

Supporting Information for New Journal of Chemistry

Rapid access to sulfate-encapsulated symmetrical and asymmetrical capsules based on silver-pyrazole complex cations

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1. General information

The preparation of complexes **1**~**3** were carried out under air atmosphere whereas complex **4** was prepared under a nitrogen atmosphere using standard Schlenk technique. Dichloromethane were distilled from CaH₂ before use. Diethyl ether was dried by distillation from sodium benzophenone prior to use. Other reagents were obtained from commercial suppliers and used as received without further purification. The ligands L¹~L³ were prepared according to literature procedures. Infrared spectra were recorded on a Bruker Alpha-T FTIR spectrometer as Nujol mulls. ¹H NMR and ¹³C NMR spectra were obtained at room temperature using Bruker Avance 600 MHz spectrometers. Mass spectra were acquired on a Finnigan TSQ 700 spectrometer. Elemental analyses were performed on a HERAEUS CHN-O-S-Rapid elemental analyzer by Instruments Center, National Chung Hsin University. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer. TGA data were recorded by Instruments Center, National Tsing Hua University.

X-ray Crystallographic Analysis of 1-4.

Crystal data collection and processing parameters are given in Table S1. Diffraction data were carried out on a Bruker APEX2 CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$). The structures **1-4** were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXL-97 program. All of the non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were located geometrically and refined in the riding mode. For complex **2**, the crystal structure is disordered at the O2, O3, O4, C37, C38, C53, C54, and C55 positions: a refined occupancy ratios of 0.70 : 0.30 for O2-O4 atoms, 0.50 : 0.50 for C37 and C38 atoms, and 0.54 : 0.46 for C53-C55. For complex **4**, the SQUEEZE option in Platon was used without the contribution of solvent molecules, leading to the presence of solvent accessible void, to refine the structure. A Platon void calculation for the solvent free form gave a total potential solvent volume of 269 \AA^3 (3.3%) which is roughly in agreement with half solvated dichloromethane (2.7%). Additional crystallographic data as CIF files are available as Supporting Information.

Table S1 X-ray crystallographic data for complexes **1** – **4**.

	1	2	3	4
Empirical Formula	C ₉₆ H ₁₁₂ N ₁₆ Ag ₄ S ₂ O ₈	C ₅₅ H ₁₀₂ N ₁₀ Ag ₂ SO ₅	C ₉₀ H ₇₂ N ₁₂ Ag ₂ SO ₄	C ₉₀ H ₇₂ N ₁₂ Cu ₂ SO ₄
Formula weight	2113.62	1231.27	1633.40	1544.74
<i>T</i> (K)	200(2)	200(2)	200(2)	200(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.384(3)	11.6173(4)	12.1323(5)	21.6261(11)
<i>b</i> (Å)	15.712(6)	14.1867(5)	17.6149(6)	13.7166(6)
<i>c</i> (Å)	17.847(7)	20.5791(5)	35.9629(14)	29.3214(11)
α (°)	65.553(12)	95.8130(10)	90	90
β (°)	86.379(10)	105.9260(10)	91.7810(10)	107.5170(10)
γ (°)	80.780(11)	94.0010(10)	90	90
<i>V</i> (Å ³)	2364.4(15)	3227.79(18)	7681.9(5)	8294.5(6)
<i>Z</i>	1	2	4	4
<i>D</i> _{calc} (Mg m ⁻³)	1.484	1.267	1.412	1.237
μ (mm ⁻¹)	0.924	0.688	0.599	0.595
<i>F</i> (000)	1084	1304	3352	3208
θ range for data collection	2.20–25.19°	2.35–25.01°	2.10–25.36°	2.48–25.06°
Reflections collected	50510	109214	135114	46462
Independent reflections (<i>R</i> _{int})	8462 (0.0760)	11355 (0.0589)	14033 (0.0290)	7316 (0.0391)
Data / restraints / parameters	8462 / 0 / 576	11355 / 2 / 644	14033 / 0 / 982	7316 / 0 / 492
Goodness-of-fit on <i>F</i> ²	1.057	1.000	1.036	1.062
<i>R</i> ₁ , <i>wR</i> ₂	0.0398, 0.0821	0.0421, 0.1110	0.0261, 0.0647	0.0359, 0.1031
CCDC No.	1906953	1906960	1906964	1906972

2 Synthesis of complex [Ag₂(L¹)₄(SO₄)] (1)

Method 1. Ag₂SO₄ (0.146 g, 0.468 mmol) was dissolved in R.O. water (50 mL). To this solution was added dropwisely a solution of L¹ (0.355 g, 1.91 mmol) in acetone (30 mL). After stirring the reaction mixture for another 30 minutes, a white precipitate was formed. The solids filtered off and washed with R.O. water and ether to yield white powder product 0.435 g (88%). Method 2. Changing the acetone solvent with dichloromethane (50 mL) to form a two-phase system. After vigorously stirring the reaction mixture for 1 hour, the organic layer was separated and concentrated under reduced pressure. Layerd with ether to give complex **1** (90% yield). ¹H NMR (600 MHz, CD₂C1₂): δ 13.57 (s, 1H), 7.26-7.08 (m, 5H), 3.71 (s, 2H), 2.08 (s, 1H) ppm; ¹³C NMR (150 MHz, CD₂C1₂): 141.1, 128.9, 128.6, 126.5, 115.0, 29.5, 12.1 ppm; IR (Nujol): ν_{N-H} 3191, 3142, 3083, 3056 cm⁻¹, ν_{C=N} 1587 cm⁻¹, ν_{SO₄⁻} 1178, 1123, 1091, 1045 cm⁻¹; Positive ESI-MS: [L+H]⁺ 187.65 (11%), [AgL₂]⁺ 481.88 (100%), [Ag₂L₃]⁺ 773.28 (10%), [Ag₃L₆(SO₄)]⁺ 1536.20 (47%). Single crystals were grown from CH₂Cl₂/Et₂O. Anal. Calcd for C₉H₁₁N₁₆Ag₄S₂O₈: C, 54.55; H, 5.34; N, 10.60. Found: C, 54.88; H, 5.38; N, 10.79 %.

3 Synthesis of complex [Ag₂(L²)₅(SO₄)(H₂O)] (2)

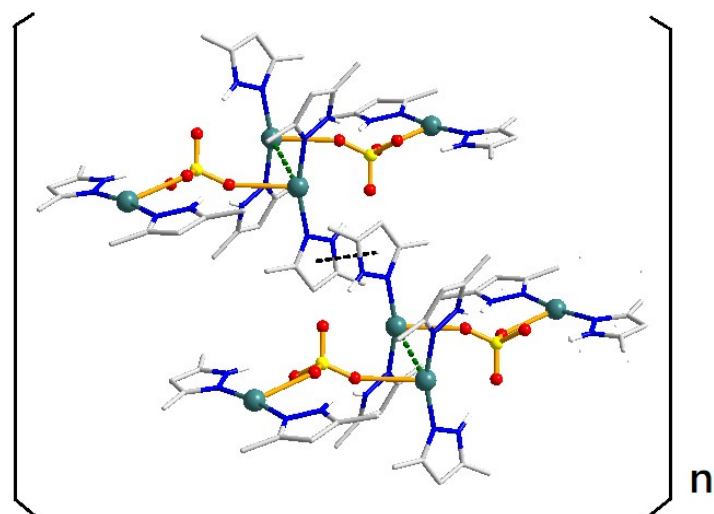
Method 1. Ag₂SO₄ (0.147 g, 0.471 mmol) was dissolved in R.O. water (50 mL). To this solution was added dropwisely a solution of L² (0.432 g, 2.40 mmol) in acetone (30 mL). After stirring the reaction mixture for another 30 minutes, a white precipitate was formed. The obtained solid was washed by R.O. water and then ether to afford white solid product 0.541 g (93%), which is identified by elemental analysis as complex **2**. Single crystals were obtained by the slow evaporation of acetonitrile (95%) solution of **2** to dryness in the air. Method 2. Changing the acetone solvent with dichloromethane (50 mL) to form a two-phase system. After vigorously stirring the reaction mixture for 1 hour, the organic layer was separated and concentrated under reduced pressure. Layerd with acetonitrile (95%) and evaporate slowly to dryness in the air to give crystals of **2** (91% yield). ¹H NMR (600 MHz, CD₂C1₂): δ 13.32 (s, 1H), 5.96 (s, 1H), 1.33 (s, 18H) ppm; ¹³C NMR (150 MHz, CD₂C1₂): 125.5, 98.6, 31.9, 30.9 ppm; IR (Nujol): ν_{O-H} 3445 cm⁻¹, ν_{N-H} 3175, 3138, 3090, 3038 cm⁻¹, ν_{C=N} 1571 cm⁻¹, ν_{SO₄⁻} 1141, 1089 cm⁻¹; Positive ESI-MS: [L+H]⁺ 181.32 (100%), [AgL₂]⁺ 467.52 (62%), [Ag₂L₄(SO₄)+H]⁺ 1033.04 (10%), [Ag₂L₅(SO₄)+H]⁺ 1213.04 (9%), [Ag₃L₆(SO₄)]⁺ 1500.92 (69%). Anal. Calcd for C₅₅H₁₀₂N₁₀Ag₂O₅S: C 53.65, H 8.35, N 11.38 %. Found: C, 53.80; H, 8.34; N, 11.48 %.

