

M₁₂L₈ metallo-supramolecular cube with cyclotriguaiacylene-type ligand: spontaneous resolution of cube and its constituent host ligand

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Supplementary information

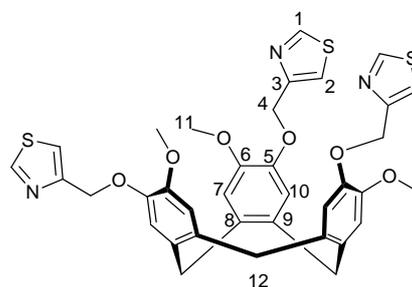
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1. Synthesis

(±)-Cyclotriguaiacylene¹ was synthesized according to literature methods. All other chemicals were obtained from commercial sources and were used without further purification. NMR spectra were recorded by automated procedures on a Bruker DPX 300 MHz NMR spectrometer. Electrospray mass spectra (ES-MS) were measured on a Bruker Maxis Impact instrument in positive ion mode. Infra-red spectra were recorded as solid phase samples on a Bruker ALPHA Platinum ATR. Elemental analyses were performed on material that had been washed with diethyl ether, subsequently dried at 80-90 °C under vacuum and then exposed to the atmosphere and were performed by the microanalytical service at University of Leeds or London Metropolitan University.

Synthesis of (±)-*tris*-(4-methylthiazolyl)cyclotriguaiacylene (**L**)

(±)-Cyclotriguaiacylene (100 mg, 0.24 mmol) and Cs₂CO₃ (797 mg, 2.4 mmol) were dissolved in



dimethylformamide (DMF, 5 mL) and stirred at rt for 30 mins. 4-(chloromethyl)thiazole.HCl (55 mg 0.32 mmol) was added and the brown solution stirred at 100 °C overnight. The dark brown mixture was cooled, water (10 mL) was added and the resultant grey precipitate filtered and washed with Et₂O, affording the title compound as a grey solid. Yield 135 mg, 0.19 mmol, 80%. HRMS (ESI⁺) 700.1621 {M+H: C₃₆H₃₄N₃O₆S₃}⁺, 1399.3143 {M₂+H: C₇₂H₆₇N₆O₁₂S₆}⁺ Calcd. for 700.1605 and 1399.3136 respectively; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 8.81 (d, 3H, *J*= 2.1 Hz, H¹), 7.38 (s, 3H, H²), 6.94 (s, 3H, H⁷), 6.77 (s, 3H, H¹⁰), 5.30 (s, 6H, H⁴), 4.71 (d, 3H, *J*= 13.6 Hz, endo-H¹²), 3.81 (s, 9H, H¹¹), 3.49 (d, 3H *J*= 13.5 Hz, exo-H¹²); ¹³C{¹H} NMR (75 MHz, CDCl₃) 154.02 (C3), 153.12 (C1), 148.52 (C6), 146.73 (C5), 133.05 (C8), 131.94 (C9), 116.31 (C2), 116.23 (C7), 114.14 (C10), 67.82 (C4), 56.51 (C11), 36.62 (C12). IR ν (cm⁻¹) 3500, 3404 (broad), 3087, 2920, 1659 (sharp), 1512 (sharp), 1262 (sharp); Elemental analysis for crude ligand. Calcd. for C₃₆H₃₃O₆S₃·N₃·(HCl)·0.5(H₂O) C 58.01 H 4.73 N 5.64 Found C 58.30 H 4.50 N 5.50 %. The crude ligand was further purified by dissolving in dichloromethane with 5% methanol, passing through a plug of silica, and solvent removed *in vacuo*. Elemental analysis calcd. for C₃₆H₃₃O₆S₃N₃ C 61.78 H 4.75 N 6.00 Found C 61.69 H 4.51 N 6.14 %.

X-ray quality crystals were obtained from crude ligand by standing a saturated DMF:water solution, and from the diffusion of diethyl ether vapours into a nitromethane solution of L.

Synthesis of [Ag₁₂L₈](ReO₄)₁₂ complex 1 Crude (±)-*tris*-(4-

methylthiazolyl)cyclotriguaiacylene (7 mg) and AgReO₄ (1.5 eq.) were dissolved in DMF (1 mL), kept in the dark, and diethyl ether vapours were diffused into the reaction vial, affording cubic crystals of complex **1**, [Ag₁₂L₈](ReO₄)₁₂·(DMF)₁₀, along with a small amount of powdered contaminant likely to be AgCl. Yield 6.1 mg, 49.3%. IR ν (cm⁻¹) 3090, 1653 (DMF C=O), 1508 (sharp), 1260 (sharp), 1086 (sharp), 903 (Re-O); Satisfactory elemental analysis could not be obtained due to high levels of solvation and the presence of minor inorganic impurities. pXRD indicates the crystalline material is phase pure, Figure S22.

[Ag₁₂L₈](ReO₄)₁₂·10(DMF) calcd. C 35.94 H 3.17 N 4.48, found C 32.74 H 2.26 N 3.59 %. HRMS (ESI⁺) 808.0561 {AgL}⁺, 1507.2125 {AgL₂}⁺, calcd. 808.0574 and 1507.2106 respectively.

Synthesis of [Ag₁₂L₈](BF₄)₁₂ complex 2 Crude (±)-*tris*-(4-

methylthiazolyl)cyclotriguaiacylene (7 mg) and AgBF₄ (1.5 eq.) were dissolved in DMF (1 mL), kept in the dark, and diethyl ether vapours were diffused into the reaction vial, affording

cubic crystals of complex **2**, $[\text{Ag}_{12}\text{L}_8]\cdot(\text{BF}_4)_{12}\cdot(\text{DMF})_{12}$, along with a small amount of powdered contaminant likely to be AgCl. Yield 7.5 mg, 75.6% IR ν (cm^{-1}) 3098, 1656 (DMF C=O), 1510 (sharp), 1256 (sharp), 1149 (sharp), 1046 (B-F). Satisfactory elemental analysis could not be obtained due to high levels of solvation and the presence of minor inorganic impurities. pXRD indicates the crystalline material is phase pure, Figure S23. $[\text{Ag}_{12}\text{L}_8](\text{BF}_4)_{12}\cdot 12(\text{DMF})$ calcd. C 44.16 H 3.98 N 5.72, found C 43.20 H 4.58 N 6.46 %.

2. NMR spectra and mass spectra

2.1 NMR spectra of (\pm)-*tris*-(4-methylthiazolyl)cyclotriguaiacylene, **L**

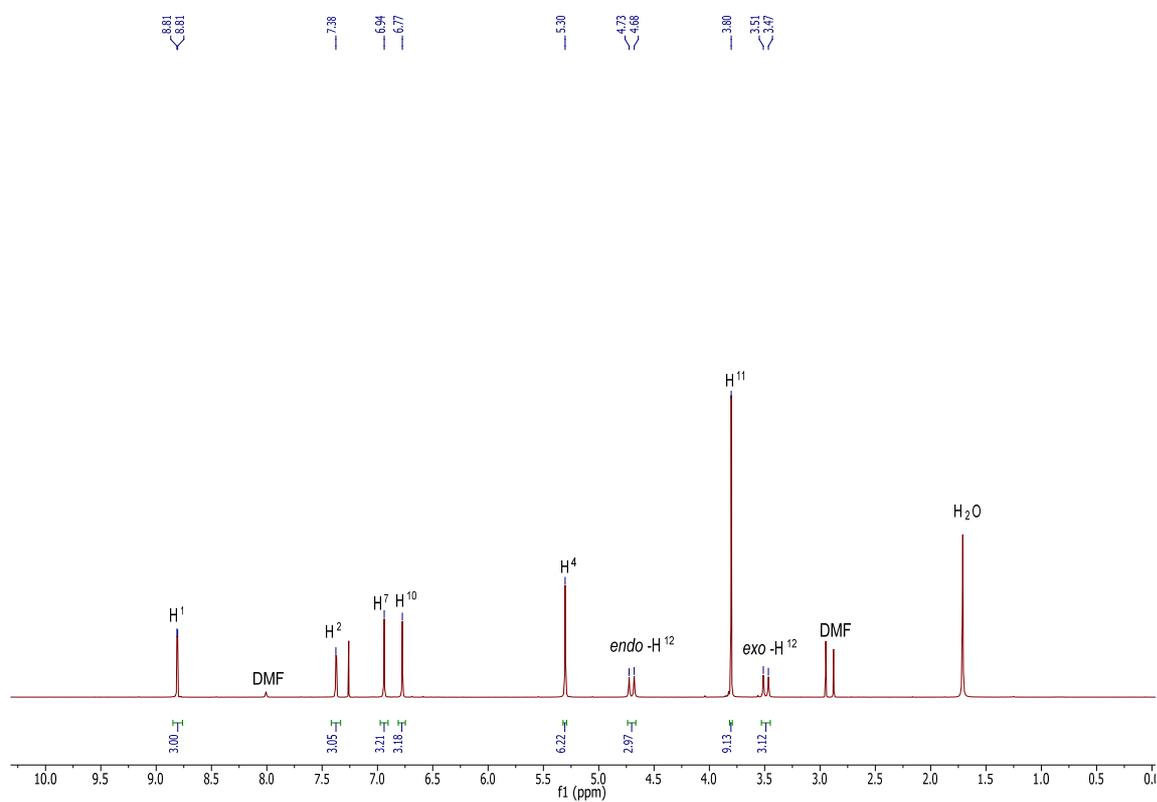


Figure S1. ^1H NMR (300 MHz, CDCl_3) spectrum of (\pm)-*tris*-(4-methylthiazolyl)cyclotriguaiacylene, **L**

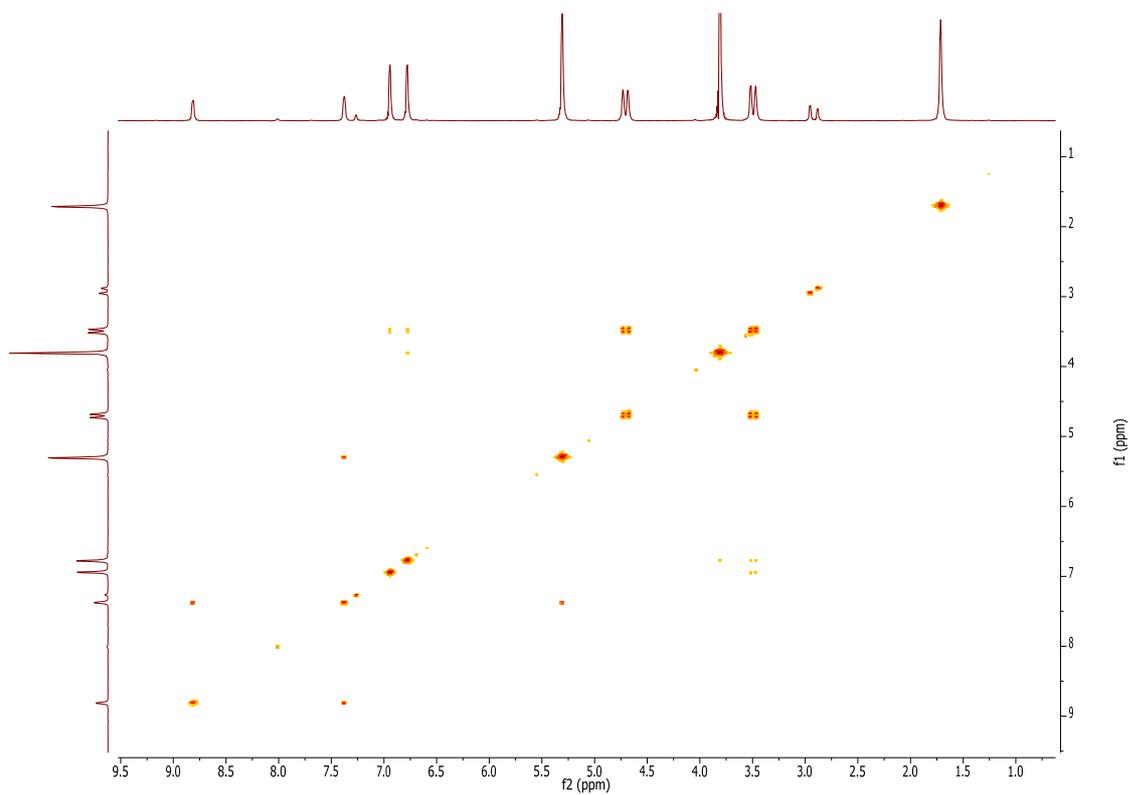


Figure S2. ^1H - ^1H COSY NMR (CDCl_3) spectrum of L.

