

**A Trigonal Prismatic Ligand in the Metal-Mediated Self-Assembly of 1D
and 2D Metallosupramolecular Polymers**

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General:

Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. Elemental analysis were performed on an Elementar Vario EL instrument. Infrared spectra were collected on a Fourier Transform IR spectrometer (using KBr pellets). ^1H and ^{13}C NMR spectra were recorded at 500 (500 MHz) or 400 (400 MHz) spectrometers with TMS as the reference. Mass spectra (ESI analysis) were recorded on a microTOF-Q spectrometer (LC/MS). Single crystal X-ray diffraction data were collected on a SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube ($\lambda = 0.71073$ Å). Data reduction included absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically.

Synthesis of bicyclo-oxacalix[2]benzene[3]pyrazine **L**

A mixture of benzene-1,3,5-triol (5.0 g, 39.7 mmol) and 2,6-dichloropyrazine (8.9 g, 59.5 mmol) in DMSO (200 ml) was stirred and heated to 85°C. Cs_2CO_3 (19.4 g, 59.5 mmol) was added in portions within 3.5 h. After the addition, the mixture was kept at this temperature for 30 min. The resultant solution was poured into 600 mL ice water, extracted by EtOAc (4 x 50 mL) and washed with brine. The organic extracts were dried with anhydrous Na_2SO_4 . After removal of the solvent, the residue was purified by column chromatography (petroleum ether/ EtOAc, 4/1) to afford **L** as white powder (1.4g, 14.9%). ^1H NMR ($\text{DMSO}-d_6$, 500 MHz, ppm): δ 8.26 (s, 6H, Py-H), 6.82 (s, 6H, Ar-H). ^{13}C NMR ($\text{DMSO}-d_6$, 125 MHz, ppm): δ 158.1, 153.7, 126.0, 115.9. HRMS (ESI): m/z calcd $[\text{M} + \text{H}]^+$ for $\text{C}_{24}\text{H}_{13}\text{N}_6\text{O}_6^+$: 481.0891; Found 481.0896.

Crystallographic data for $\text{L}\cdot\text{CH}_3\text{OH}$: $[\text{C}_{25}\text{H}_{12}\text{N}_6\text{O}_7]$; $M_r = 508.41$; $T = 296(2)$ K; triclinic; space group $P\bar{1}$; $a = 12.3325(6)$; $b = 13.9068(7)$; $c = 14.5927(8)$ Å; $\alpha =$

110.871(2); $\beta = 90.663(2)$; $\gamma = 95.055(2)$; $V = 2326.9(2) \text{ \AA}^3$; $Z = 4$; $\rho_{\text{calcd}} = 1.451 \text{ g/cm}^3$; crystal size = 0.44 x 0.27 x 0.15 mm; $\mu = 0.110 \text{ mm}^{-1}$; reflections collected 27239; unique reflections 8146; data/restraints/parameters 8146 /6/685; *GOF* on F^2 1.046; R_{int} for independent data 0.0233; final $R_I = 0.0593$, $wR_2 = 0.1799$; R indices (all data) $R_I = 0.0593$, $wR_2 = 0.1799$; largest diff. peak and hole: 1.227 and -0.376 e\AA^{-3} .

Synthesis of silver-containing supramolecular complex 1

To a 5 mL vial **L** (2.2 mg, 0.0046 mmol) dissolved in benzene (1 ml) was added first, a blank solution of 3 ml benzene and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, AgBF_4 (6.0 mg, 0.031 mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of silver-containing complex **1** were obtained by slow evaporation of the above solution in air and under DMF atmosphere at room temperature.

Crystals of complex $\{[\text{Ag}_3(\text{L})_4(\text{BF}_4)_3](\text{L})(\text{Ph})_2\}_n$ **1** obtained in open air (2.0 mg, 56.7 %), IR (KBr): 3441.1, 3090.8, 1585.2, 1543.99, 1446.4, 1416.2, 1256.0, 1187.2, 1154.5, 1113.7, 1083.2, 1060.5, 1007.3, 991.5, 868.5, 686.2, 664.5, 635.5, 567.3, 484.1. Anal. Calcd for $\text{C}_{132}\text{H}_{72}\text{N}_{30}\text{O}_{30}\text{Ag}_3\text{B}_3\text{F}_{12}$: C, 54.13; H, 2.46; N, 14.35. Found: C, 52.02; H, 2.62; N, 13.01.

Crystallographic data for complex 1 obtained in open air:

$[\text{C}_{163}\text{H}_{48}\text{Ag}_3\text{B}_2\text{F}_8\text{N}_{24}\text{O}_{32}]$; $M_r = 3351.48$; $T = 173(2) \text{ K}$; Orthorhombic; space group $Pba2$; $a = 24.0892(10)$; $b = 40.0165(16)$; $c = 7.9746(3) \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$; $V = 7687.2(5) \text{ \AA}^3$; $Z = 2$; $\rho_{\text{calcd}} = 1.448 \text{ g/cm}^3$; crystal size = 0.36 x 0.32 x 0.28 mm; $\mu = 0.471 \text{ mm}^{-1}$; reflections collected 88233; unique reflections 12713; data/restraints/parameters 12713/44/839; *GOF* on F^2 1.144; R_{int} for independent data 0.0397; final $R_I = 0.0822$, $wR_2 = 0.2319$; R indices (all data) $R_I = 0.0863$, $wR_2 = 0.2364$; largest diff. peak and hole: 1.708 and -0.949 e\AA^{-3} .

Crystals of complex $\{[\text{Ag}_3(\text{L})_4(\text{BF}_4)_3](\text{DMF})(\text{Ph})_2\}_n$ **1** obtained under DMF

atmosphere (1.0 mg, 32.5 %), IR (KBr): 3441.1, 3090.8, 1585.2, 1543.99, 1446.4, 1416.2, 1256.0, 1187.2, 1154.5, 1113.7, 1083.2, 1060.5, 1007.3, 991.5, 868.5, 686.2, 664.5, 635.5, 567.3, 484.1. Anal. Calcd for $C_{111}H_{67}N_{25}O_{25}Ag_3B_3F_{12}$: C, 48.70; H, 2.28; N, 12.80. Found: C, 47.76; H, 2.01; N, 12.35.