4 Synthesis of [Ag₂(L³)₆(SO₄)] (3)

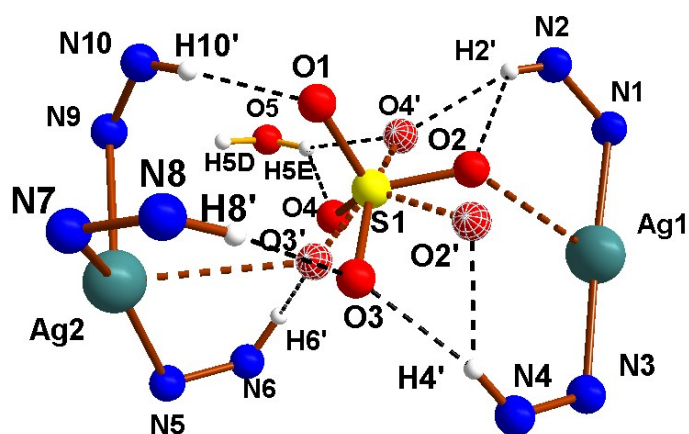
Method 1. Ag₂SO₄ (0.146 g, 0.468 mmol) was dissolved in R.O. water (50 mL). To this solution was added dropwisely a solution of L³ (0.627 g, 2.85 mmol) in acetone (30 mL). After stirring the reaction mixture for another 30 minutes, a white precipitate formed was filtered and washed by R.O. water and ether. Vacuum dry to afford 0.702 g (92%) of a white powder. Method 2. Changing the acetone solvent with dichloromethane to form a two-phase system. After vigorously stirring the reaction mixture for 1 hour, the organic layer was separated and concentrated under reduced pressure. Layerd with ether to give complex **3** (88% yield). ¹H NMR (600 MHz, CD₂Cl₂): δ 13.81 (s, 1H), 7.71-7.02 (m, 10H), 6.77 (s, 1H) ppm; ¹³C NMR (150 MHz, CD₂Cl₂): 149.5, 131.2, 129.4, 128.8, 126.3, 100.9 ppm; IR (Nujol): ν_{N-H} 3190, 3138, 3112, 3097 cm⁻¹, ν_{C=N} 1571 cm⁻¹, ν_{SO₄⁻} 1124, 1110, 1075, 1052 cm⁻¹; Positive ESI-MS: [L+H]⁺ 221.70 (72%), [AgL₂]⁺ 549.86 (100%), [Ag₃L₆(SO₄)]⁺ 1740.38 (10%). Single crystals suitable for X-ray structure determination are grown from CH₂Cl₂/Et₂O. Anal. Calcd for C₉₀H₇₂N₁₂Ag₂O₄S: C 66.18, H 4.44, N 10.29 %. Found: C 66.57, H 4.51, N 10.23 %.

5 Synthesis of [Cu₂(Hpz^{Ph,Ph})₆(SO₄)] (4)

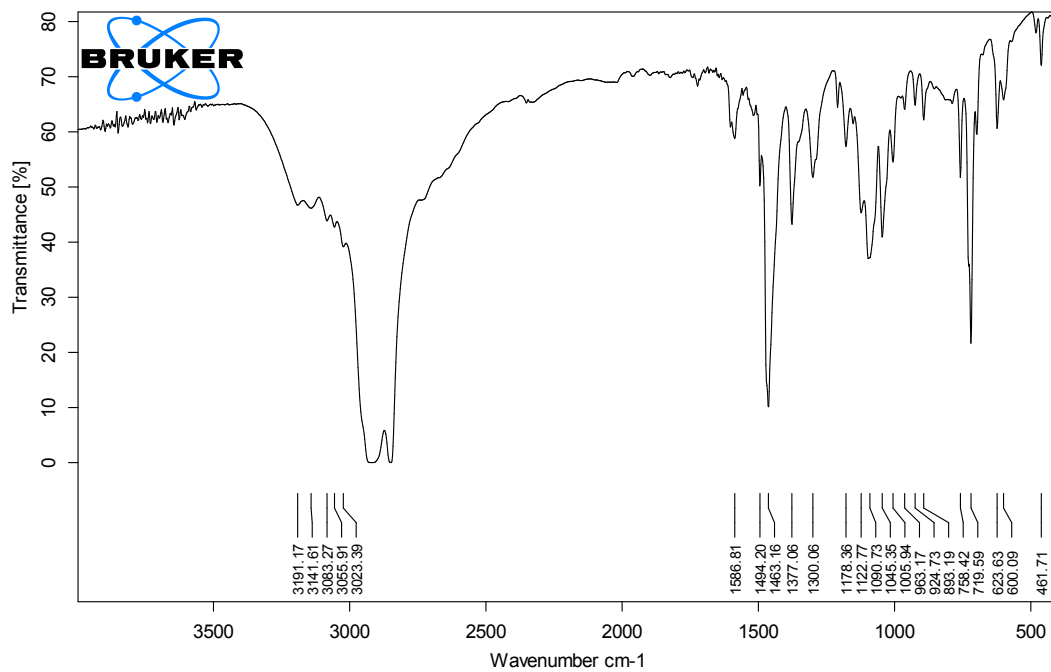
A mixture of complex **3** (0.214g, 0.131 mmol) and CuBr (0.0384g, 0.268 mmol) was stirred in 5 mL CH₂Cl₂ for 30 min under N₂ at room temperature. The reaction was filtered and the filtrate was evaporated under reduced pressure to afford white solid. The solid was washed by diethyl ether and dried *in vacuo*. Single crystals were grown by layering a CH₂Cl₂ solution with diethyl ether (0.178g, 86% yield). The purity is confirmed by X-ray powder diffraction patterns as shown in S12. Anal. Calcd for [Cu₂C₉₀H₇₂N₁₂SO₄]. (CH₂Cl₂)_{0.5}: N, 10.59; C, 68.48; H, 4.64. Found: N, 10.64; C, 68.35; H, 4.32 %. ¹H NMR (600 MHz, CD₂Cl₂): δ 14.56 (s, 1H), 7.74 (d, *J* = 7.4 Hz, 4H), 7.13 (t, *J* = 7.3 Hz, 2H), 7.00 (dd, *J* = 7.4, 7.3 Hz, 4H), 6.79 (s, 1H) ppm; ¹³C NMR (150 MHz, CD₂Cl₂): 148.9, 130.9, 129.1, 128.7, 126.5, 101.0 ppm; IR (Nujol): ν_{N-H} 3139, 3090 cm⁻¹, ν_{C=N} 1572 cm⁻¹, ν_{SO₄⁻} 1125, 1109, 1074, 1052 cm⁻¹; Positive ESI-MS: [L+H]⁺ 221.47 (100%), [CuL₂]⁺ 503.31 (74%).