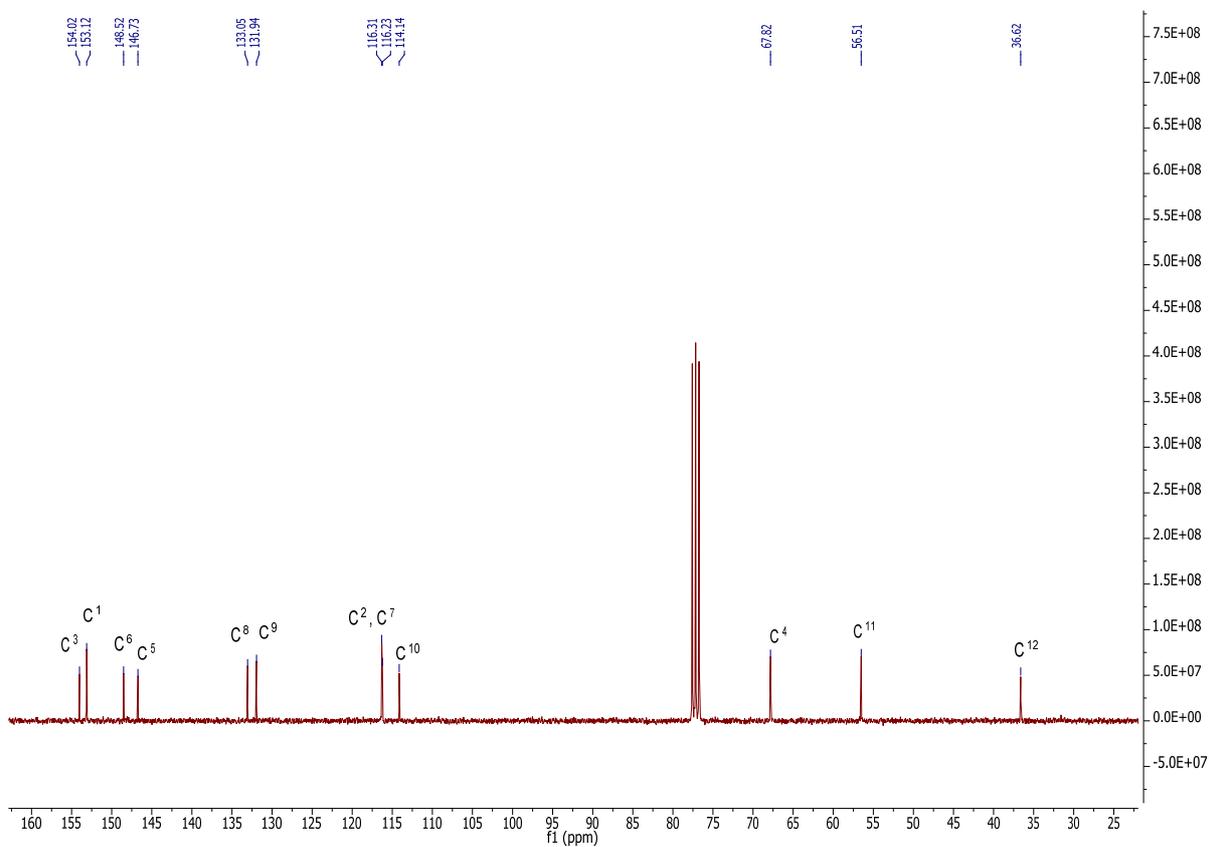


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) spectrum of L.

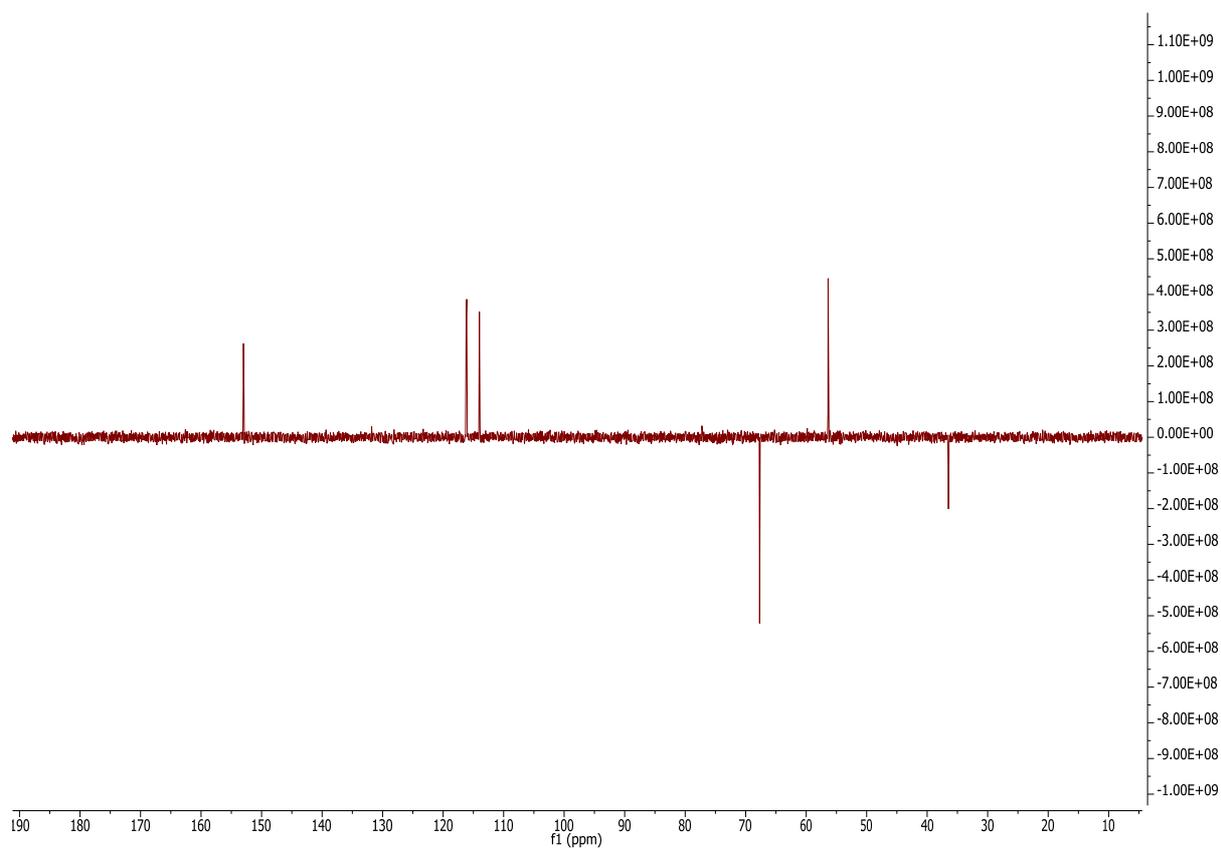


Figure S4. DEPT-135 (CDCl_3) spectrum for L.

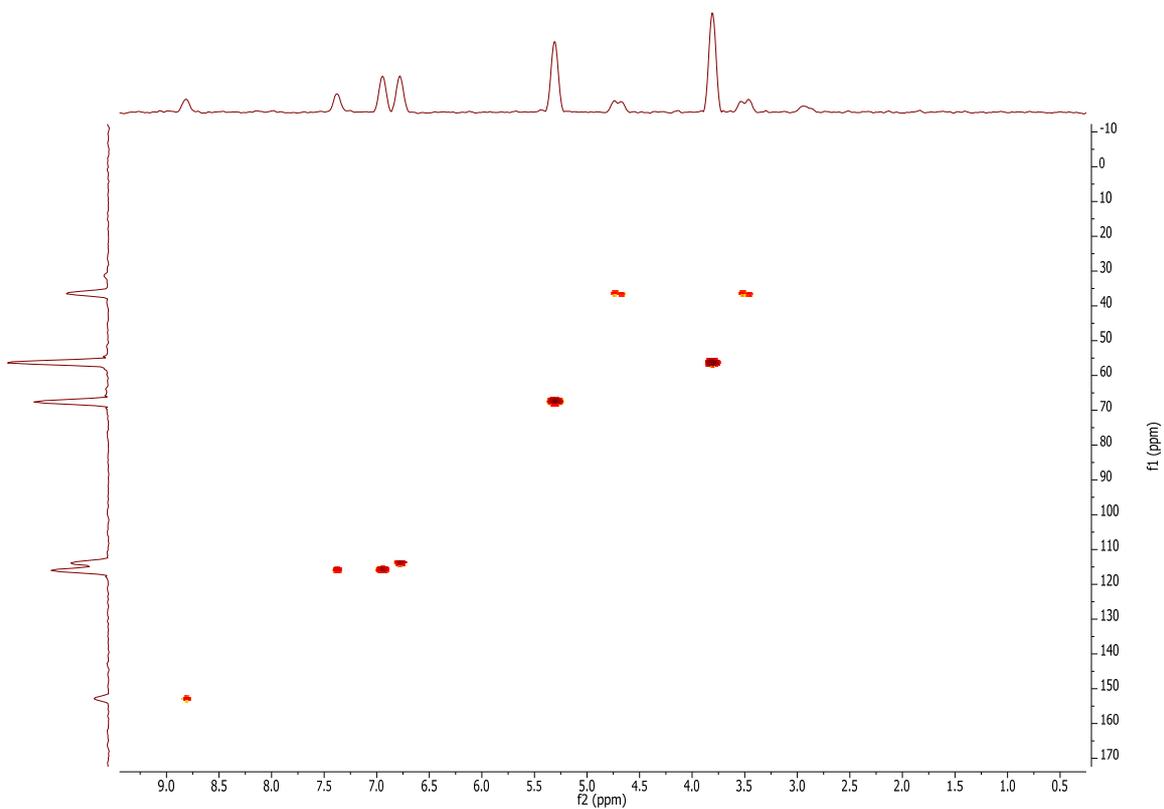


Figure S5. ^1H - ^{13}C HMQC (CDCl_3) spectrum of L.