Crystallographic data for complex 1 obtained under DMF atmosphere:

$[C_{120}H_{80}Ag_3B_3F_{12}N_{26}O_{26}]$; $Mr = 2886.14$; $T = 296(2)$ K; Orthorhombic; space group $Pba2$; $a = 24.111(2)$; $b = 39.900(4)$; $c = 7.9191(8)$ Å; $\alpha = \beta = \gamma = 90^\circ$; $V = 7618.4(13)$ Å³; $Z = 2$; $\rho_{\text{calcd}} = 1.258$ g/cm³; crystal size = 0.15 x 0.12 x 0.06 mm; $\mu = 0.465$ mm⁻¹; reflections collected 35095; unique reflections 13378; data/restraints/parameters 13378/76/858; GOF on F^2 1.221; R_{int} for independent data 0.0300; final $R_I = 0.1130$, $wR_2 = 0.2958$; R indices (all data) $R_I = 0.1135$, $wR_2 = 0.2961$; largest diff. peak and hole: 1.575 and -2.596 eÅ⁻³.

Synthesis of silver-containing supramolecular complex $\{[Ag_4(L)_4(NO_3)_4](Ph)_2\}_n$ 2

To a 5 mL vial **L** (2.1 mg, 0.0044 mmol) dissolved in benzene (1 ml) was added first, a blank solution of 3 ml benzene and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, $AgNO_3$ (4.0 mg, 0.024mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of silver-containing complex **2** were obtained by slow evaporation of the above solution in air at room temperature (1.8 mg, 60.6 %). IR (KBr): 3448.8, 3086.9, 2361.9, 1666.2, 1543.4, 1445.8, 1416.0, 1385.7, 1305.7, 1252.7, 1189.1, 1153.4, 1114.8, 1050.1, 992.1, 872.8, 857.2, 737.0, 695.0, 663.4, 635.9, 557.1, 488.3. Anal. Calcd for $C_{108}H_{60}N_{28}O_{36}Ag_4$: C, 47.00; H, 2.18; N, 14.22. Found: C, 46.11; H, 2.10; N, 13.70.

Crystallographic data for complex 2: $[C_{57}H_{33}Ag_2N_{14}O_{18}]$; $Mr = 1417.71$; $T = 173(2)$

K; Monoclinic; space group $P2(1)/c$; $a = 29.2291(11)$; $b = 20.7698(8)$; $c = 9.1567(4)$ Å; $\alpha = \gamma = 90^\circ$; $\beta = 98.3360(10)$; $V = 5500.1(4)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.712$ g/cm³; crystal size = 0.56 x 0.53 x 0.11 mm; $\mu = 0.804$ mm⁻¹; reflections collected 62819; unique reflections 9675; data/restraints/parameters 9675/0/808; GOF on F^2 1.050; R_{int} for

independent data 0.0222; final $R_I = 0.0279$, $wR_2 = 0.0680$; R indices (all data) $R_I = 0.0314$, $wR_2 = 0.0708$; largest diff. peak and hole: 0.989 and -0.893 eÅ⁻³.

Synthesis of silver-containing supramolecular complex [(AgL·NO₃)·DMF]_n **3**

To a 5 mL vial **L** (2.0 mg, 0.0042 mmol) dissolved in THF (1 ml) was added first, a blank solution of 3 ml THF and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, AgNO₃ (7.5 mg, 0.044 mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of silver-containing complex **3** were obtained by slow evaporation of the above solution under DMF atmosphere at room temperature (1.9 mg, 62.5 %). IR (KBr): 3435.1, 3084.4, 1590.3, 1546.7, 1472.7, 1447.5, 1414.0, 1384.3, 1308.1, 1254.2, 1186.7, 1154.3, 1113.6, 1007.8, 991.5, 874.0, 847.2, 663.5, 494.0. Anal. Calcd for C₂₇H₁₉N₈O₁₀Ag: C, 44.79; H, 2.63; N, 15.48. Found: C, 44.28; H, 2.66; N, 15.27.

Crystallographic data for complex 3: [C₂₇H₁₉AgN₈O₁₀]; Mr = 723.37; T = 173(2) K; Monoclinic; space group *P2(1)/c*; a = 13.646(2); b = 10.0009(17); c = 20.571(3) Å; α = γ = 90°; β = 104.816(2); V = 2714.1(8) Å³; Z = 4; ρ_{calcd} = 1.770 g/cm³; crystal size = 0.25 x 0.15 x 0.06 mm; μ = 0.820 mm⁻¹; reflections collected 15808; unique reflections 5043; data/restraints/parameters 5043/6/415; GOF on F² 1.157; R_{int} for independent data 0.0279; final $R_I = 0.0732$, $wR_2 = 0.1965$; R indices (all data) $R_I = 0.0762$, $wR_2 = 0.1986$; largest diff. peak and hole: 1.556 and -1.251 eÅ⁻³.

Synthesis of copper-containing complex {[Cu₂(L)₂(NO₃)₄·ACN](Ph)₄]_n **4** and {[CuL(NO₃)₂](Ph)₂]_n **5**

To a 5 mL vial **L** (2.5 mg, 0.0052 mmol) dissolved in benzene (1 ml) was added first, a blank solution of 3 ml benzene and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, Cu(NO₃)₂ (7.5 mg, 0.0400 mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. Single crystals of copper-containing supramolecular complex **4** (green, major) and **5** (yellow, minor) were obtained by slow evaporation of the above solution in air at room temperature

(2.0 mg in total). IR (KBr) for complex **4** and **5**: 3443.5, 3435.2, 3101.0, 2361.6, 1596.2, 1593.2, 1546.9, 1545.4, 1506.9, 1503.0, 1473.4, 1457.7, 1448.0, 1447.8, 1436.7, 1416.9, 1384.0, 1329.4, 1304.7, 1252.7, 1196.1, 1193.5, 1150.3, 1113.9, 1059.5, 992.5, 873.0, 619.1, 664.3, 570.2, 482.1. We were unable to separate complexes **4** (green) and **5** (yellow), thus, elemental analysis was not carried out.

Crystallographic data for complex 4: [C₇₄H₄₈Cu₂N₁₇O₂₄]; Mr = 1686.4; T = 173(2) K; Monoclinic; space group *P2(1)/c*; a = 14.2224(7); b = 19.3544(9); c = 27.9524(11) Å; $\alpha = \gamma = 90^\circ$; $\beta = 110.187(2)$; $V = 7221.7(6)$ Å³; Z = 4; $\rho_{\text{calcd}} = 1.551$ g/cm³; crystal size = 0.26 x 0.19 x 0.14 mm; $\mu = 0.684$ mm⁻¹; reflections collected 83048; unique reflections 12713; data/restraints/parameters 12713 /0/1054; *GOF* on F^2 1.026; R_{int} for independent data 0.0370; final $R_I = 0.0487$, $wR_2 = 0.1187$; R indices (all data) $R_I = 0.0651$, $wR_2 = 0.1331$; largest diff. peak and hole: 1.052 and -0.803 eÅ⁻³.

