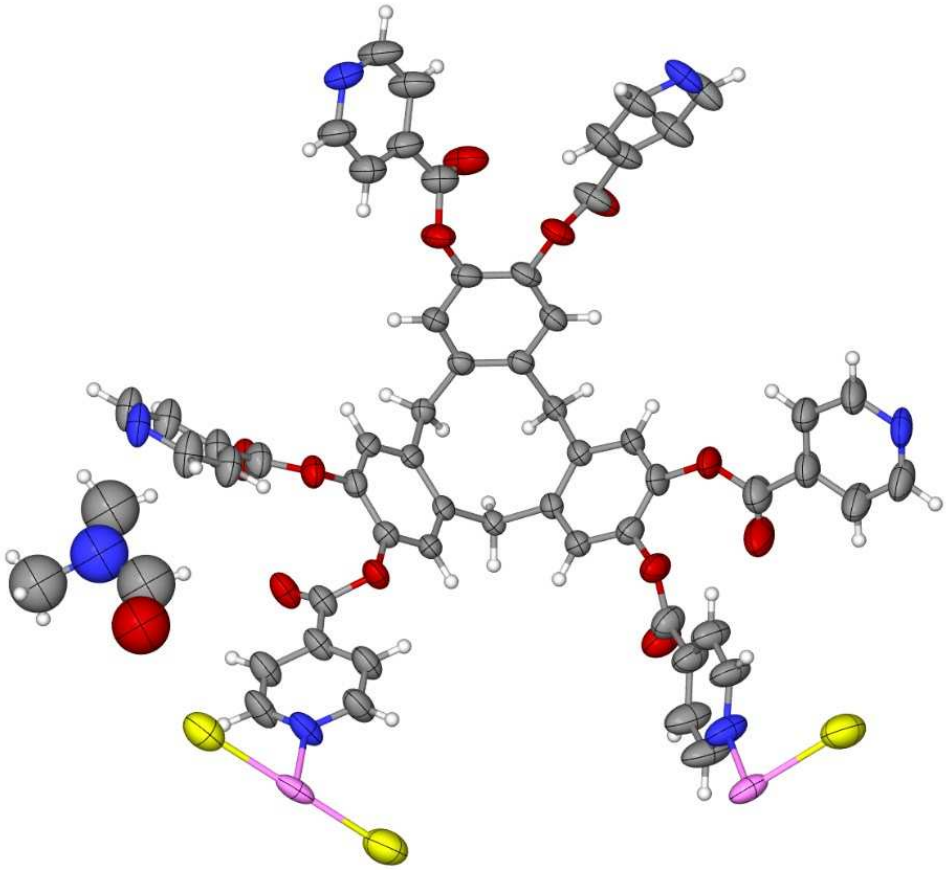


*Figure S29: Asymmetric unit of **3b** with ellipsoids shown at 50% probability levels. Isotropic atoms are solvent DMF.*