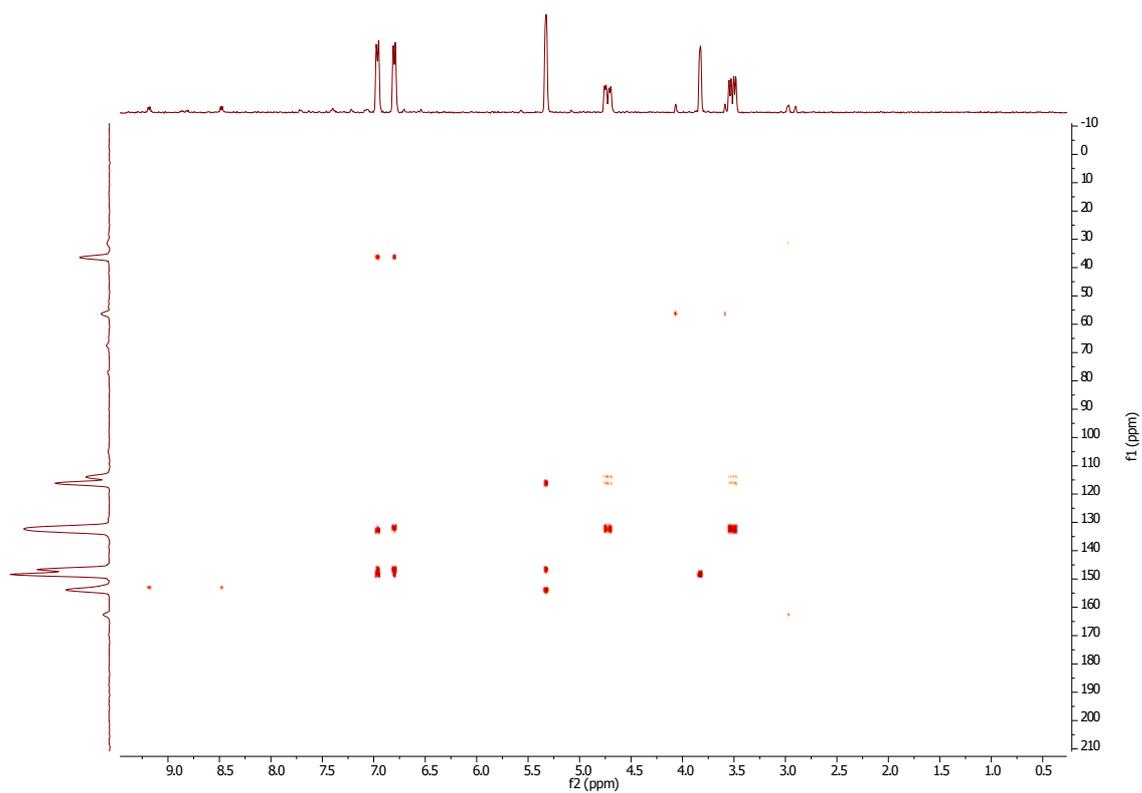


Figure S6. ^1H - ^{13}C HMBC (CDCl_3) spectrum for L.

2.2 Mass spectrum of (\pm)-*tris*-(4-methylthiazolyl)cyclotriguaiacylene, L

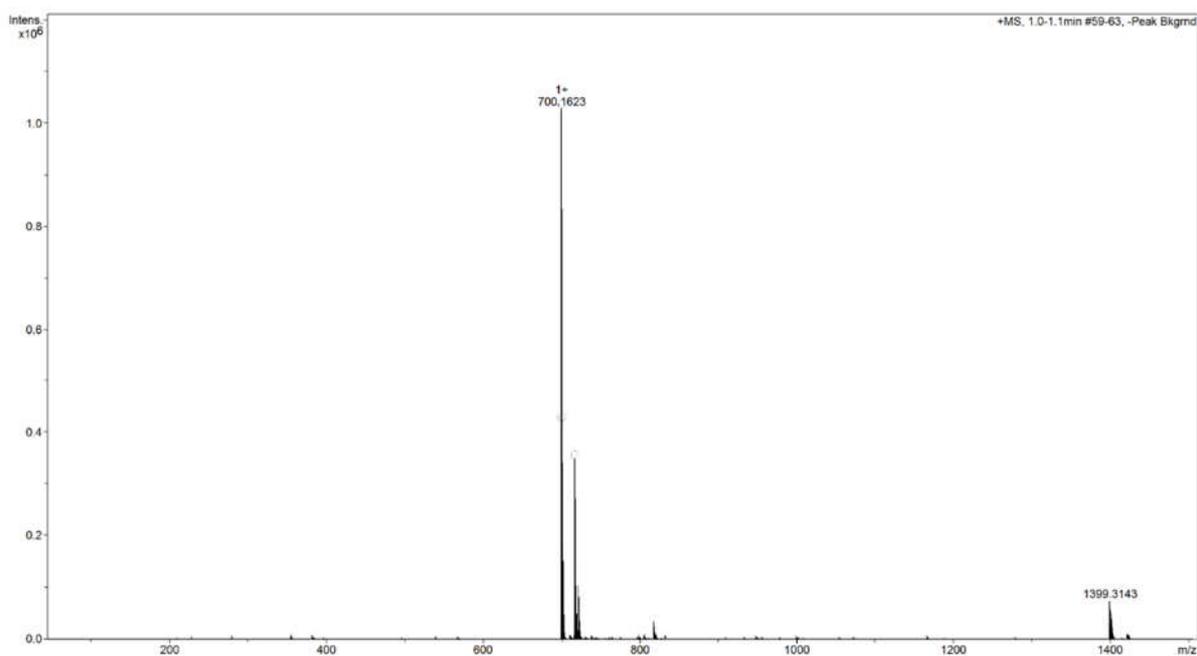


Figure S7. HRMS spectrum of L. $\{\text{LH}\}^+ = 700.1623$ and $\{\text{L}_2\text{H}\}^+ = 1399.3143$.

2.3 Infrared spectrum of (\pm)-*tris*-(4-methylthiazolyl)cyclotriguaiacylene, L

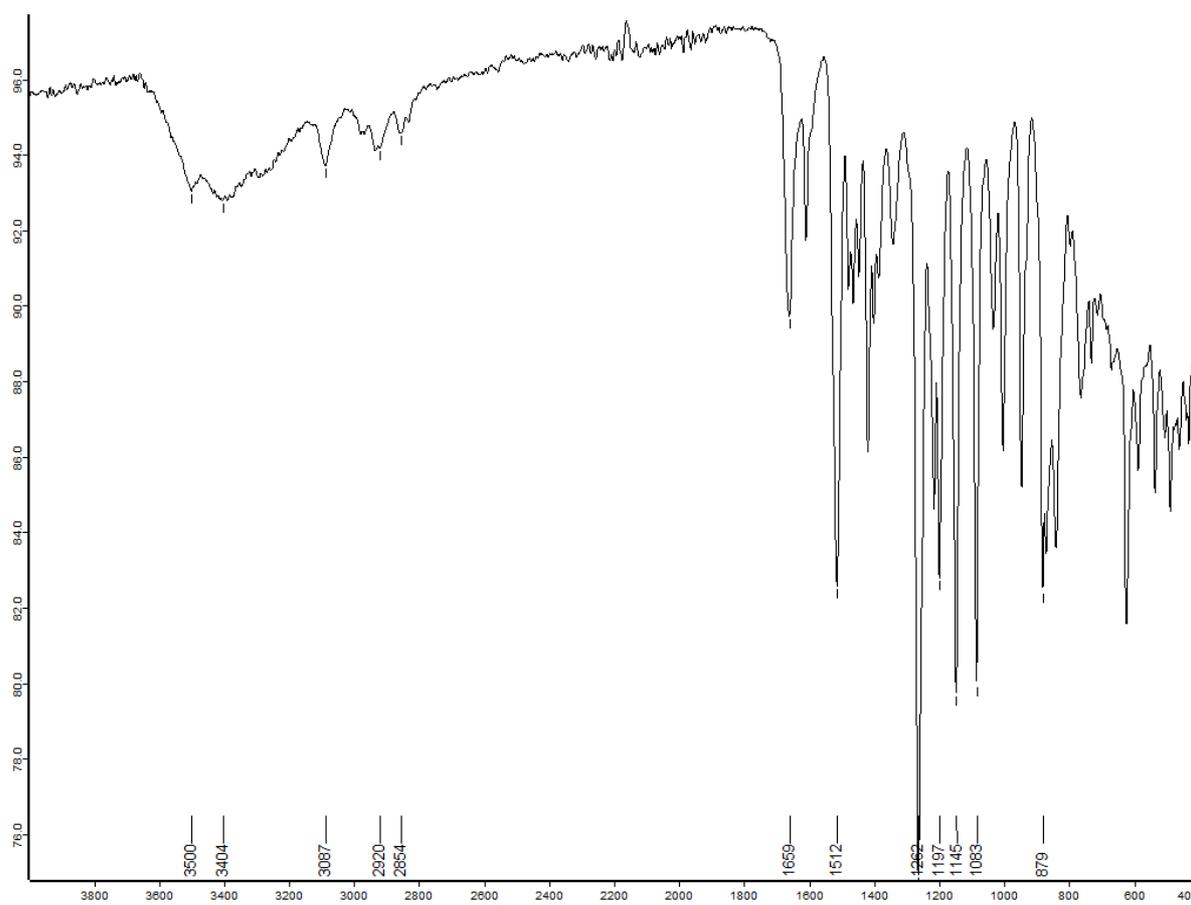


Figure S8. IR spectrum of L.

2.4 NMR spectra of AgBF₄ and L in d₇-DMF

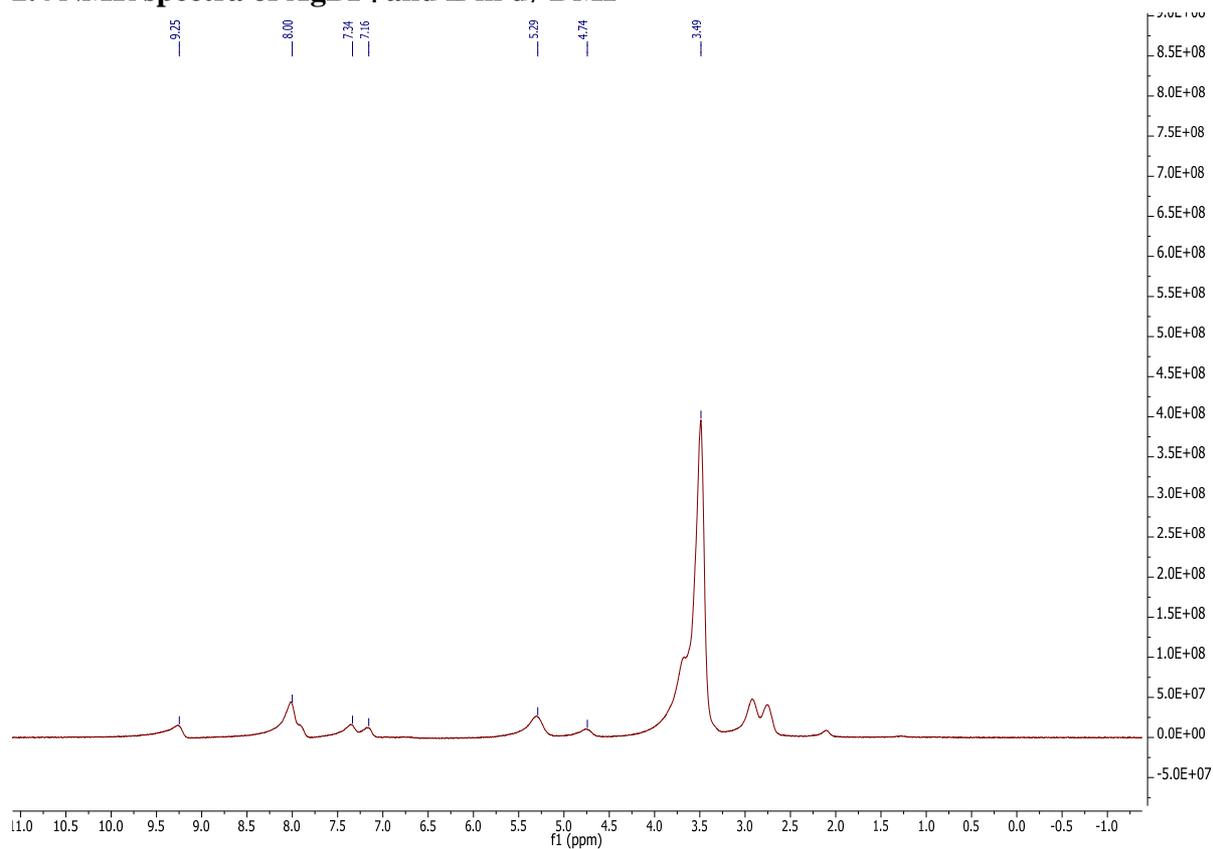


Figure S9. ¹H NMR (300 MHz, d₇-DMF) of mixture of AgBF₄ and L. Peaks at 2.73, 2.95 and 8.03 ppm are solvent.