Crystallographic data for complex 5: [C₃₀H₁₈CuN₈O₁₂]; Mr = 746.06; T = 173(2) K; Triclinic; space group *P1̄*; a = 8.9664(3); b = 12.5605(5); c = 13.3868(5) Å; $\alpha = 99.7180(10)$; $\beta = 95.0440(10)$; $\gamma = 101.3990(10)$; $V = 1445.19(9)$ Å³; Z = 2; $\rho_{\text{calcd}} = 1.714$ g/cm³; crystal size = 0.48 x 0.43 x 0.28 mm; $\mu = 0.842$ mm⁻¹; reflections collected 16823; unique reflections 5066; data/restraints/parameters 5066/0/460; *GOF* on F^2 1.029; R_{int} for independent data 0.0251; final $R_I = 0.0314$, $wR_2 = 0.0786$; R indices (all data) $R_I = 0.0392$, $wR_2 = 0.0834$; largest diff. peak and hole: 0.504 and -0.537 eÅ⁻³.

Synthesis of copper-containing supramolecular complex {[CuL(NO₃)₂](THF)₂]_n

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To a 5 mL vial **L** (2.7 mg, 0.0056 mmol) dissolved in THF (1 ml) was added first, a blank solution of 3 ml THF and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, Cu(NO₃)₂ (39 mg, 0.2079 mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of

complex **6** were obtained by slow evaporation of the above solution in air at room temperature (2.4 mg, 52.2 %). IR (KBr): 3091.6, 2426.4, 1595.9, 1546.7, 1507.0, 1473.0, 1447.8, 1415.0, 1383.7, 1314.0, 1253.6, 1195.3, 1150.2, 1114.3, 1058.1, 1004.3, 992.4, 873.2, 727.9, 663.6, 637.0, 572.8, 533.6, 481.4. Anal. Calcd for $C_{32}H_{28}N_8O_{14}Cu$: C, 47.28; H, 3.45; N, 13.79. Found: C, 45.45; H, 3.34; N, 13.56.

Crystallographic data for complex 6: $[C_{35}H_{12}CuN_8O_{15}]$; $Mr = 848.07$; $T = 173(2)$ K; Orthorhombic; space group $Pnma$; $a = 22.2075(6)$; $b = 12.3261(3)$; $c = 12.2305(3)$ Å; $\alpha = \beta = \gamma = 90^\circ$; $V = 3347.88(15)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.683$ g/cm³; crystal size = 0.51 x 0.35 x 0.22 mm; $\mu = 0.745$ mm⁻¹; reflections collected 37419; unique reflections 3083; data/restraints/parameters 3083/0/281; GOF on F^2 1.056; R_{int} for independent data 0.0305; final $R_I = 0.0421$, $wR_2 = 0.1199$; R indices (all data) $R_I = 0.0475$, $wR_2 = 0.1269$; largest diff. peak and hole: 0.722 and -0.714 eÅ⁻³.

Synthesis of copper-containing supramolecular complex $\{[(CuL\cdot Cl_2)](THF)_2\}_n$ **7**

To a 5 mL vial **L** (2.7 mg, 0.0057 mmol) dissolved in THF (1 ml) was added first, a blank solution of 3 ml THF and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, $CuCl_2\cdot 2H_2O$ (33.5 mg, 0.1965 mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of complex **7** were obtained by slow evaporation of the above solution in air at room temperature (2.0 mg, 46.2 %). IR (KBr): 3434.5, 3096.4, 1593.9, 1546.8, 1507.1, 1473.1, 1457.3, 1446.3, 1414.6, 1385.4, 1362.8, 1327.2, 1306.4, 1253.5, 1193.2, 1151.3, 1113.7, 1057.3, 1004.9, 992.2, 873.1, 850.8, 663.6, 528.5, 480.3. Anal. Calcd for $C_{32}H_{28}N_6O_8CuCl_2$: C, 50.59; H, 3.69; N, 11.07. Found: C, 49.64; H, 3.48; N, 10.83.

Crystallographic data for complex 7: $[C_{32}H_{28}Cl_2CuN_6O_8]$; $Mr = 759.04$; $T = 173(2)$ K; Monoclinic; space group $c2/c$; $a = 14.4555(3)$; $b = 18.4604(4)$; $c = 13.0973(5)$ Å; $\alpha = \gamma = 90^\circ$; $\beta = 112.3280(10)$; $V = 3233.02(16)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.559$ g/cm³; crystal size = 0.37 x 0.28 x 0.17 mm; $\mu = 0.903$ mm⁻¹; reflections collected 18567; unique

reflections 2841; data/restraints/parameters 2841/0/223; GOF on F^2 1.060; R_{int} for independent data 0.0263; final $R_I = 0.0421$, $wR_2 = 0.1116$; R indices (all data) $R_I = 0.0475$, $wR_2 = 0.1169$; largest diff. peak and hole: 0.861 and -0.767 eÅ⁻³.

Synthesis of zinc-containing supramolecular complex {[ZnL'(NO₃)₂](Ph)₂]_n **8**

To a 5 mL vial **L** (2.0 mg, 0.0042 mmol) dissolved in benzene (1 ml) was added first, a blank solution of 3 ml benzene and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, Zn(NO₃)₂·6H₂O (15 mg, 0.0504 mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of complex **8** were obtained by slow evaporation of the above solution in air at room temperature (2.4 mg, 66.6 %). IR (KBr): 3451.2, 3087.7, 1586.7, 1545.7, 1503.56, 1447.7, 1418.3, 1384.1, 1331.9, 1304.2, 1254.6, 1197.4, 1153.7, 1114.8, 1049.2, 1007.2, 992.5, 875.5, 855.3, 735.7, 685.6, 664.9, 636.5, 569.3, 516.7, 483.9. Anal. Calcd for C₃₆H₂₄N₈O₁₂Zn: C, 52.30; H, 2.91; N, 13.56. Found: C, 50.61; H, 2.72; N, 13.14.