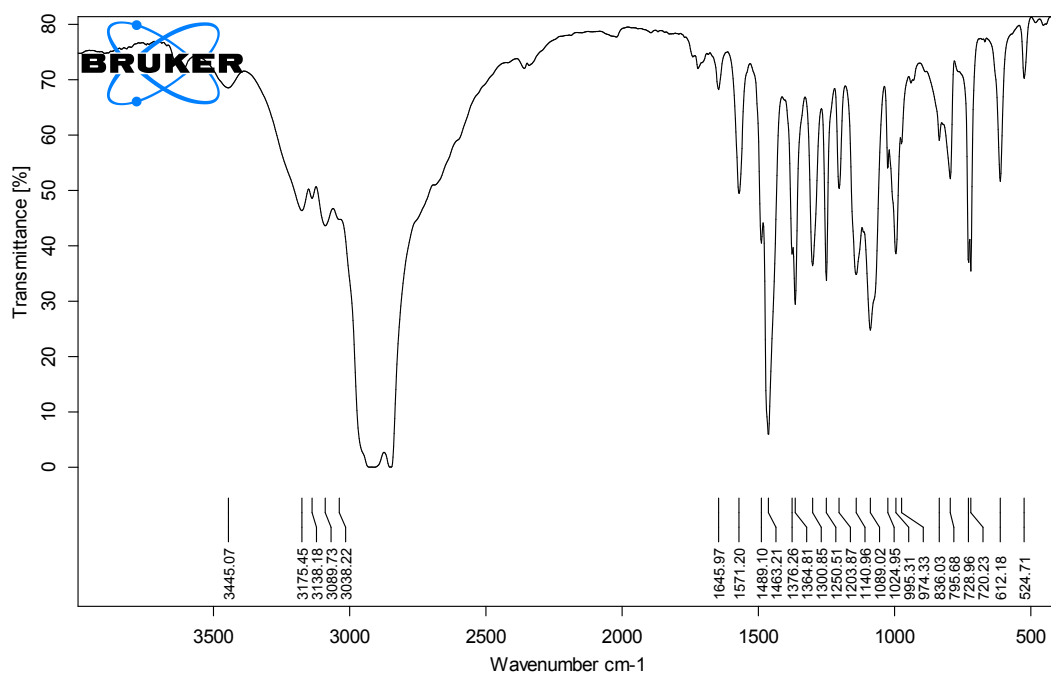
6 Figure S2. The 1-D polymeric array of complex **1**, which is mainly composed of alternative Ag...Ag and π ... π interactions.



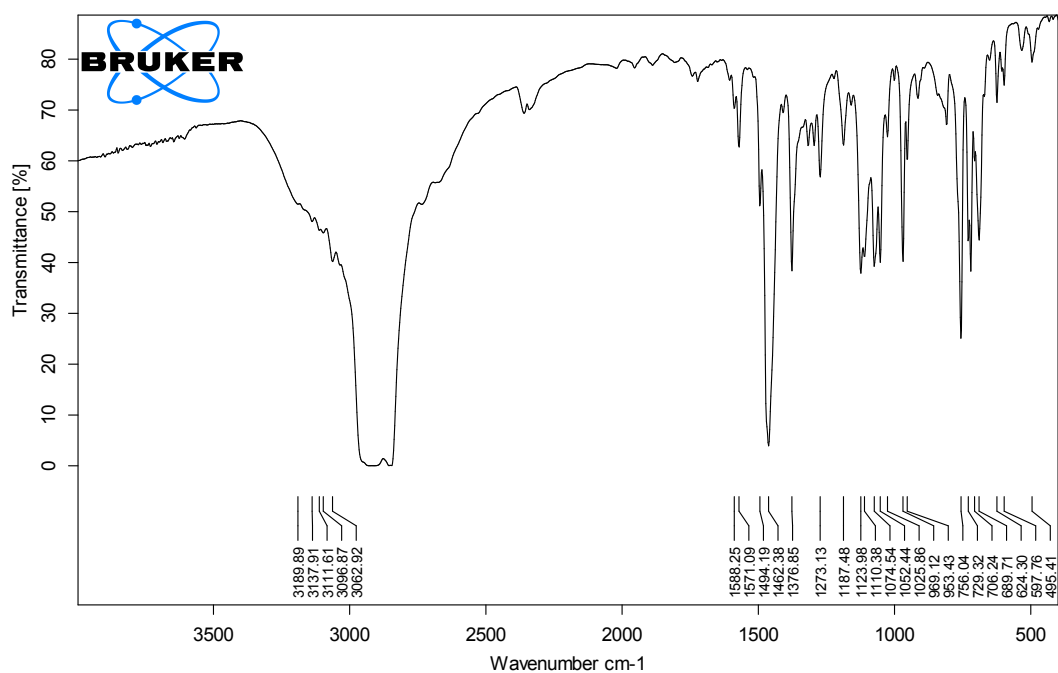
7. Figure S3. The hydrogen bonds and dative bonds around disordered sulfate for complex **2**: H2'...O2 2.04(1), H2'...O4' 1.89(1), H4'...O2' 1.94(1), H4'...O3 1.99 (1), H5E...O4 1.97(1), H5E...O4' 2.24(1), H6'...O3' 2.03(1), H8'...O3 2.09(1), H10'...O1 1.92 (1). Ag1...O2 2.75(2), Ag1...O2 2.56 (1).