2.5 Mass spectrum of $[\text{Ag}_{12}\text{L}_8](\text{ReO}_4)_{12}$ complex 1

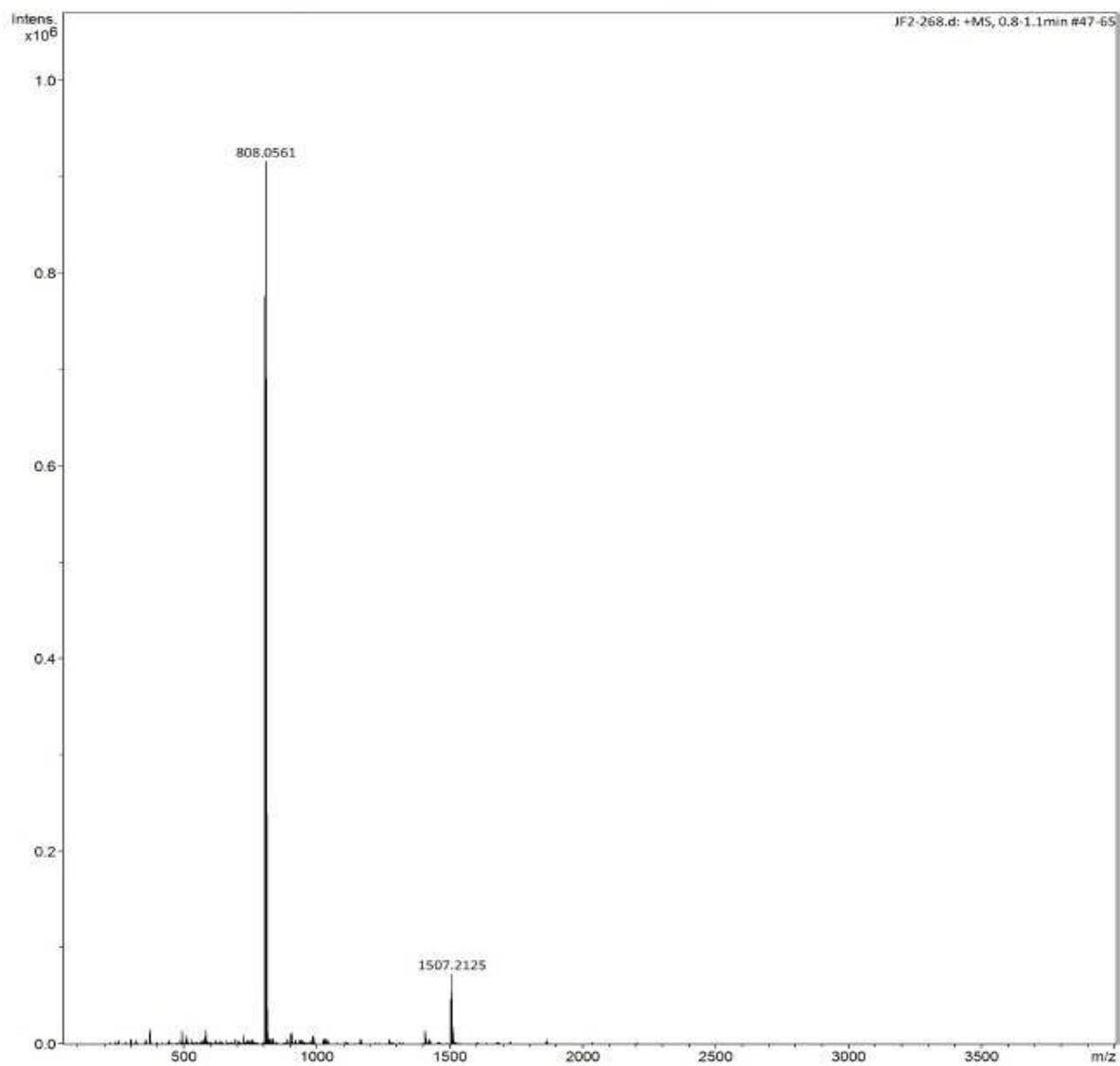


Figure S10. HRMS spectrum of complex **1**, 808.0561 and 1507.2125 are $[\text{AgL}]^+$ and $[\text{AgL}_2]^+$ respectively.

2.6 Infrared spectra of $[Ag_{12}L_8]^{12+}$ complexes

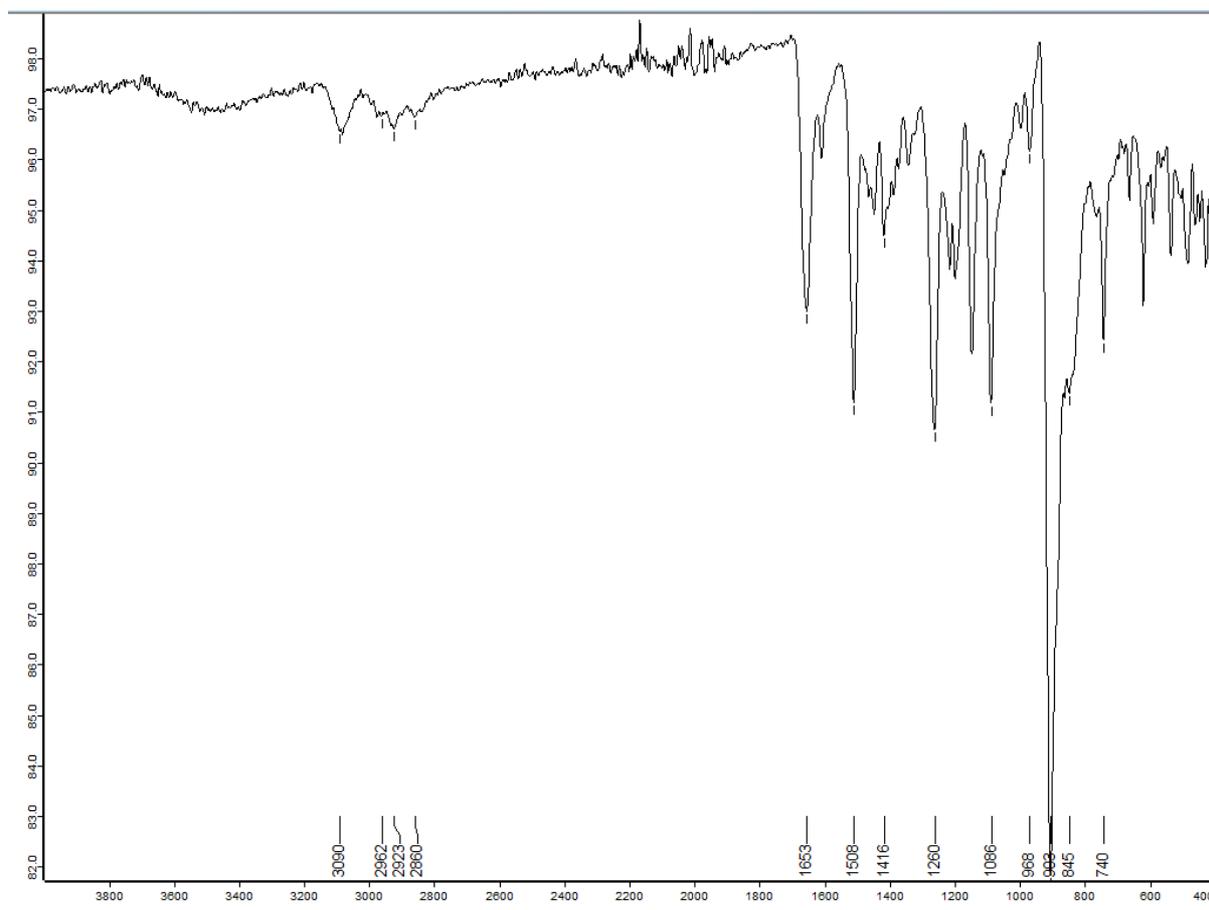


Figure S11. Infrared spectrum of complex $[Ag_{12}L_8](ReO_4)_{12} \cdot n(DMF) \mathbf{1}$

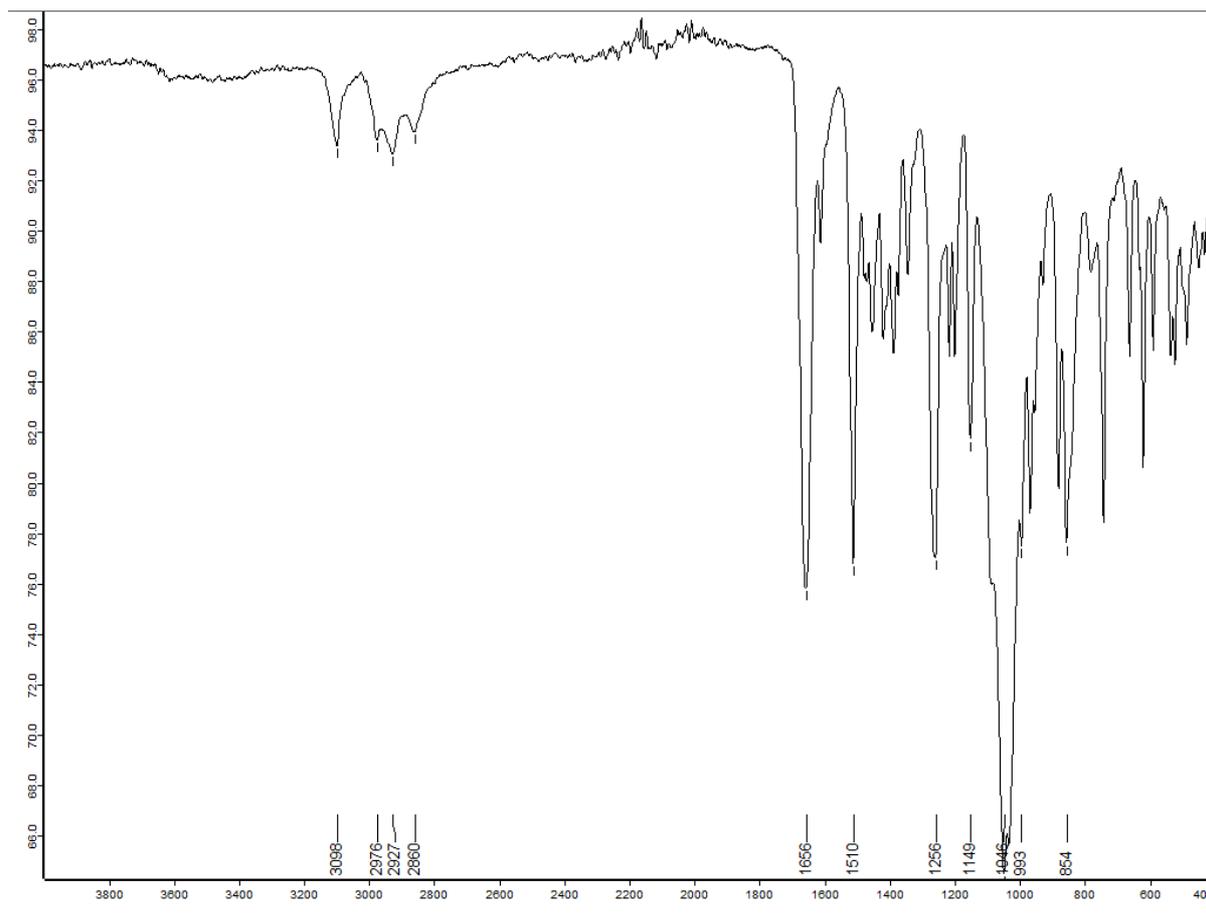


Figure S12. Infrared spectrum of complex $[\text{Ag}_{12}\text{L}_8](\text{BF}_4)_{12}\cdot n(\text{DMF}) \mathbf{2}$

3. X-Ray Crystallography

3.1 Single Crystal Experimental Details

Crystals were mounted under inert oil on a MiTeGen tip and flash frozen using an OxfordCryosystems low temperature device. X-ray diffraction data were collected using $\text{Cu-}K_{\alpha}$ radiation ($\lambda = 1.54184 \text{ \AA}$) using an Agilent Supernova dual-source diffractometer with Atlas S2 CCD detector and fine-focus sealed tube generator. Data were corrected for Lorentzian and polarization effects and absorption corrections were applied using multi-scan methods. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix on F^2 using SHELXL-97.² Unless otherwise specified, all non-hydrogen atoms were refined as anisotropic, and hydrogen positions were included at geometrically estimated positions. For complex **1** the O positions of the ReO_4^- anions were refined isotropically and Re-O distances were restrained to be chemically reasonable. One anion was refined with group U_{iso} for the O sites. One ReO_4 was of low occupancy for charge balance and was sited on a 4-fold axis, hence also showed symmetry-induced disorder. Highest residual peak was a

Fourier ripple at 0.24 Å from Re1. For complex **2** there was significantly more disorder observed as the anion sites could not be located in the difference map. Residual electron density which could not be meaningfully modelled as anions nor solvent, hence the SQUEEZE routine of PLATON was employed,³ which gave calculated void space at ca. 45% of unit cell volume. Global restraints were employed on the anisotropic displacement parameters for complex **2**. Additional details of data collections and structure solutions are given in Table S1, given formulas correspond to the levels of solvation shown by crystallography.