Crystallographic data for complex 8: [C₃₀H₁₈N₈O₁₂Zn]; $M_r = 747.89$; $T = 173(2)$ K; Triclinic; space group $P\bar{1}$; $a = 8.8580(2)$; $b = 12.6024(3)$; $c = 13.4956(4)$ Å; $\alpha = 100.8000(10)$; $\beta = 93.5000(10)$; $\gamma = 100.6030(10)$; $V = 1447.45(6)$ Å³; $Z = 2$; $\rho_{calcd} = 1.716$ g/cm³; crystal size = 0.59 x 0.24 x 0.19 mm; $\mu = 0.934$ mm⁻¹; reflections collected 16851; unique reflections 5056; data/restraints/parameters 5056/0/460; GOF on F^2 1.054; R_{int} for independent data 0.0162; final $R_I = 0.0241$, $wR_2 = 0.0643$; R indices (all data) $R_I = 0.0255$, $wR_2 = 0.0653$; largest diff. peak and hole: 0.333 and -0.265 eÅ⁻³.

Synthesis of zinc-containing supramolecular complex {[ZnL'(NO₃)₂](THF)₂]_n **9**

To a 5 mL vial **L** (2.5 mg, 0.0052 mmol) dissolved in THF (1 ml) was added first, a blank solution of 3 ml THF and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, Zn(NO₃)₂·6H₂O (10 mg, 0.0336 mmol) dissolved in

acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of complex **9** were obtained by slow evaporation of the above solution in air at room temperature (3.0 mg, 70.9 %). IR (KBr): 3485.5, 3095.4, 2973.2, 1658.2, 1640.9, 1596.5, 1546.8, 1499.8, 1473.3, 1447.2, 1421.7, 1300.2, 1253.3, 1220.1, 1187.7, 1152.3, 1113.5, 1061.5, 988.2, 867.8, 811.7, 735.3, 689.6, 663.9, 635.1, 570.4, 522.9, 511.2, 483.9. Anal. Calcd for C₃₂H₂₈N₈O₁₄Zn: C, 47.18; H, 3.44; N, 13.76. Found: C, 45.49; H, 3.24; N, 13.15.

Crystallographic data for complex 9: [C₂₈H₂₆N₁₂O₁₄Zn]; *Mr* = 819.98; *T* = 173(2) K; Monoclinic; space group *C2/c*; *a* = 14.5638(16); *b* = 18.863(2); *c* = 13.3530(14) Å; $\alpha = \gamma = 90^\circ$; $\beta = 113.3550(10)$; *V* = 3367.8(6) Å³; *Z* = 4; $\rho_{\text{calcd}} = 1.617 \text{ g/cm}^3$; crystal size = 0.15 x 0.14 x 0.12 mm; $\mu = 0.818 \text{ mm}^{-1}$; reflections collected 10174; unique reflections 3121; data/restraints/parameters 3121/0/251; *GOF* on *F*² 1.062; *R*_{int} for independent data 0.0139; final *R*_I = 0.0593, *wR*₂ = 0.1582; *R* indices (all data) *R*_I = 0.0608, *wR*₂ = 0.1596; largest diff. peak and hole: 1.124 and -1.032 eÅ⁻³.

Synthesis of zinc-containing supramolecular complex [(ZnL·I₂)(Ph)₂]_n **10**

To a 5 mL vial **L** (2.1 mg, 0.0044 mmol) dissolved in benzene (1 ml) was added first, a blank solution of 3 ml benzene and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, ZnI₂ (7.5 mg, 0.0235 mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of complex **10** were obtained by slow evaporation of the above solution in air at room temperature (2.5 mg, 59.5 %). IR (KBr): 3084.3, 1594.4, 1584.1, 1506.9, 1497.2, 1489.4, 1473.5, 1446.1, 1421.5, 1416.0, 1385.0, 1374.9, 1362.8, 1325.6, 1306.7, 1252.8, 1197.4, 1150.3, 1113.8, 1059.6, 1004.7, 991.8, 876.1, 851.9, 694.8, 674.9, 668.6, 636.4, 572.9, 517.8, 481.3. Anal. Calcd for C₃₆H₂₄N₆O₆ZnI₂: C, 45.20; H, 2.51; N, 8.79. Found: C, 45.94; H, 2.45; N, 8.56.

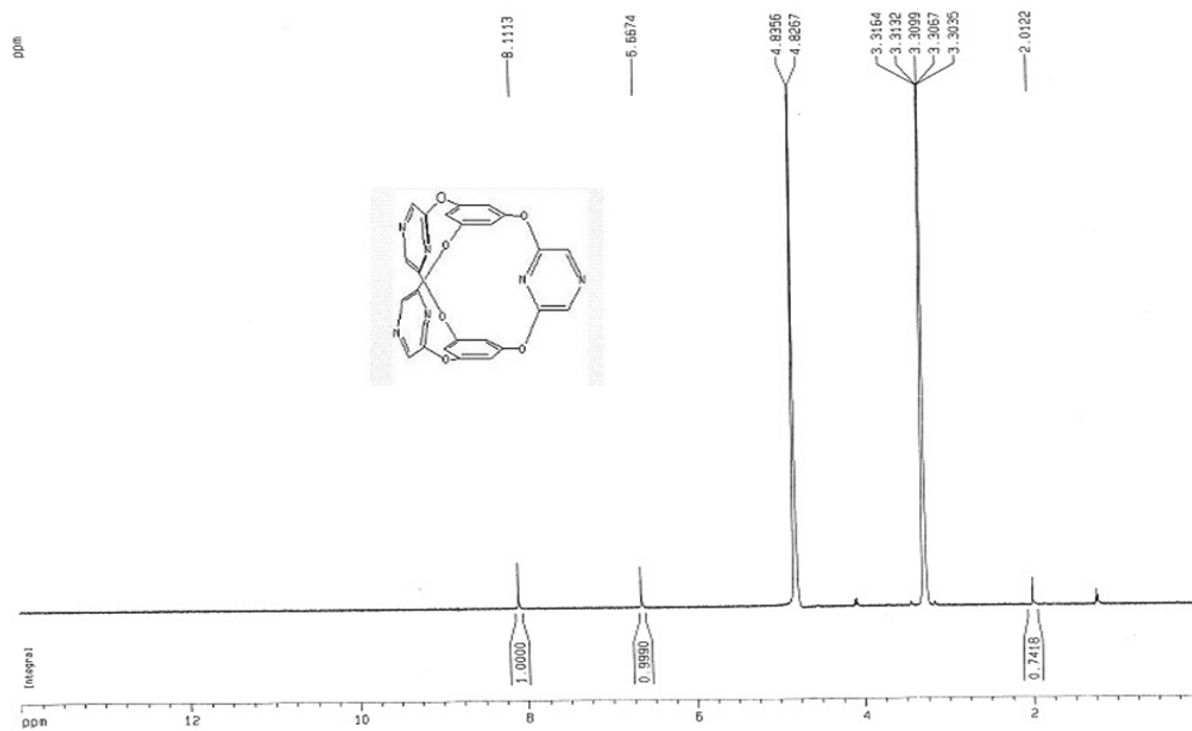
Crystallographic data for complex 10: [C₃₀H₁₈I₂N₆O₆Zn]; *Mr* = 877.67; *T* = 173(2)