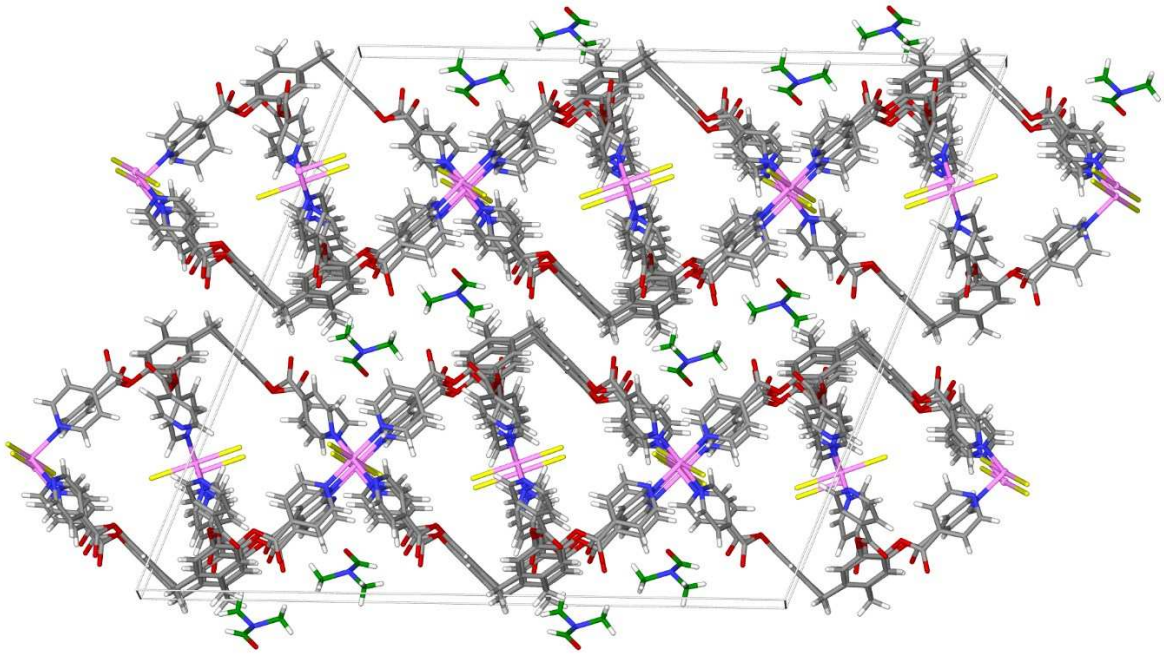


*Figure S30: Unit cell packing diagram of **3b** viewed down b. DMF shown in green.*

$[Co_3I_{1.5}(H_2O)_{4.5}L1)_2]\cdot 4.5I\cdot m(DMF)$ 4

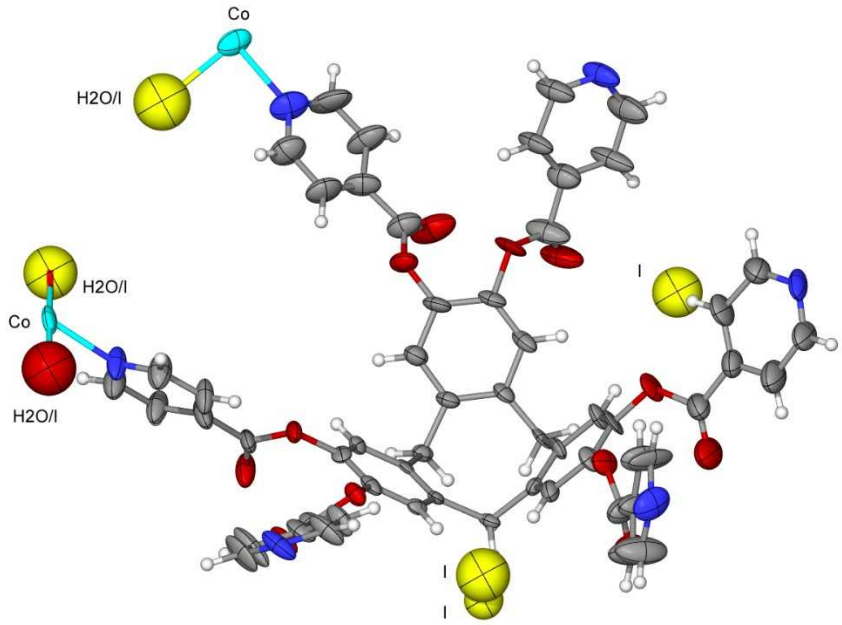


*Figure S31: Asymmetric unit of **4** with ellipsoids shown at 50% probability levels. Isotropic atoms are disordered I- anions and disordered H_2O/I ligands with position refined as 25% I, 75% O.*

$[Ag_2(L1)(DMF)_2]\cdot 2BF_4\cdot 2(H_2O)\cdot 6(DMF)$ 6

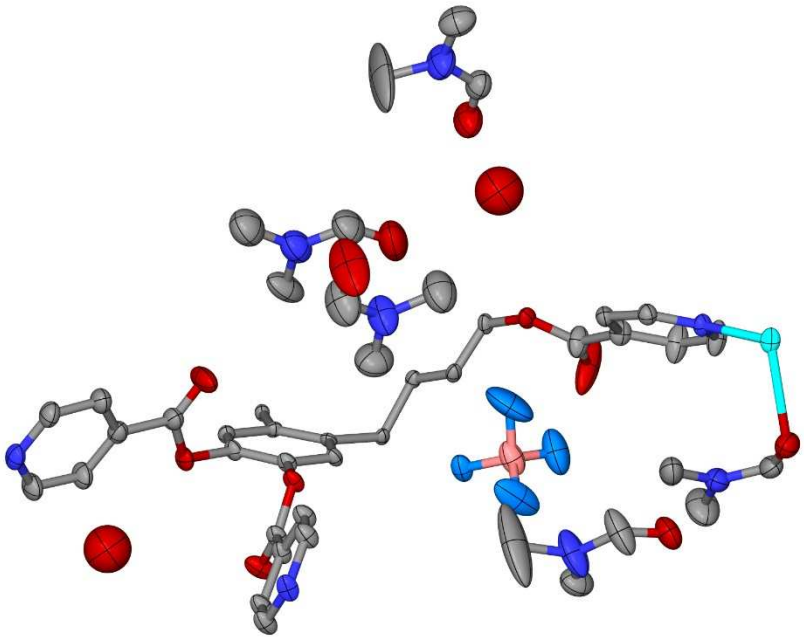


*Figure S32: Asymmetric unit of **6** with ellipsoids shown at 50% probability levels. Isotropic atoms are disordered water. Hydrogen atoms excluded for clarity.*