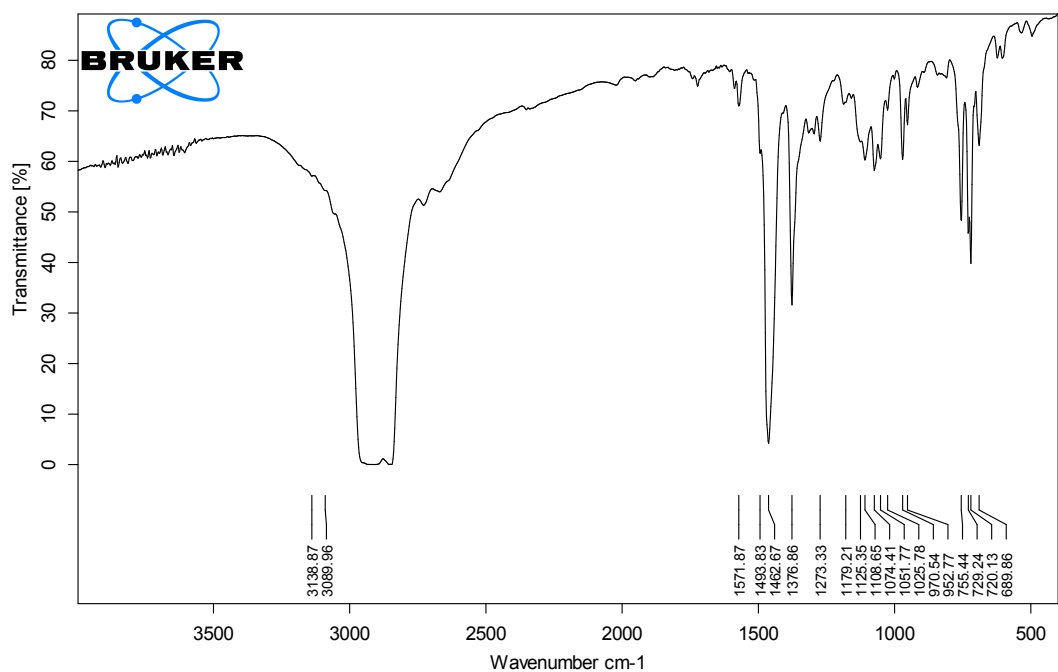
8 Figure S4 IR spectrum of complex 1



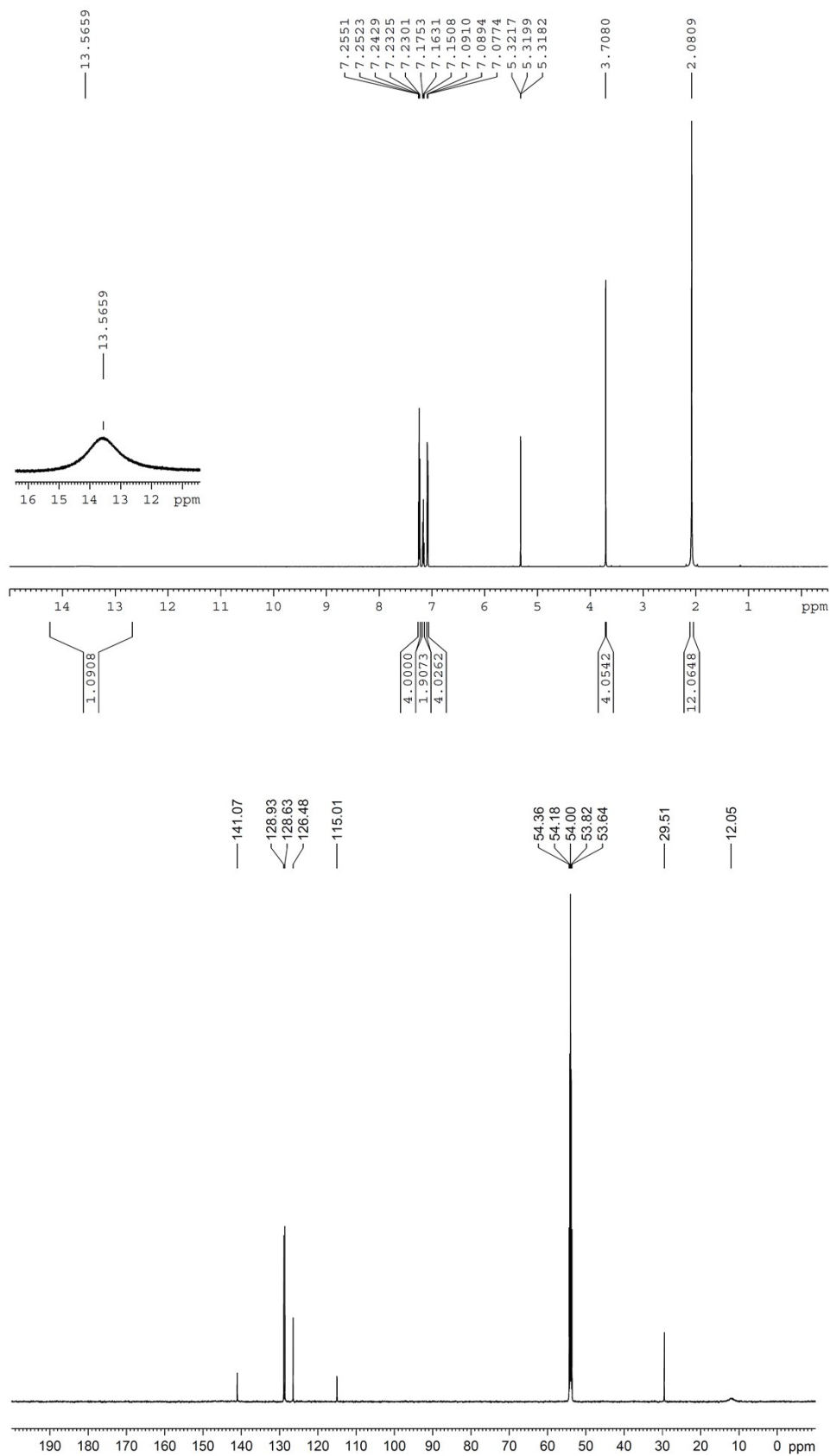
9 Figure S5 IR spectrum of complex 2



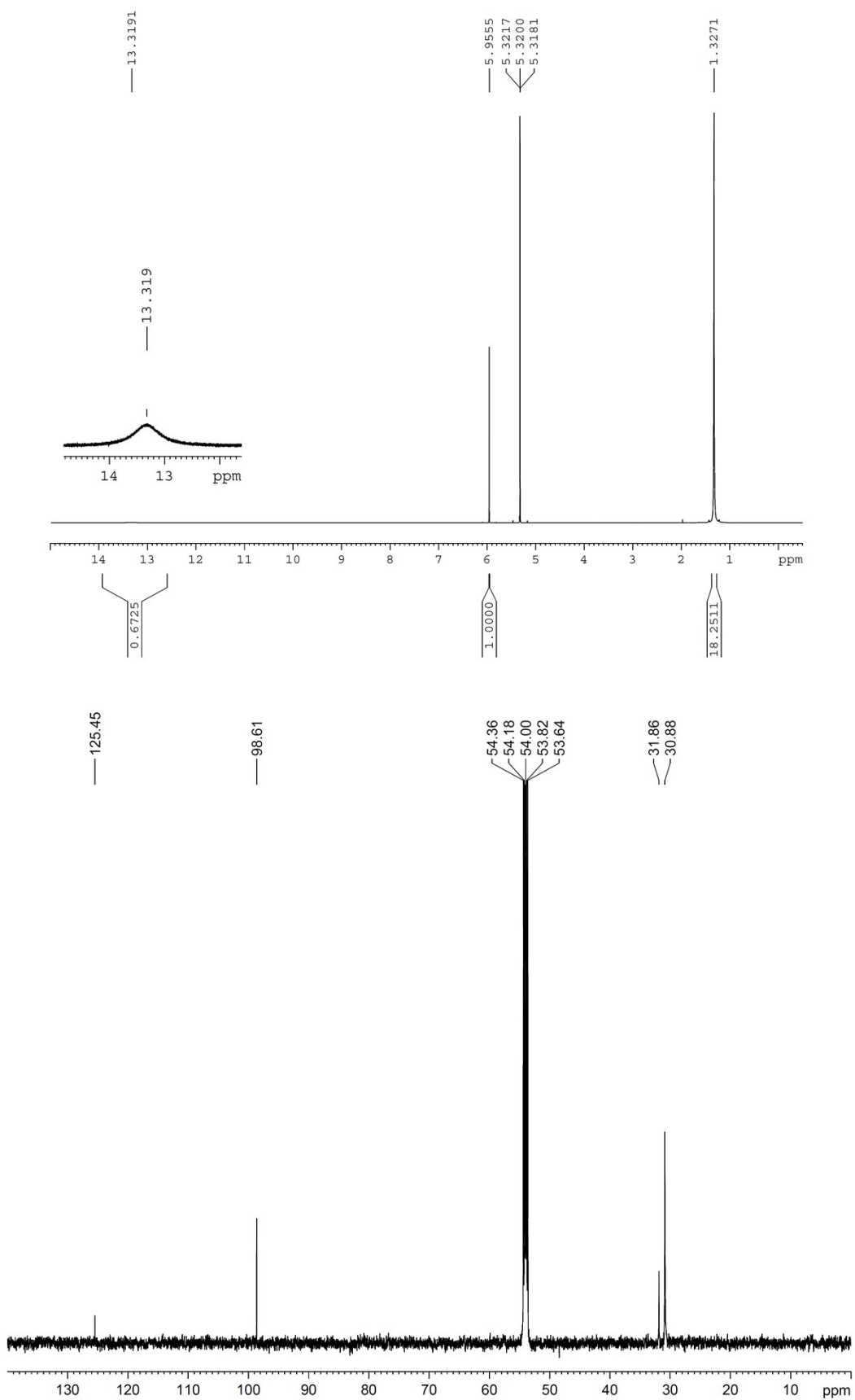
10 Figure S6 IR spectrum of complex 3