K; Triclinic; space group $P\bar{1}$; $a = 9.6503(6)$; $b = 12.7719(6)$; $c = 13.0096(7)$ Å; $\alpha = 102.8800(10)$; $\beta = 93.4560(10)$; $\gamma = 107.4480(10)$; $V = 1477.21(14)$ Å³; $Z = 2$; $\rho_{\text{calcd}} = 1.973$ g/cm³; crystal size = 0.52 x 0.46 x 0.22 mm; $\mu = 2.977$ mm⁻¹; reflections collected 17012; unique reflections 5135; data/restraints/parameters 5135/0/460; *GOF* on F^2 1.070; R_{int} for independent data 0.0223; final $R_I = 0.0211$, $wR_2 = 0.0537$; R indices (all data) $R_I = 0.0243$, $wR_2 = 0.0533$; largest diff. peak and hole: 0.751 and -0.323 eÅ⁻³.

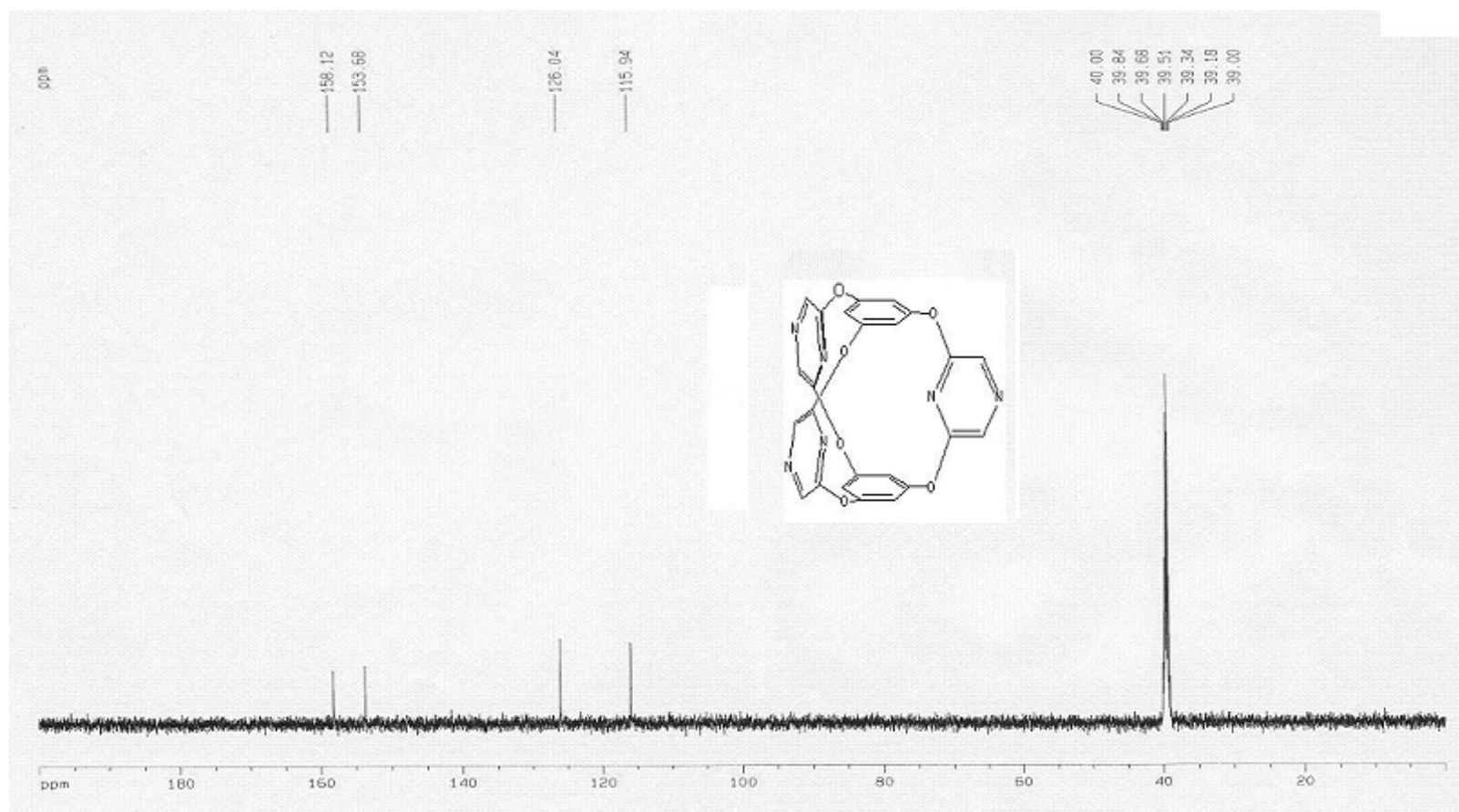
Synthesis of zinc-containing supramolecular complex [(ZnL·I₂)(THF)₂]_n **11**

To a 5 mL vial **L** (2.9 mg, 0.0060 mmol) dissolved in THF (1 ml) was added first, a blank solution of 3 ml THF and acetonitrile (1:1) was then layered on top of the **L** solution, and finally, ZnI₂ (30 mg, 0.0940 mmol) dissolved in acetonitrile (1 ml) was layered on top of the blank solution. X-ray quality single crystals of complex **11** were obtained by slow evaporation of the above solution in air at room temperature (1.6 mg, 28.6 %). IR (KBr): 3435.1, 3081.0, 2969.1, 1587.6, 1546.8, 1521.8, 1507.2, 1489.4, 1472.9, 1447.3, 1421.9, 1415.5, 1329.9, 1306.1, 1199.4, 1153.1, 1114.7, 992.4, 876.0, 850.7, 663.1, 520.4. Anal. Calcd for C₃₂H₂₈N₆O₈ZnI₂: C, 40.69; H, 2.97; N, 8.90. Found: C, 40.15; H, 2.86; N, 8.47.