Table S1. Details of data collections and structure refinements.

Compound	L·4(H ₂ O)	L·3(CH ₃ NO ₂)	1	2
Formula	C ₃₆ H ₄₁ N ₃ O ₁₀ S ₃	C ₃₉ H ₄₂ N ₆ O ₁₂ S ₃	C ₂₈₈ H ₂₆₄ Ag ₁₂ N ₂₄ O ₉₆ Re ₁₂ S ₂₄	C ₂₈₈ H ₂₆₄ Ag ₁₂ B ₁₂ F ₄₈ N ₂₄ O ₄₈ S ₂₄
<i>Mr</i>	771.9	882.97	9895.52	7934.84
Crystal color and shape	Yellow, needle	Colourless, rod	Pale orange, block	Pale orange, block
Crystal size (mm)	0.15 x 0.05 x 0.02	0.20 x 0.03 x 0.02	0.15 x 0.10 x 0.10	0.15 x 0.12 x 0.07
Crystal system	Hexagonal	Trigonal (hexagonal axes)	Cubic	Cubic
Space group	<i>P</i> 6 ₃	<i>R</i> 3	<i>F</i> 432	<i>F</i> 432
<i>a</i> (Å)	14.5223(19)	28.138(3)	35.7237(4)	35.4548(7)
<i>b</i> (Å)	14.5223(19)	28.138(3)	35.7237(4)	35.4548(7)
<i>c</i> (Å)	10.2701(12)	4.4445(5)	35.7237(4)	35.4548(7)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	120	120	90	90
<i>V</i> (Å ³)	1875.8(4)	3047.4(5)	45590.0(9)	44568.2(15)
<i>Z</i>	2	3	4	4
<i>T</i> /K	110(1)	120(1)	120(1)	120(1)
ρ_{calc} (g·cm ⁻³)	1.367	1.443	1.442	1.183
θ range (°)	3.51 – 73.42	5.45 – 73.82	3.50–73.74	3.53–73.63
No. data collected	4447	4449	9948	4858
No. unique data	2239	2150	3794	2572
<i>R</i> _{int}	0.0604	0.0786	0.0341	0.0286
No. obs. Data (<i>I</i> > 2σ(<i>I</i>))	1394	1635	2667	1639
No. parameters	158	183	168	152
No. restraints	1	1	4	42
<i>R</i> ₁ (obs data)	0.0886	0.0719	0.0847	0.0718
<i>wR</i> ₂ (all data)	0.2598	0.1873	0.2886	0.2256
Flack parameter	-0.07(7)	0.08(5)	0.03(4)	0.15(3)
<i>S</i>	0.996	1.052	1.036	1.042
Max. shift/esd	0.000	0.000	0.001	0.001
Largest difference peak and hole/ (e Å ⁻³)	1.332, -0.326	0.399, -0.315	2.000, -2.126	0.778, -0.479

3.2 Additional diagrams of $[tris-(4\text{-methylthiazolyl})cyclotriguaicyclene]\cdot 4H_2O$, $L\cdot 4(H_2O)$

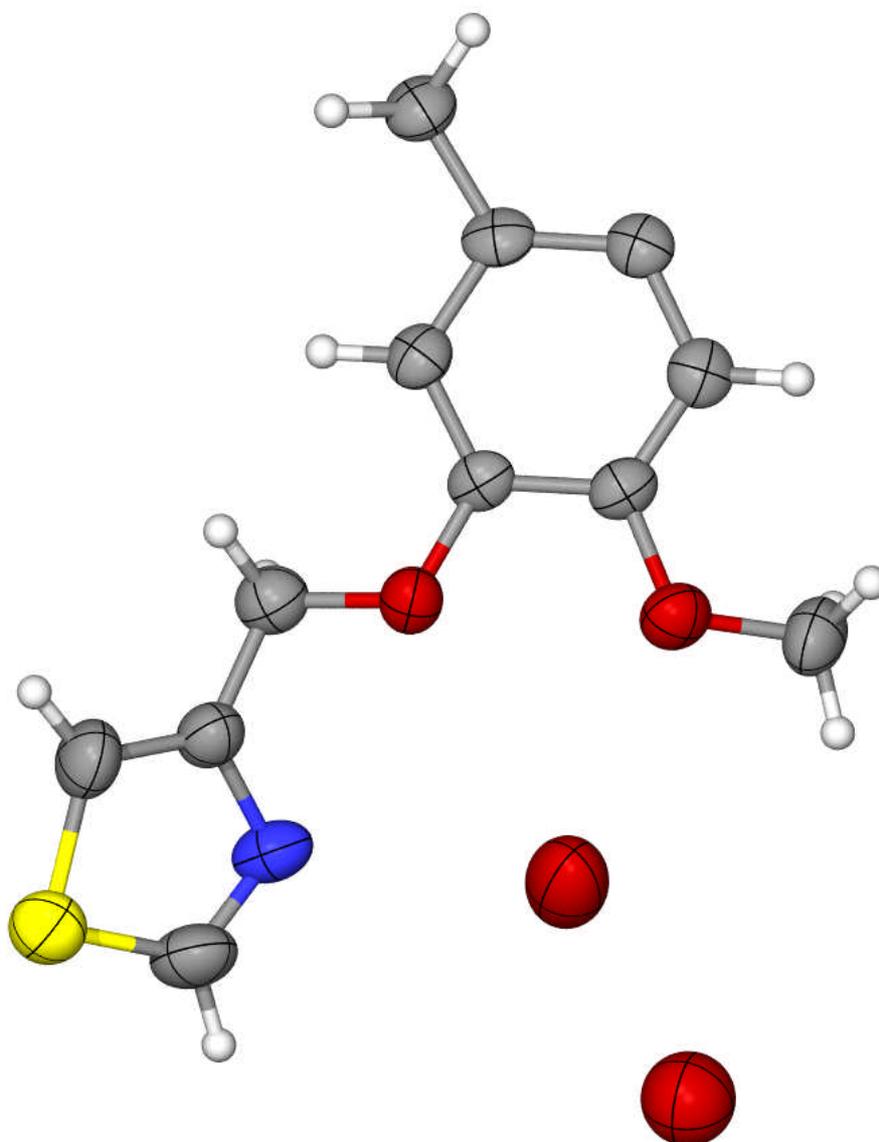


Figure S13: Asymmetric unit of crystal structure of $L\cdot 4(H_2O)$ with ellipsoids shown at 50% probability level. C, grey; H, white; O, red; N, blue; S, yellow; Ag, light blue.

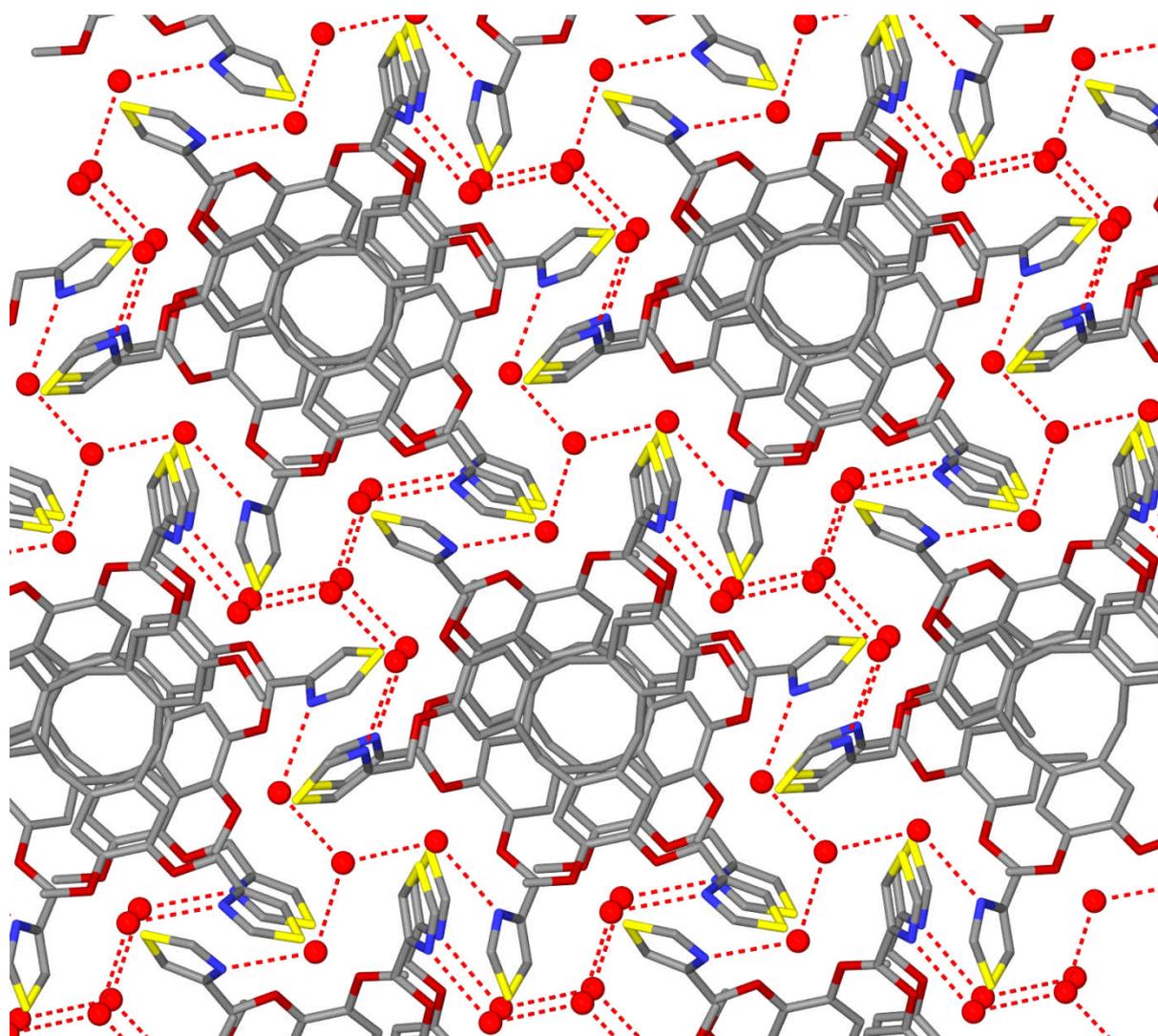


Figure S14: Packing diagram of L·4(H₂O) viewed down *c*. Hydrogen atoms excluded for clarity, water molecules shown as spheres.