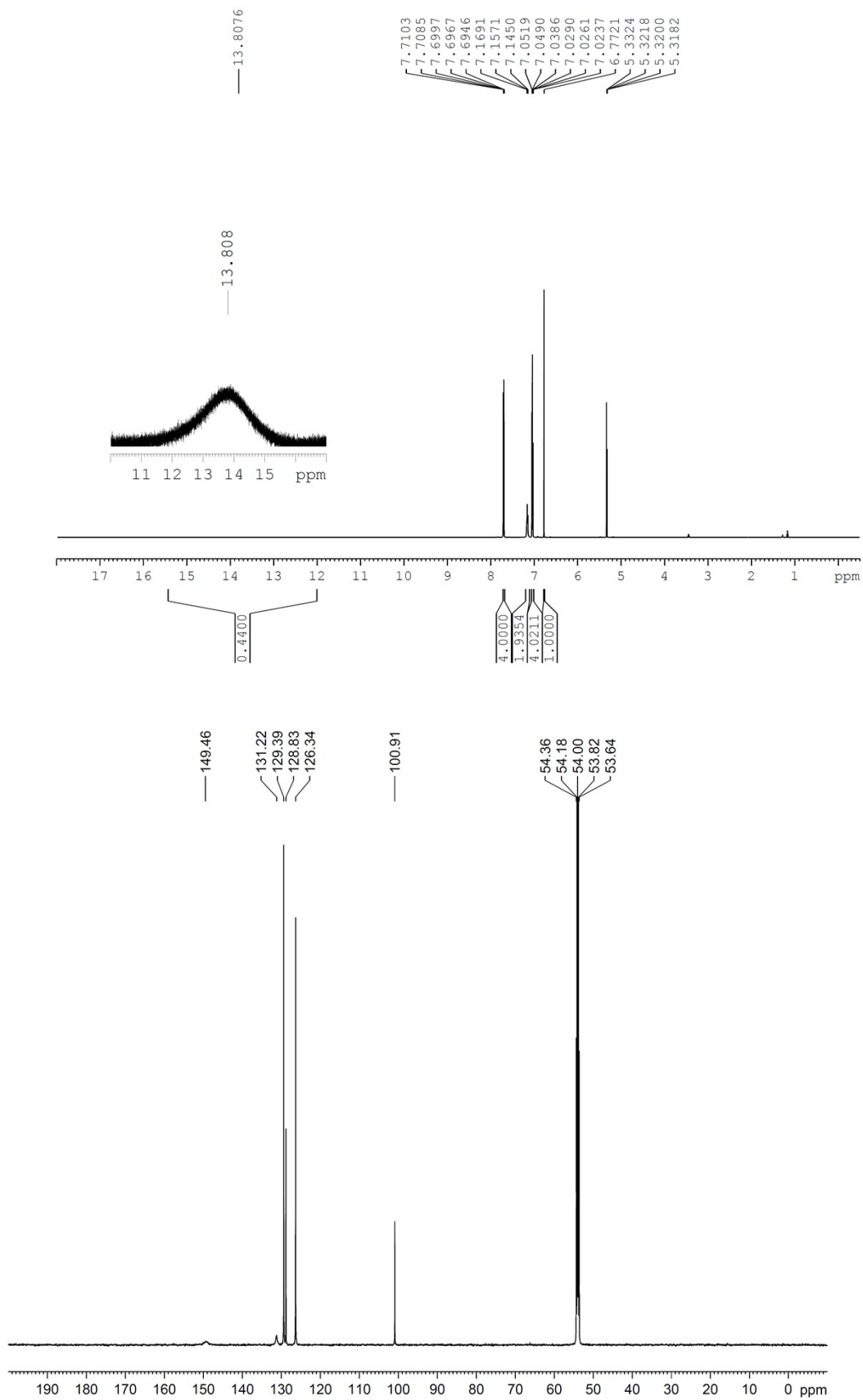
11 Figure S7 IR spectrum of complex 4



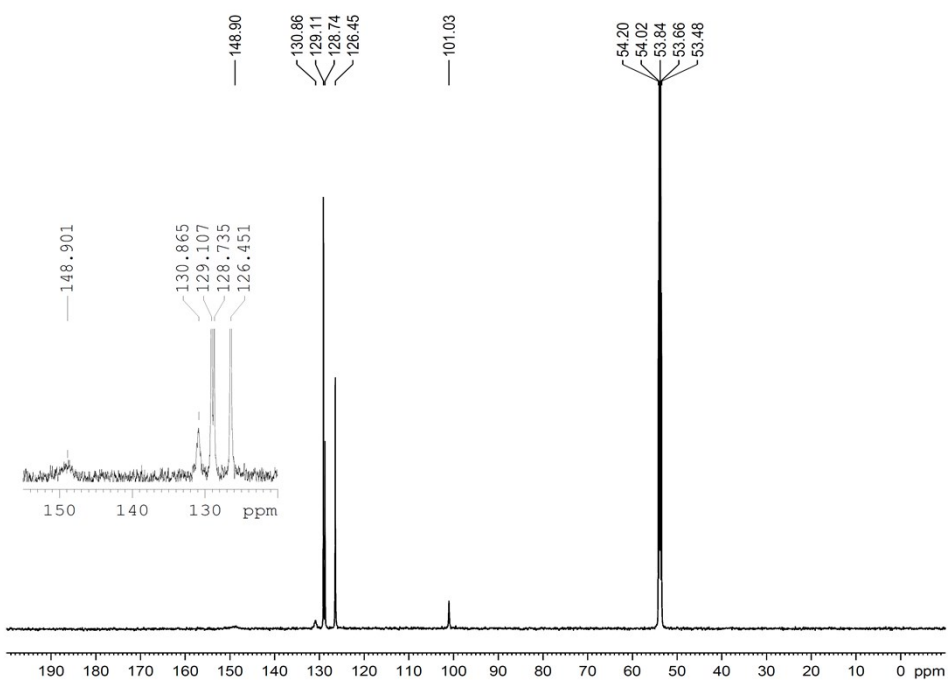
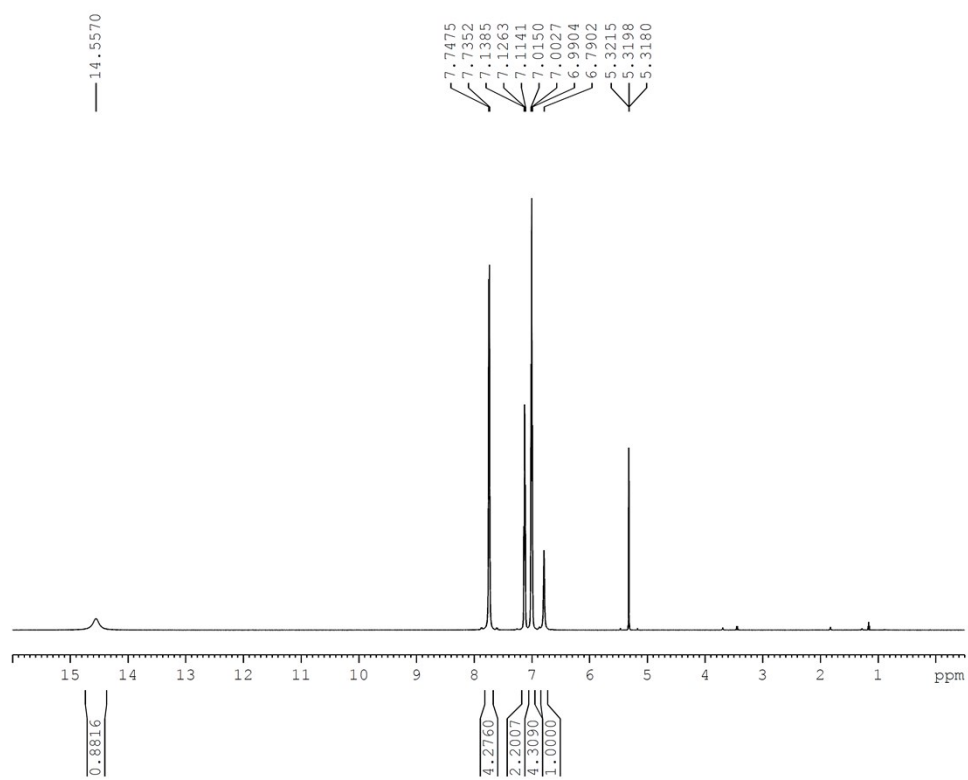
12 Figure S8 ^1H & ^{13}C NMR spectra of complex 1