Crystallographic data for complex 11: [C₃₂H₂₈I₂N₆O₈Zn]; $M_r = 943.77$; $T = 173(2)$ K; Monoclinic; space group $C2/c$; $a = 15.3062(17)$; $b = 18.444(2)$; $c = 13.3803(15)$ Å; $\alpha = \gamma = 90^\circ$; $\beta = 115.3070(10)$; $V = 3414.8(7)$ Å³; $Z = 4$; $\rho_{\text{calcd}} = 1.836$ g/cm³; crystal size = 0.15 x 0.12 x 0.10 mm; $\mu = 2.587$ mm⁻¹; reflections collected 9929; unique reflections 3025; data/restraints/parameters 3025/0/228; *GOF* on F^2 0.870; R_{int} for independent data 0.0178; final $R_I = 0.0360$, $wR_2 = 0.1607$; R indices (all data) $R_I = 0.0377$, $wR_2 = 0.1750$; largest diff. peak and hole: 1.229 and -0.956 eÅ⁻³.



¹H NMR spectrum of ligand **L** in CD₃NO₂.



^{13}C NMR spectrum of ligand **L** in CD_3NO_2 .

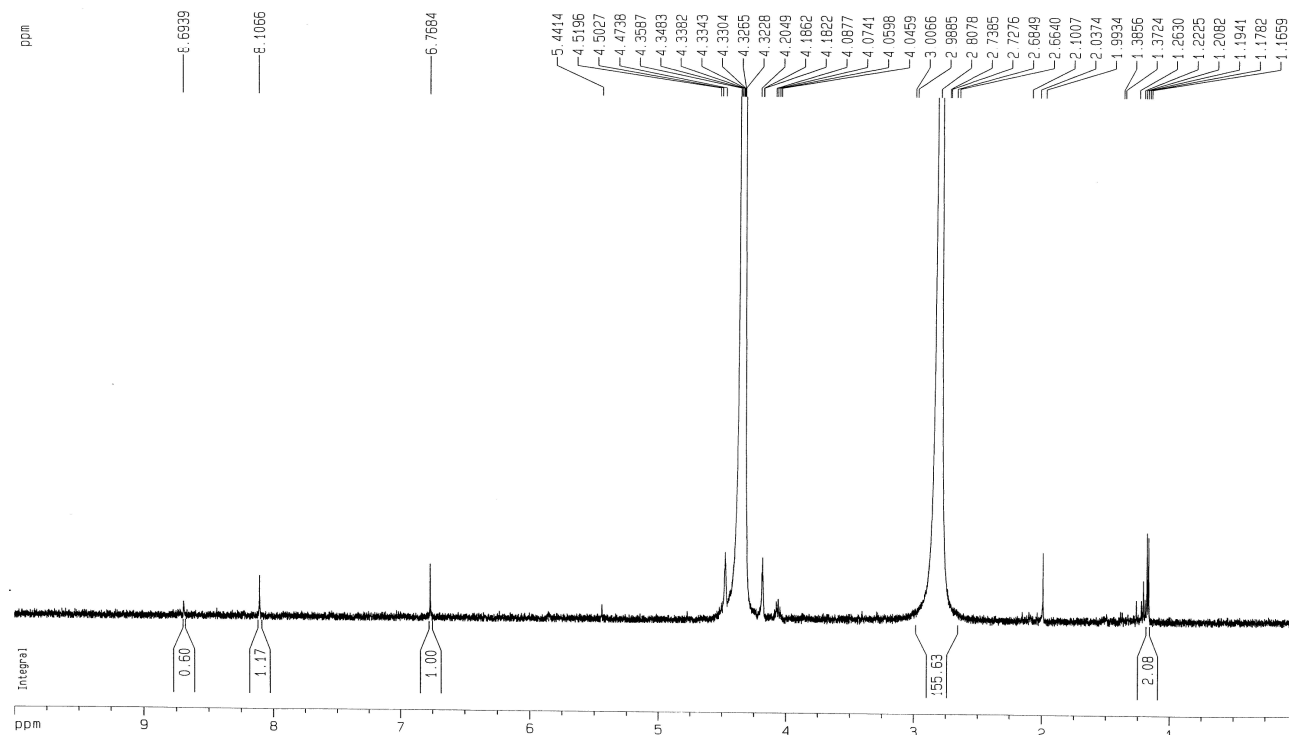


Figure S1: ^1H NMR spectrum of complex **1** (obtained by reaction of **L** with AgBF_4 in benzene and acetonitrile) in CD_3NO_2 .

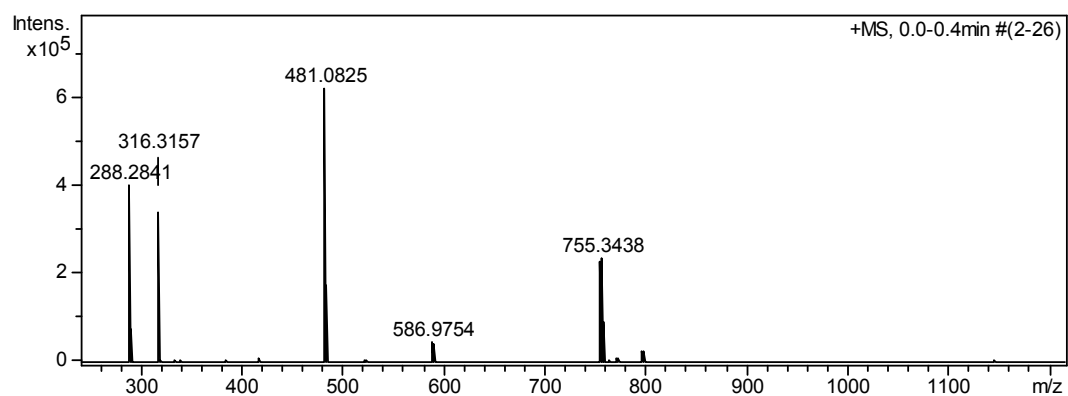


Figure S2: ESI mass spectrum of Ag complex **1** (obtained by reaction of **L** with AgBF₄ in benzene and acetonitrile) in CH₃CN. Peaks at m/z 586.98 and 755.34 can be assigned to the 1:1 complex species of [Ag(**L**)]⁺ and [Ag(**L**)(ACN).(BF₄)].