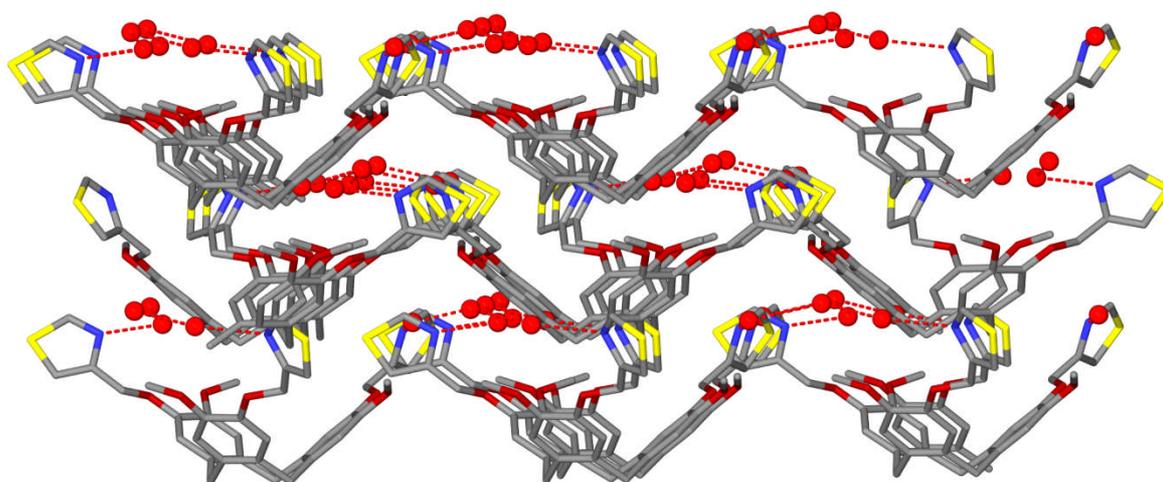


Figure S15: Packing diagram of L·4(H₂O) viewed down *a*. Hydrogen atoms excluded for clarity, water molecules shown as spheres.

3.3 Additional diagrams of [*tris*-(4-methylthiazolyl)cyclotriguaiacylene]·3CH₂NO₂, L·3(CH₃NO₂)

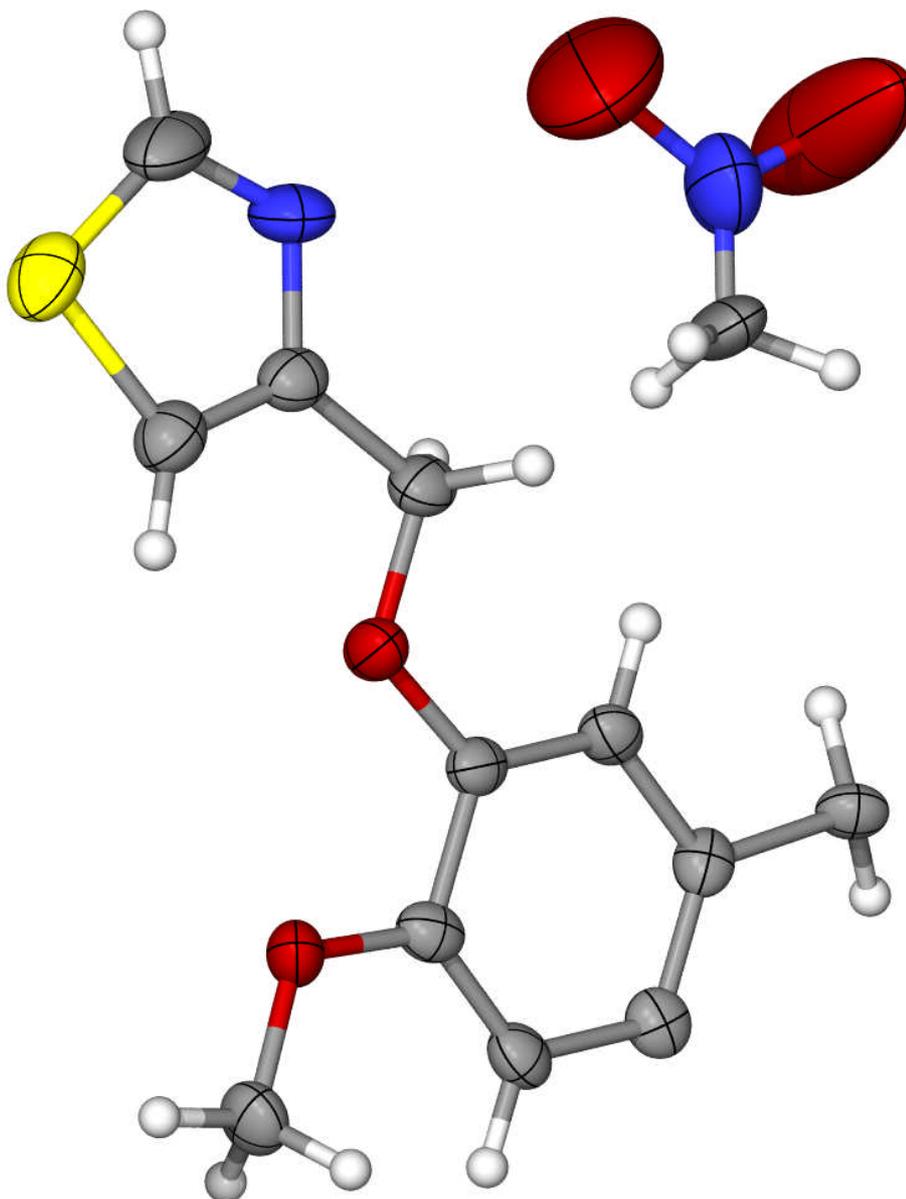
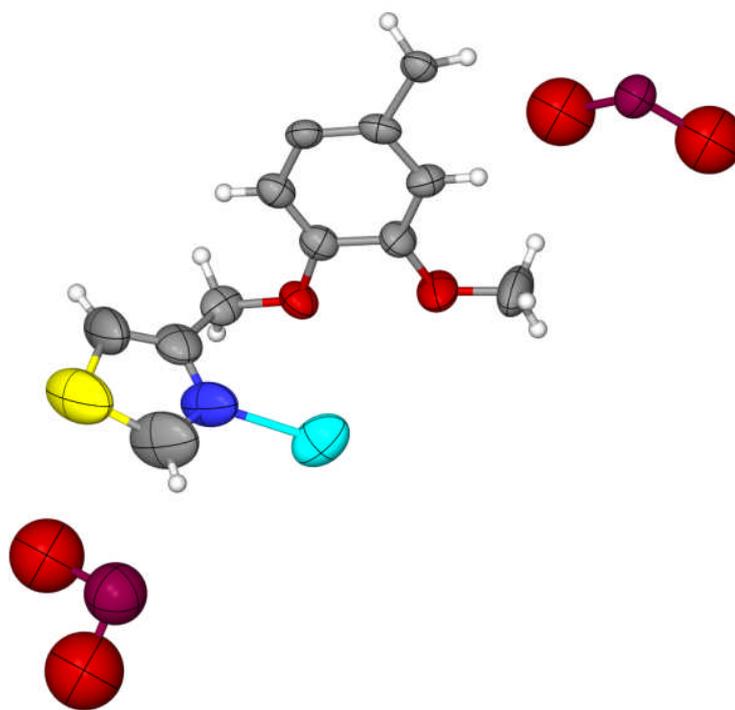
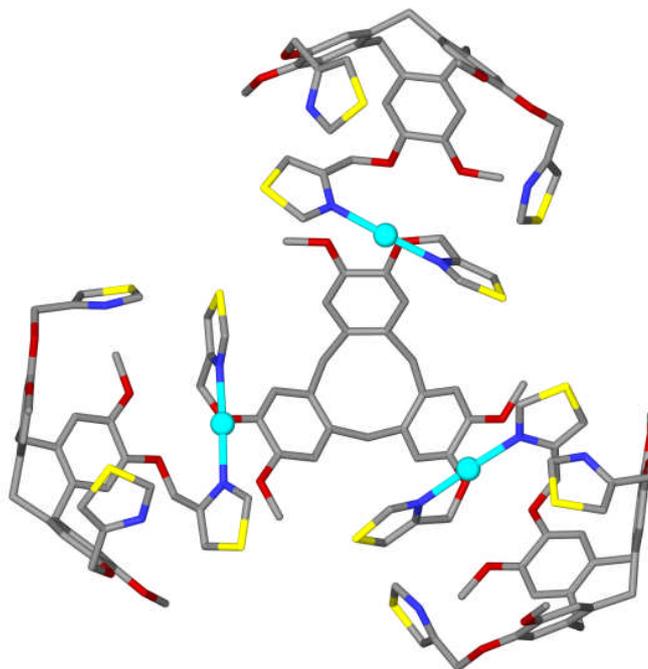


Figure S16: Asymmetric unit of crystal structure of L·3(CH₃NO₂) with ellipsoids shown at 50% probability level. C, grey; H, white; O, red; N, blue; S, yellow; Ag, light blue.

3.4 Additional diagrams of complex **1**, [Ag₁₂L₈] \cdot 12(ReO₄) \cdot 10(DMF)



(a)



(b)

Figure S17: (a) Asymmetric unit of crystal structure of complex **1** with ellipsoids shown at 50% probability level. (b) section showing Ag(I) coordination and ligand bridging behavior. C, grey; H, white; O, red; N, blue; S, yellow; Ag, light blue; Re, dark red.

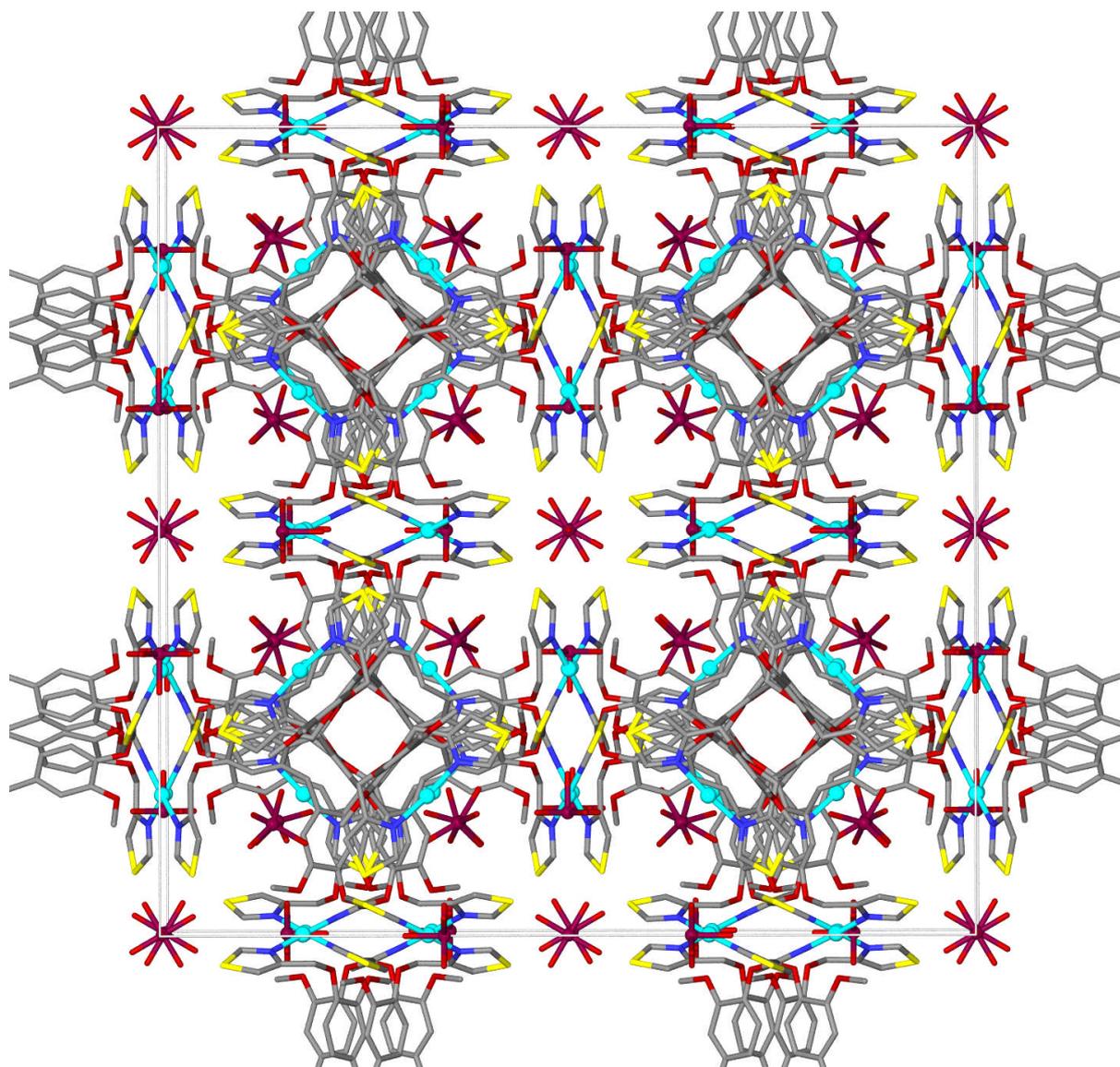


Figure S18: Packing diagram of complex **1** viewed down *c*. Hydrogen atoms excluded for clarity, Ag and Re sites shown as spheres.