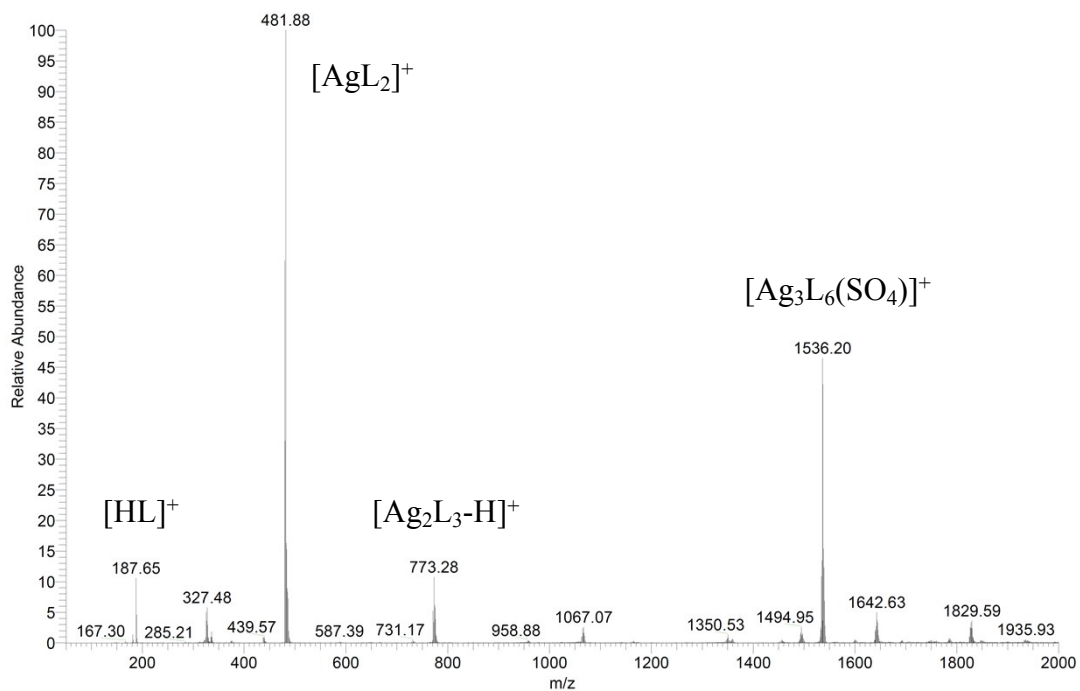
13 Figure S9 ^1H & ^{13}C NMR spectra of complex 2



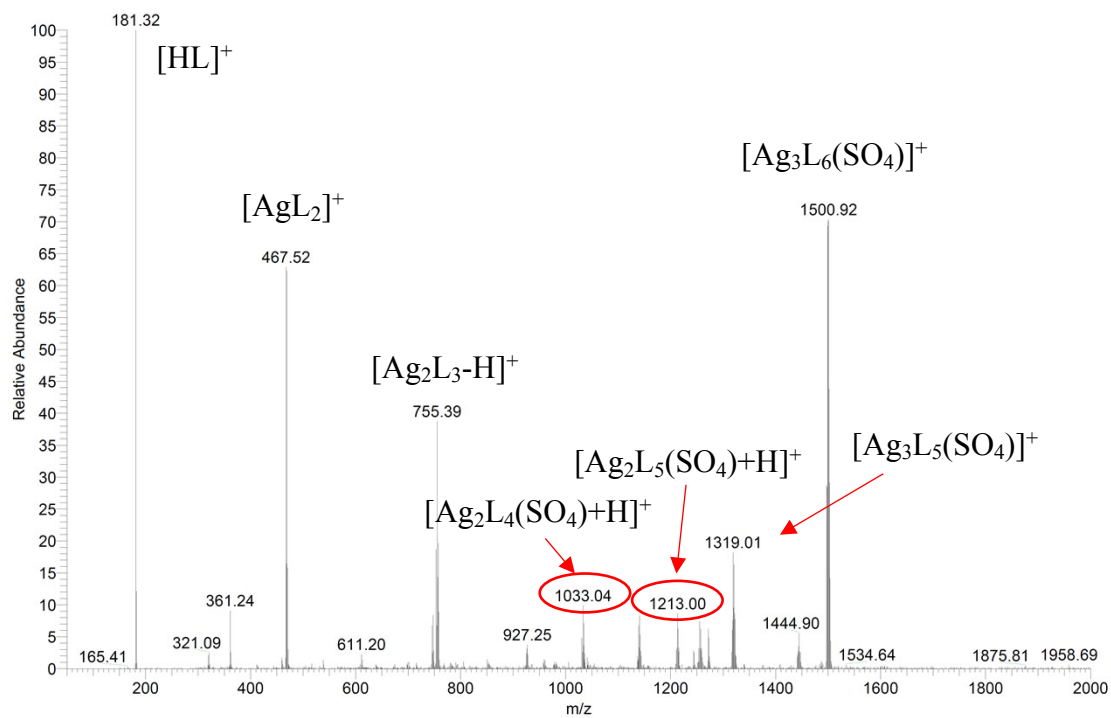
14 Figure S10 ^1H & ^{13}C NMR spectra of complex 3



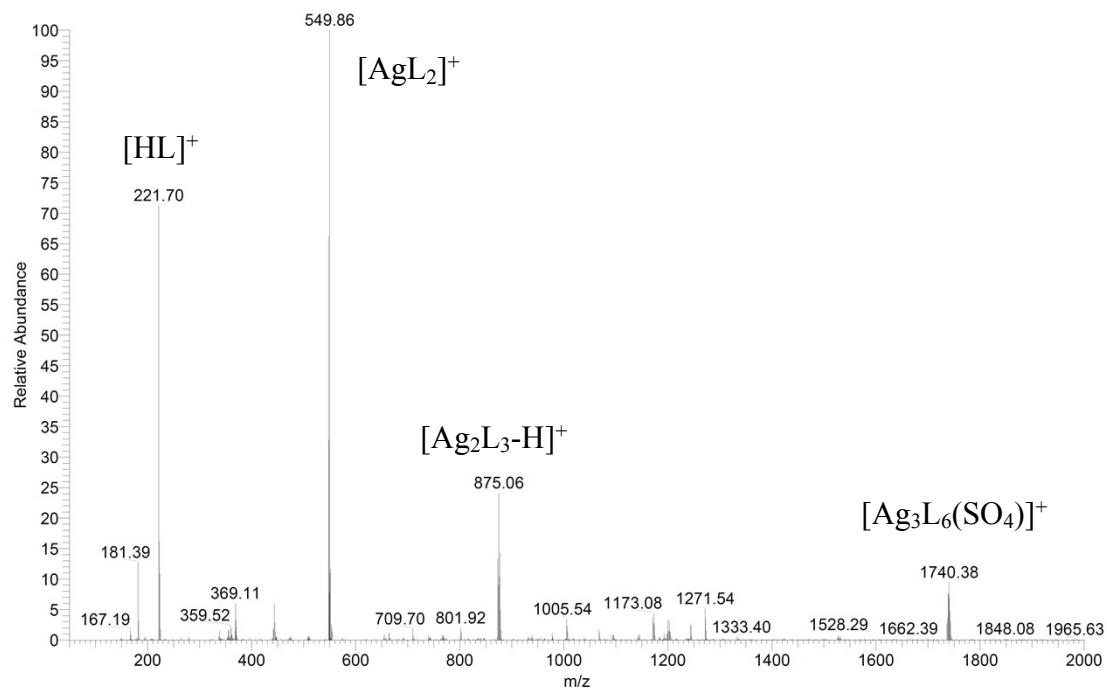
15 Figure S11 ^1H & ^{13}C NMR spectra of complex 4