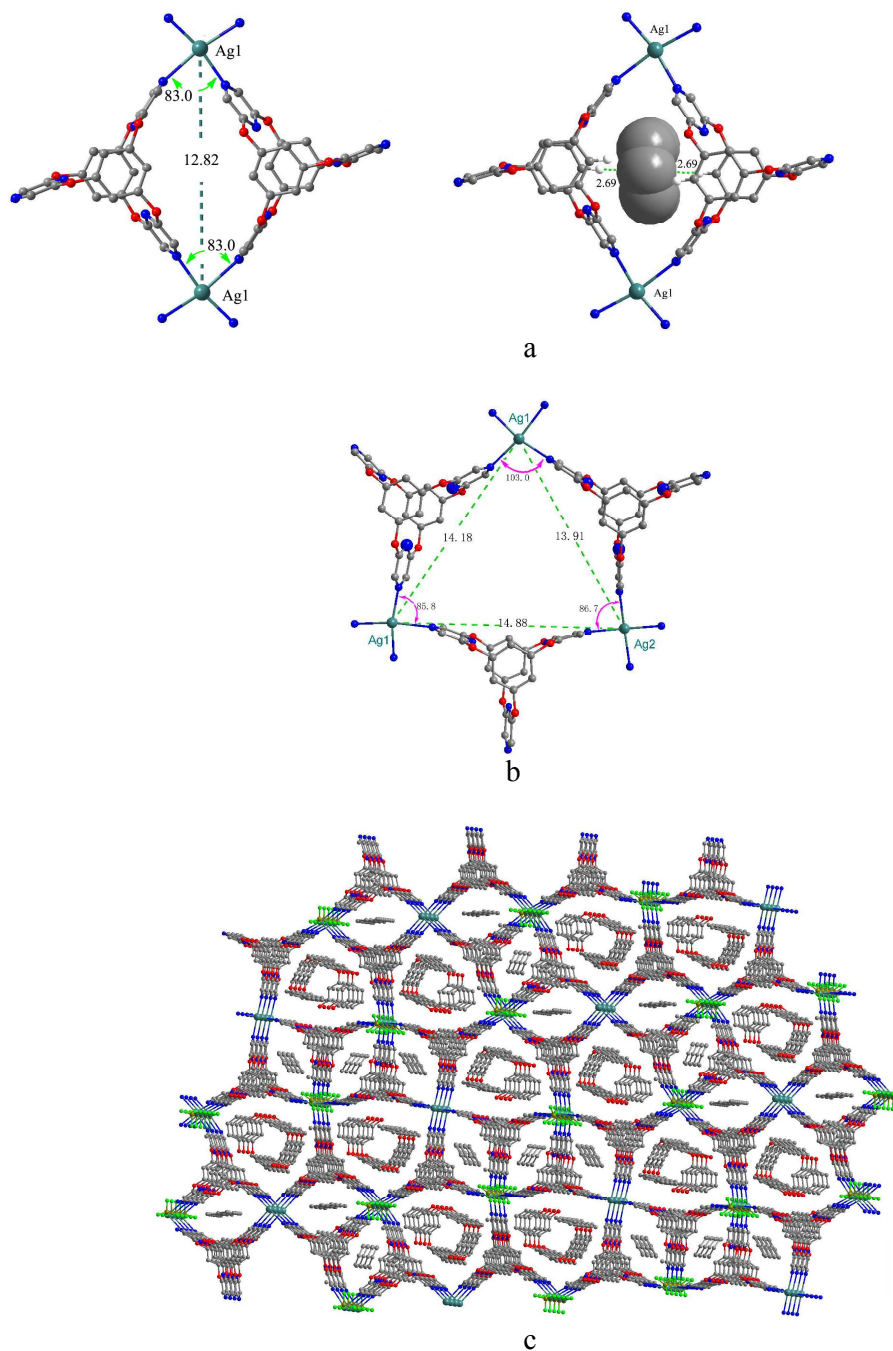


Figure S3: The Ag...Ag distance and N-Ag1-N angle of the $[\text{Ag}_2(\text{L}^3)_2]$ rhomboidal cage unit in **1**, and its hosting of a benzene guest *via* C-H... π interactions (a), the Ag...Ag distances and N-Ag-N angles of the distorted $[(\text{Ag}1)_2(\text{Ag}2)(\text{L}^3)_3]$ hexagonal cage unit in **1** (b), the layered packing of **1** (obtained by reaction of **L** with AgBF_4 in benzene and acetonitrile) viewed along *c*-axis, and the 1D rhomboidal and hexagonal channels are filled by guest molecules of benzenes and ligands **L**, respectively (c).

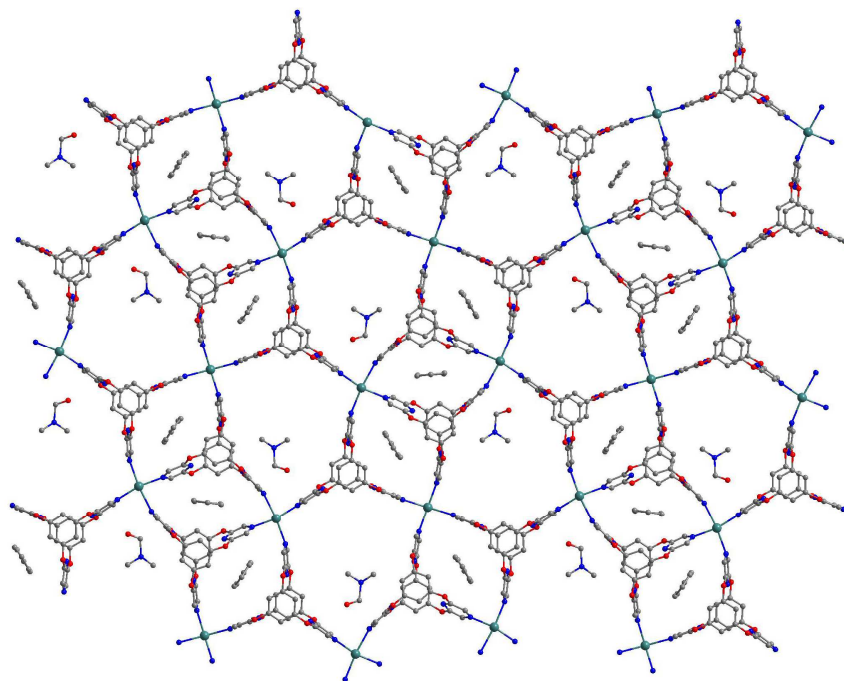


Figure S4: The 2D network structure of **1** obtained by reaction of **L** with AgBF_4 in benzene and acetonitrile under DMF atmosphere, DMF is the guest molecule included in the distorted $[\text{Ag}_3(\text{L}^3)_3]$ hexagonal cage unit, replacing **L** in the corresponding structure shown in **Figure S3**.