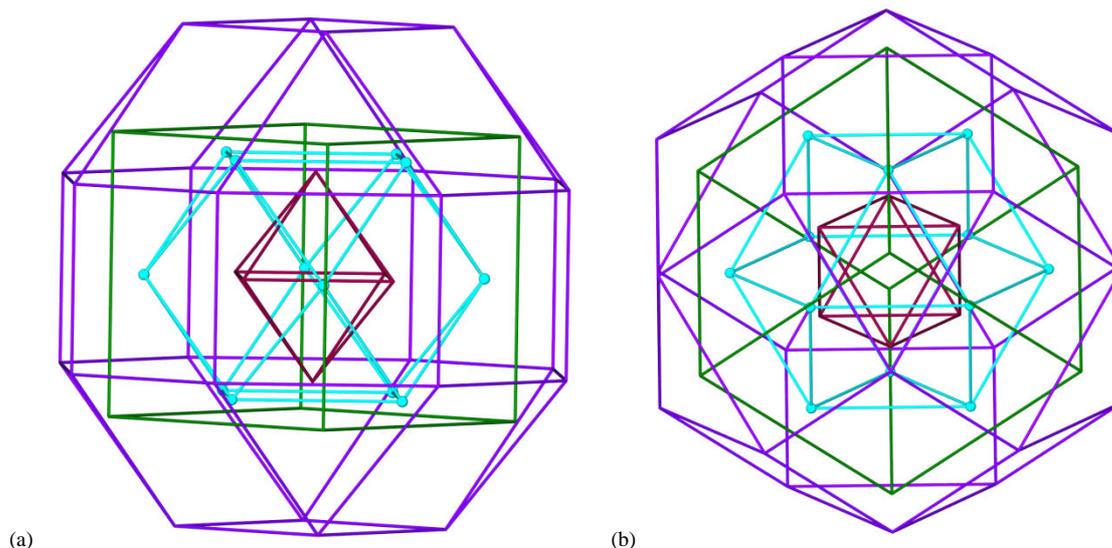


Figure S19: Matryoshka (Russian Doll) arrangement of components in complex **1** shown with in framework view. Octahedron of *endo*-ReO₄ sites shown in dark red; cuboctahedron of Ag(I) sites in light blue; cube of ligand positions in green; and rhombicuboctahedron of *exo*-ReO₄ sites in purple.

3.5 Diagrams of complex 2, [Ag₁₂L₈] \cdot 12(BF₄) \cdot 12(DMF)

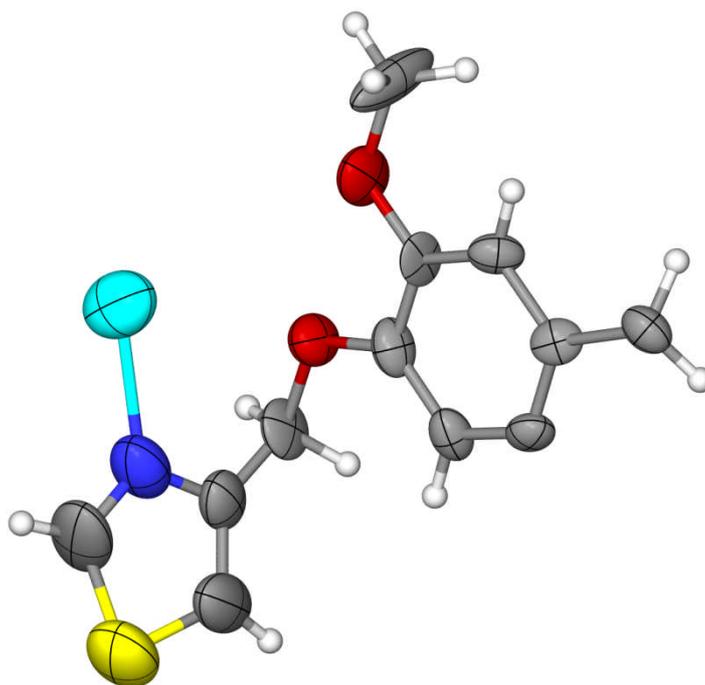


Figure S20: Asymmetric unit of crystal structure of complex **2** with ellipsoids shown at 50% probability level. Anions and solvent were not located in the difference map for this structure. C, grey; H, white; O, red; N, blue; S, yellow; Ag, light blue.

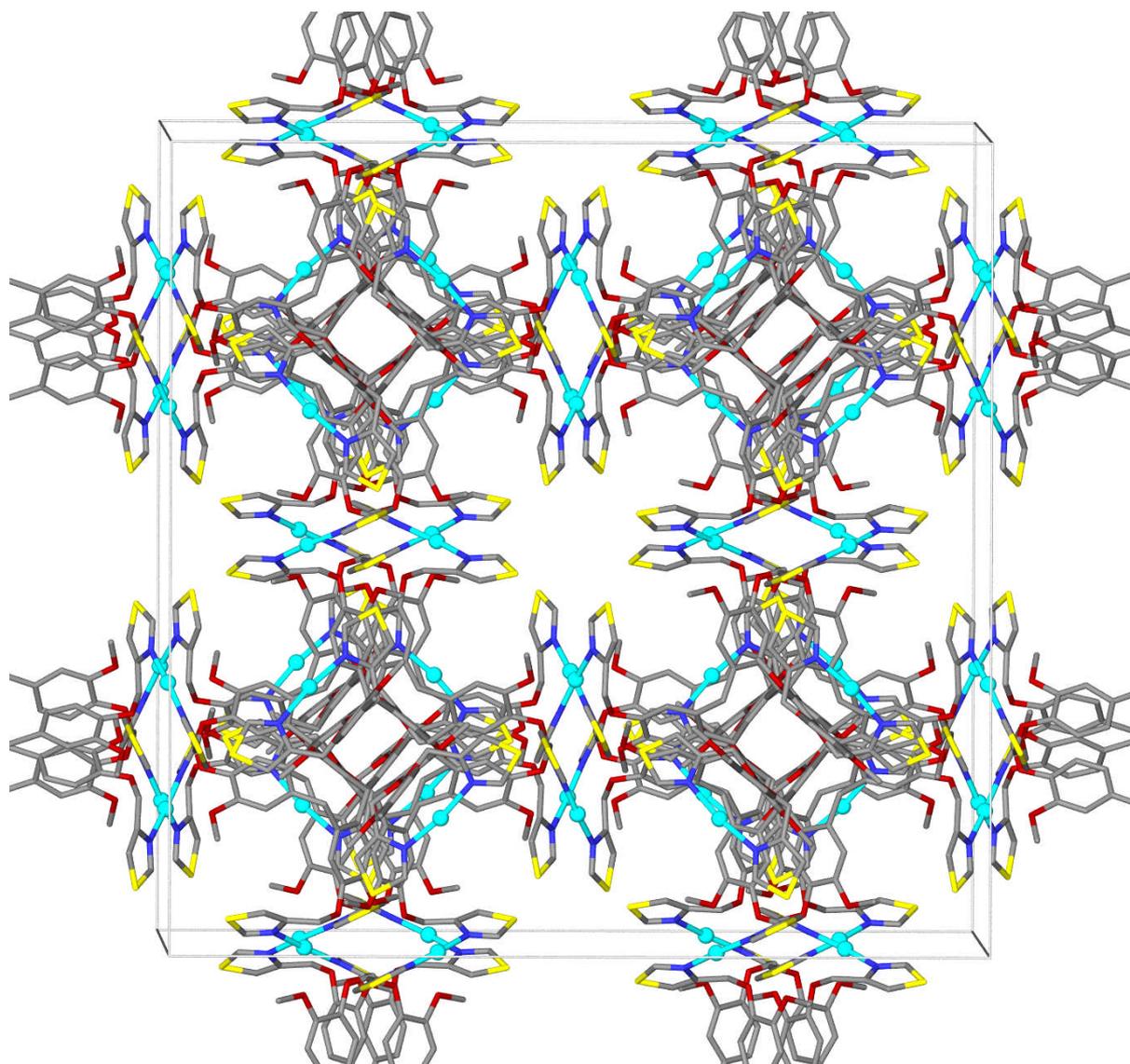


Figure S21: Packing diagram of complex **2** viewed down *a*. Hydrogen atoms excluded for clarity, Ag sites shown as spheres.