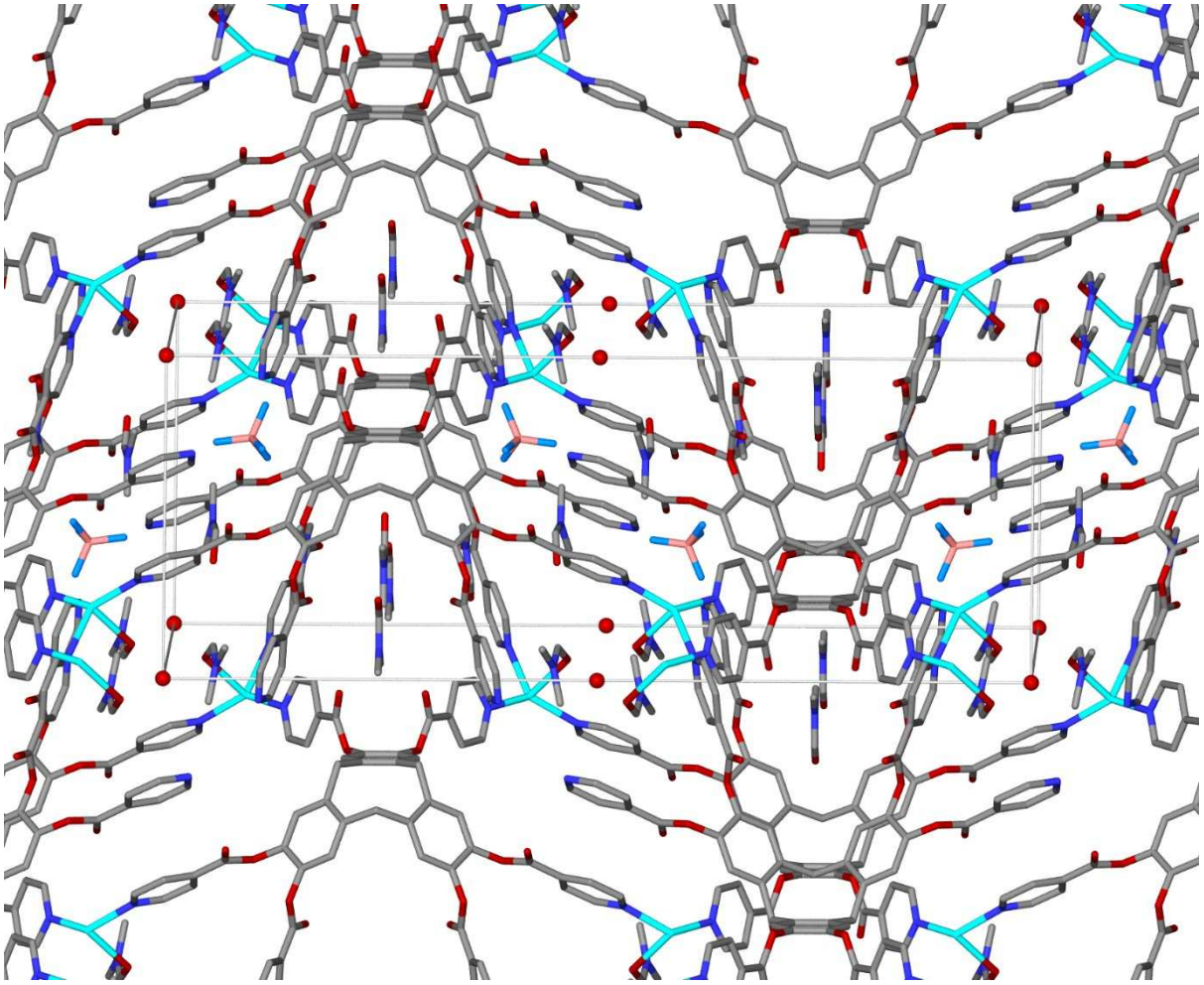


*Figure S33: Packing diagram of **6** viewed down the a axis. Hydrogen atoms excluded for clarity*