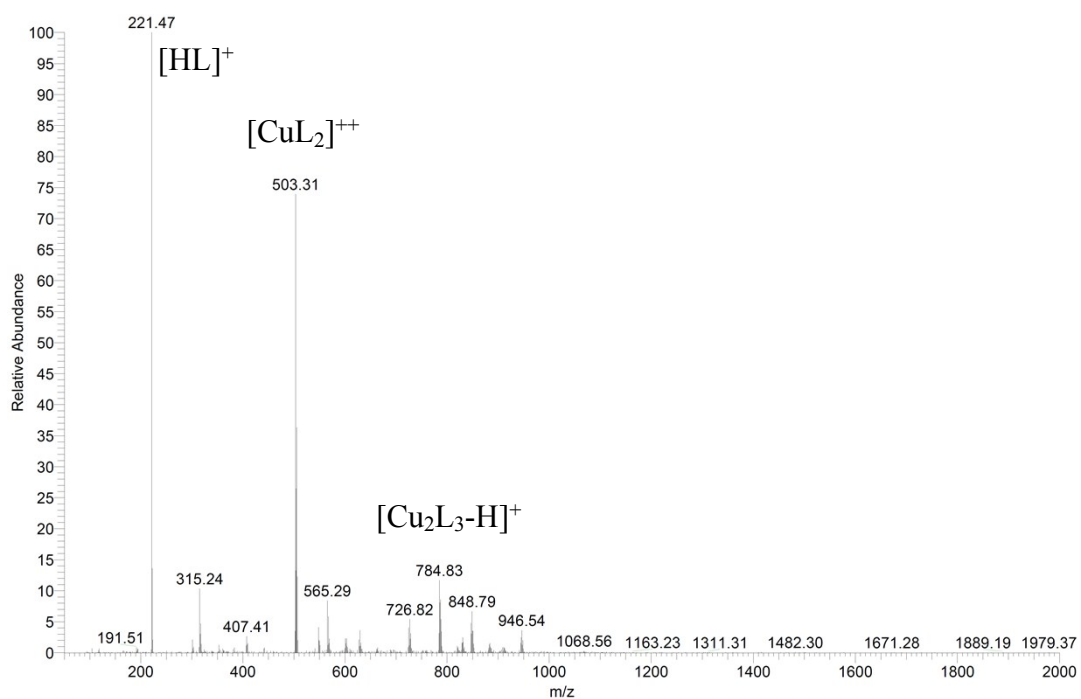
16 Figure S12. ESI-MS of complex 1.



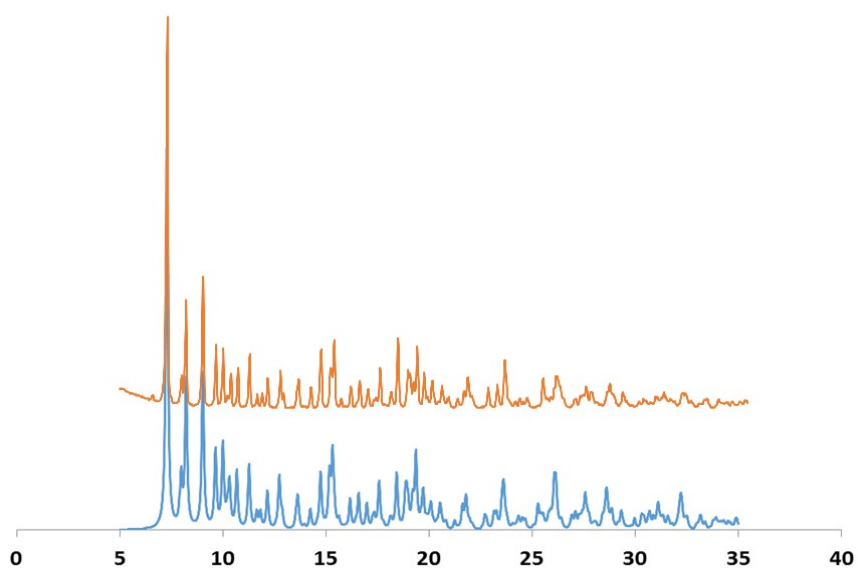
17 Figure S13. ESI-MS of complex 2.



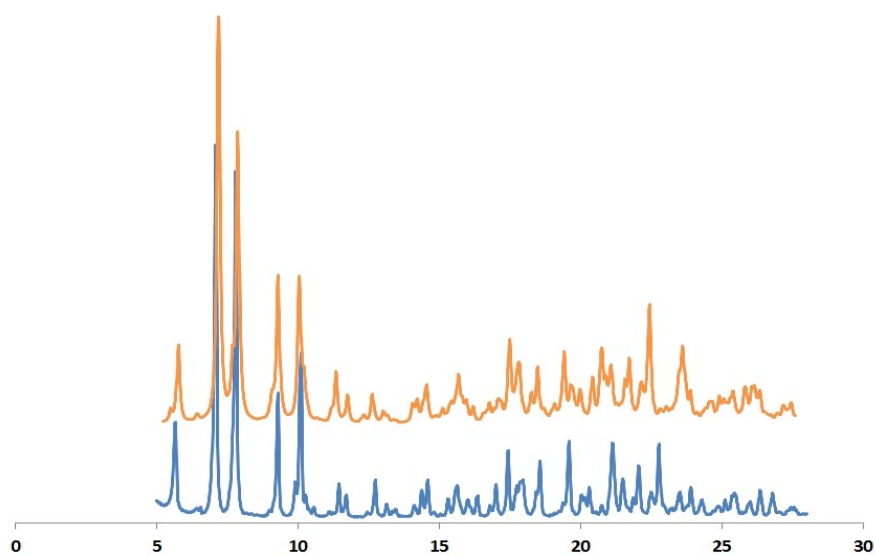
18 Figure S14. ESI-MS of complex 3.



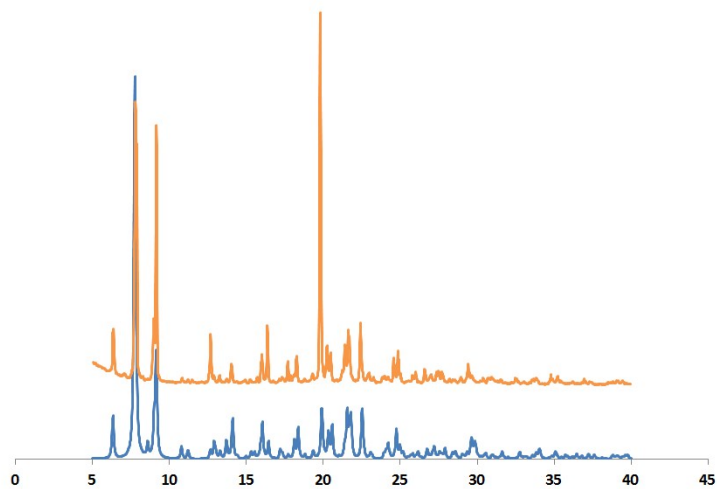
19 Figure S15. ESI-MS of complex 4.