3.6 Powder XRD Data

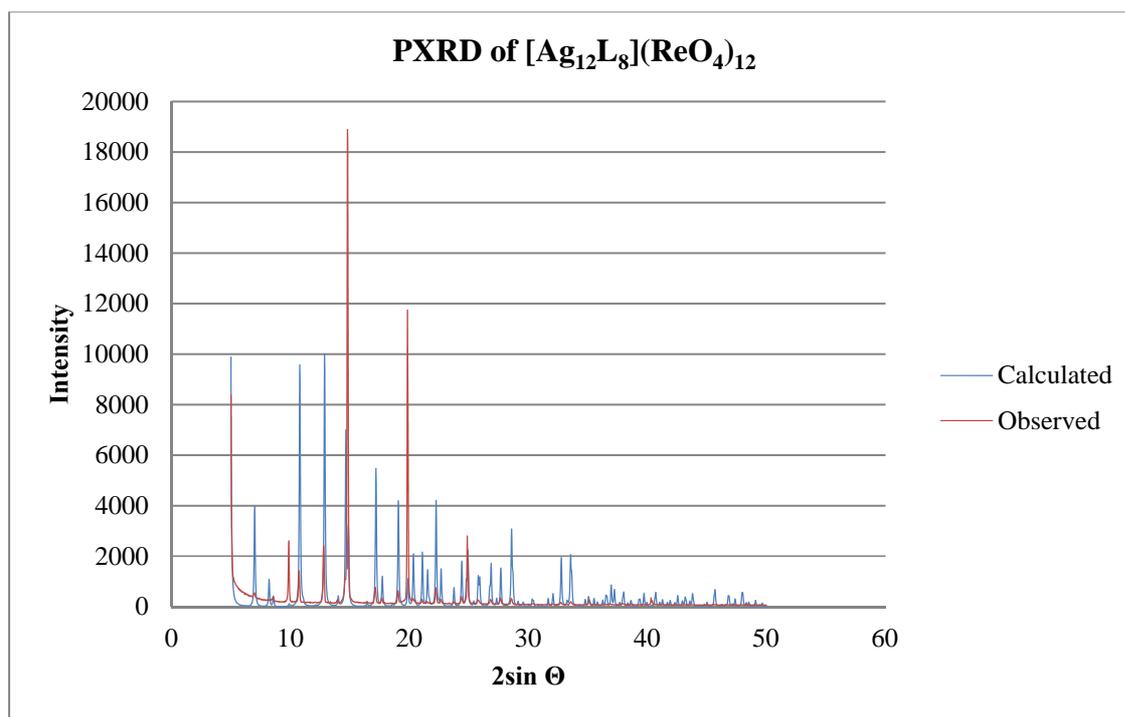


Figure S22: Powder XRD pattern of complex 1

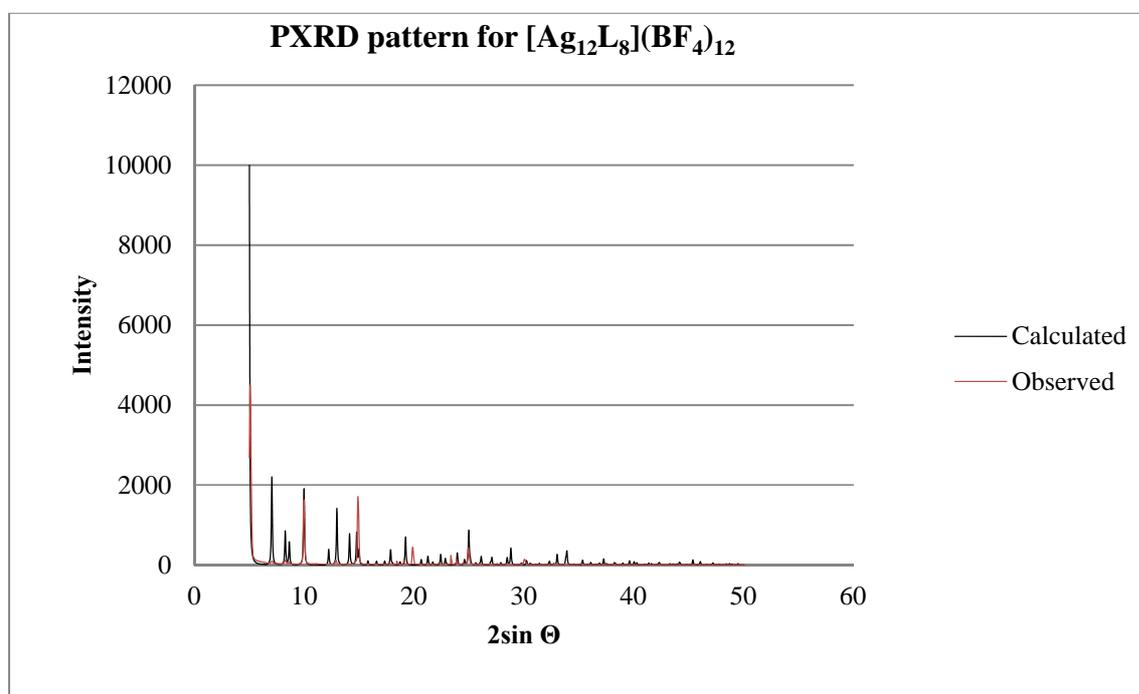


Figure S23: Powder XRD pattern of complex 2

4. Thermogravimetric Analysis

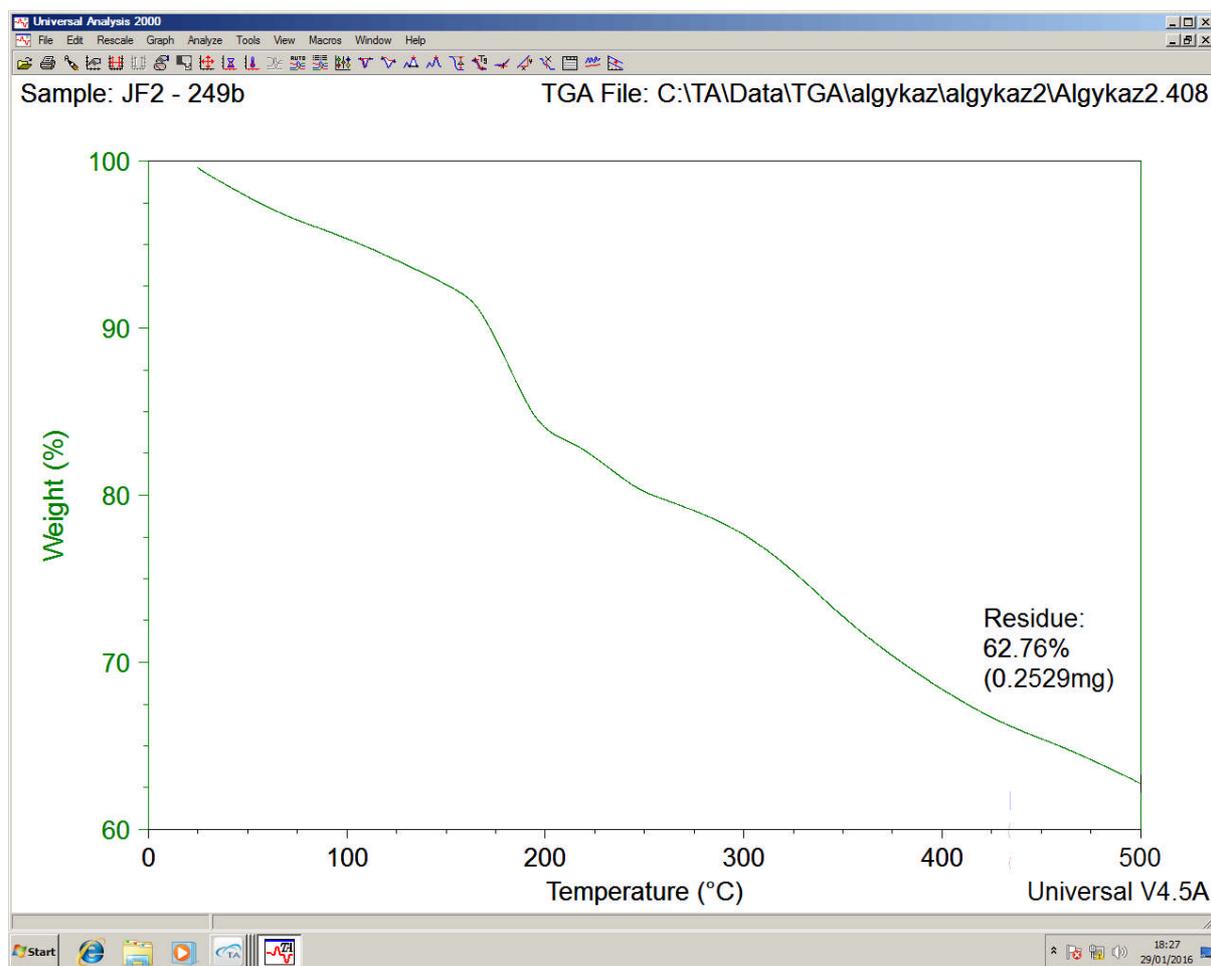


Figure S24: TGA of complex 1.

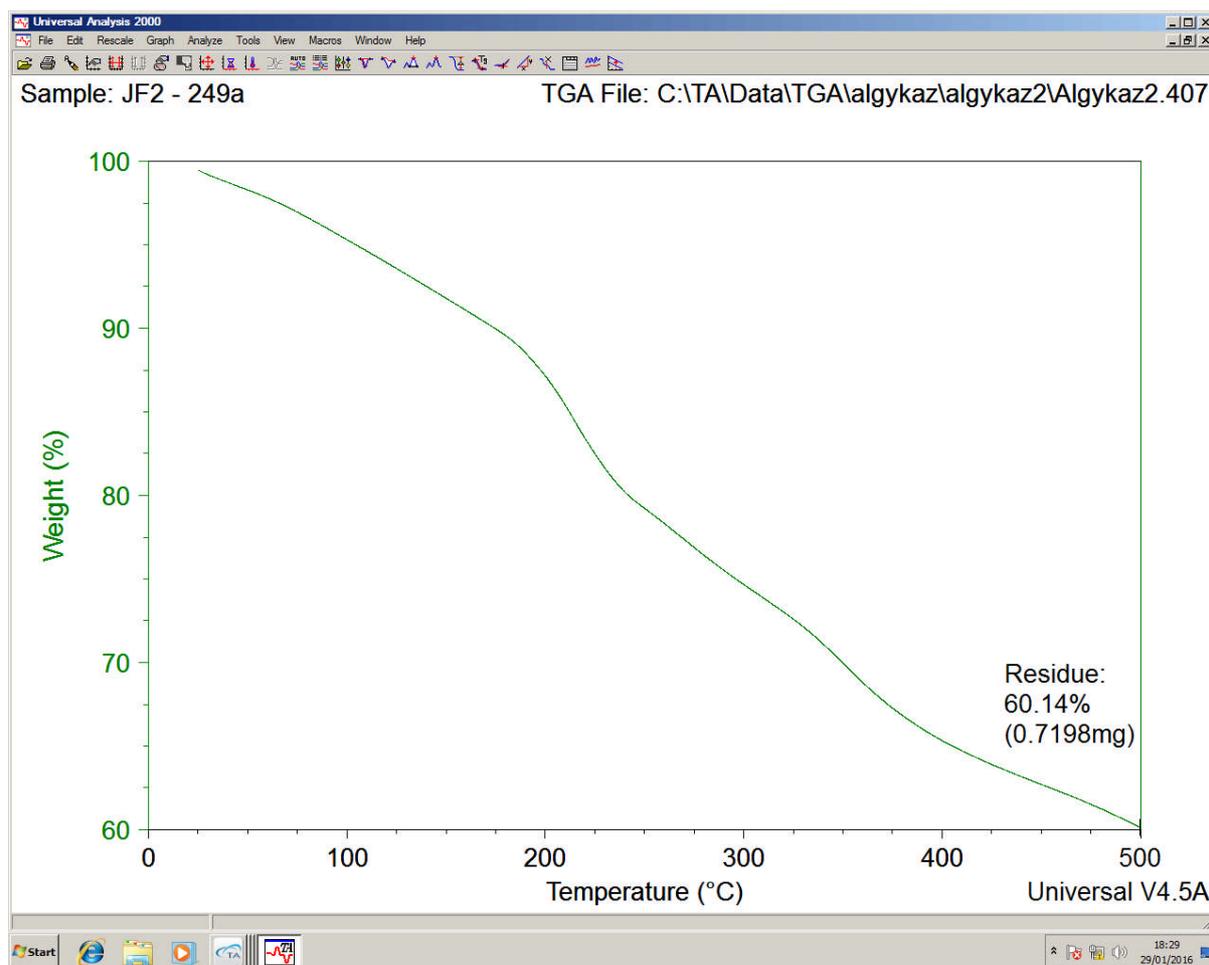


Figure S25: TGA of complex 2.

5. EDX measurements

Table S2: SEM/EDX analysis data (Weight %)

Sample reference	Carbon (Wt. %)	Oxygen (Wt. %)	Fluorine (Wt. %)	Sulphur (Wt. %)	Silver (Wt. %)	Rhenium (Wt. %)
Complex 1	38.84	18.96	-	6.02	12.21	23.98
Complex 1	43.40	20.46	-	5.22	10.59	20.33
Complex 1	38.38	16.68	-	6.03	12.73	26.18
Complex 2	47.20	15.07	14.80	8.47	14,46	-
Complex 2	47.93	14.62	16.41	7.94	13.10	-

Complex 2	46.50	14.81	14.18	9.37	15.14	-
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Table S3: SEM/EDX analysis data (Atomic %)

Sample reference	Carbon (At. %)	Oxygen (At. %)	Fluorine (At. %)	Sulphur (At. %)	Silver (At. %)	Rhenium (At. %)
Complex 1	66.69	24.44	-	3.87	2.33	2.66
Complex 1	68.66	24.30	-	3.09	1.87	2.08
Complex 1	68.21	22.25	-	4.01	2.52	3.00
Complex 2	64.97	15.57	12.88	4.37	2.22	-
Complex 2	65.03	14.89	14.07	4.04	1.98	-
Complex 2	64.79	15.49	12.49	4.89	2.35	-

6. References

1. (a) J. L. Scott, D. R. MacFarlane, C. L. Raston and C. M. Teoh, *Green Chem.*, 2000, **2**, 123-126; (b) J. Canceill, A. Collet and G. Gottarelli, *J. Am. Chem. Soc.*, 1984, **106**, 5997-6003.
2. G. M. Sheldrick, G. M. *Acta Cryst.*, 2008, **A64**, 112-122.
3. A. L. Spek, A. L. *Acta Cryst.*, 1990, **A46**, C34