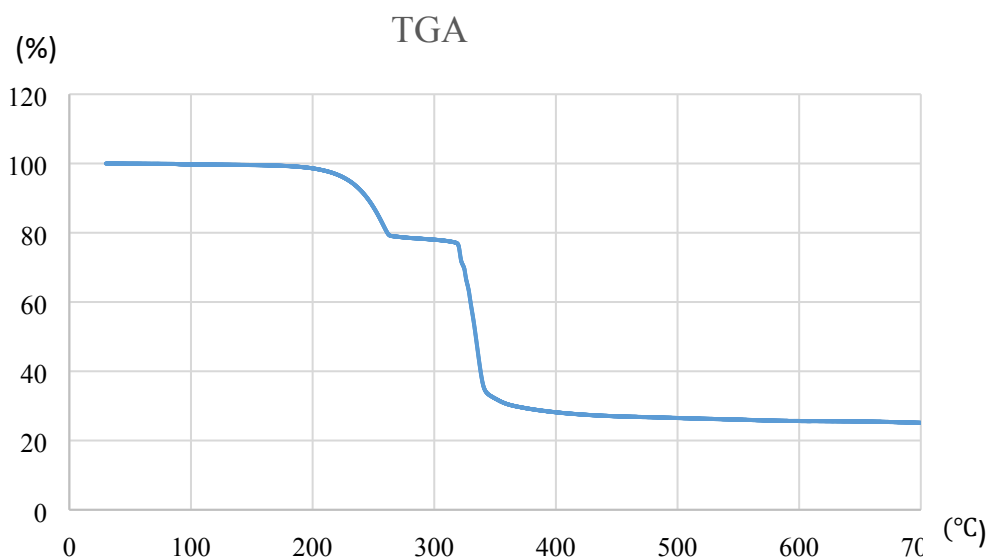
20 Figure S16. PXRD of complex **2**. Experimental (up) and simulated (down) results



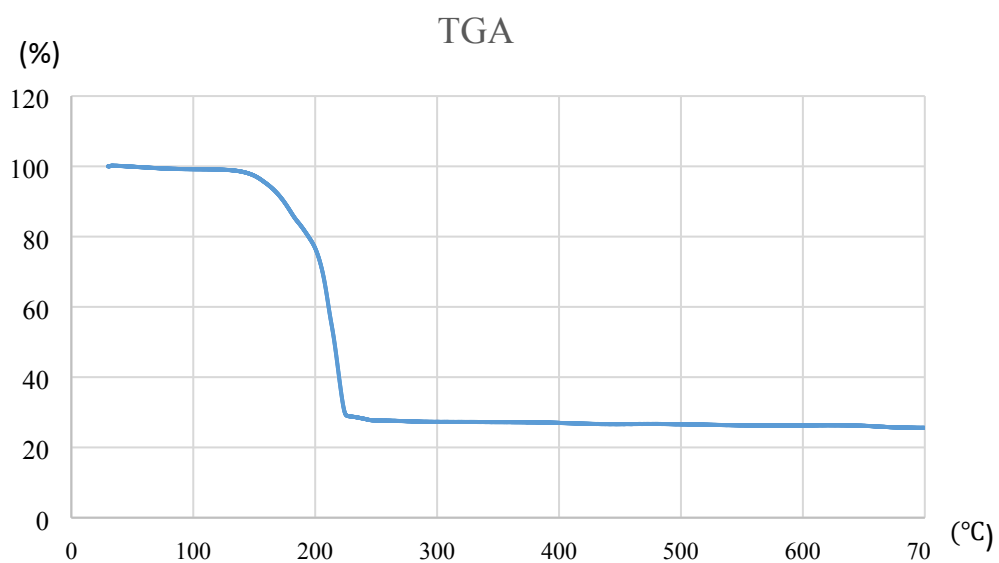
21 Figure S17. PXRD of complex **3**. Experimental (up) and simulated (down) results



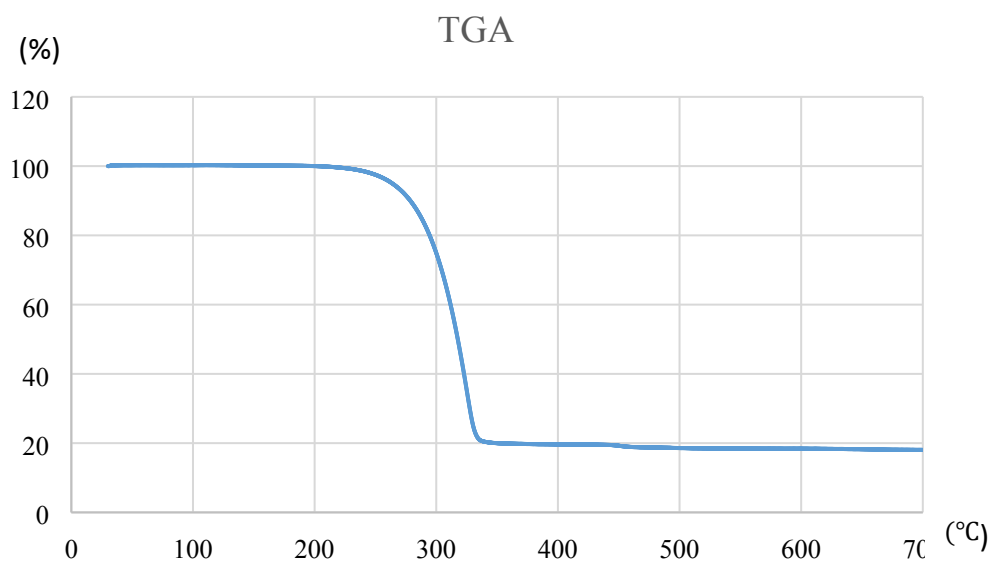
22 Figure S18. PXR D of complex **4**. Experimental (up) and simulated (down) results.



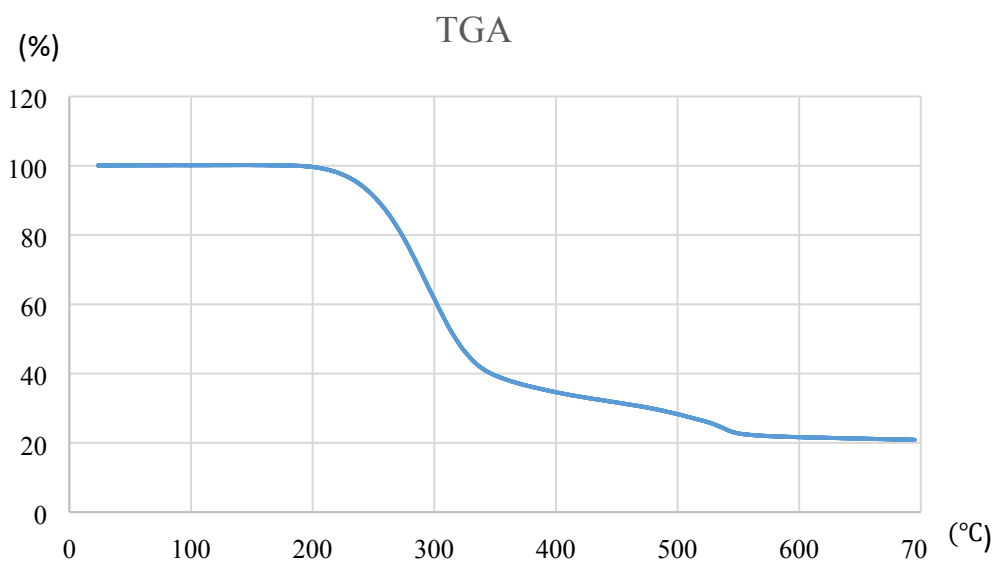
23 Figure S19. TGA of complex **1**.



24 Figure S20. TGA of complex 2.



25 Figure S21. TGA of complex 3.



26 Figure S22. TGA of complex 4.