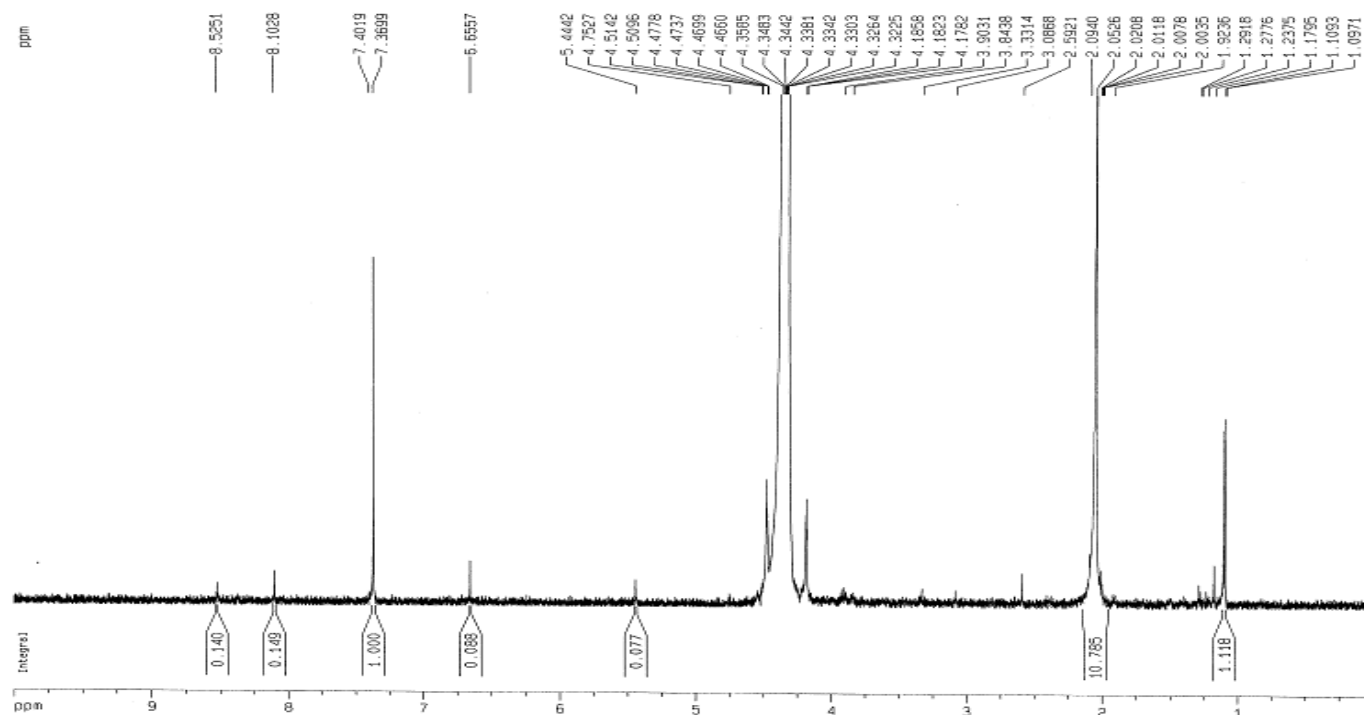


Figure S5: ¹H NMR spectrum of complex **2** (obtained by reaction of **L** with AgNO₃ in benzene and acetonitrile) in CD₃NO₂.

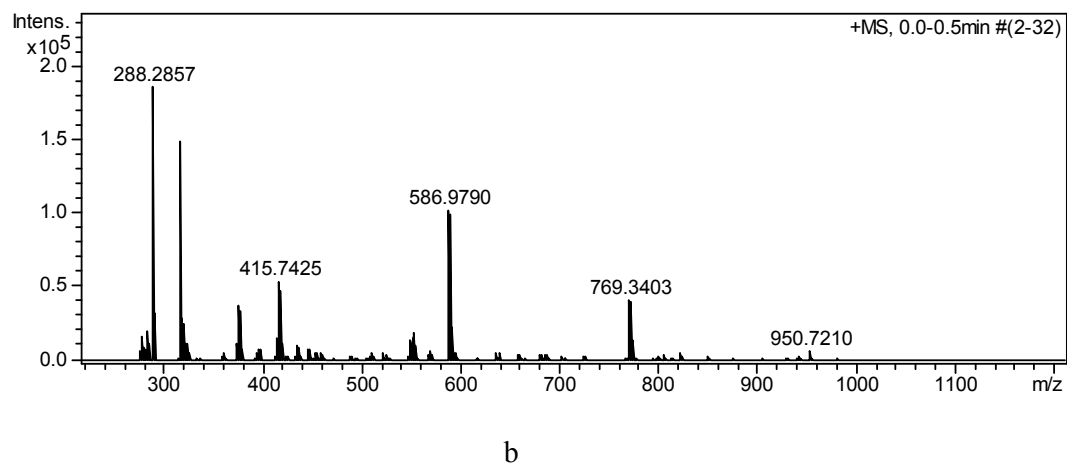
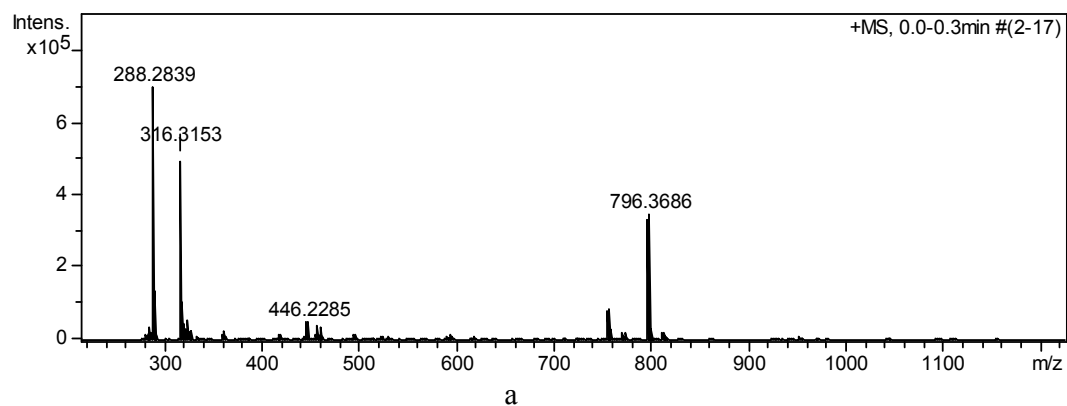


Figure S6: (a) ESI mass spectrum of Ag complex **2** (obtained by reaction of **L** with AgNO₃ in benzene and acetonitrile) in CH₃CN. Peaks at *m/z* 796.37 can be assigned to the complex specie of [Ag₂(**L**)(ACN).NO₃]⁺. (b) ESI mass spectrum of complex **3** (obtained by reaction of **L** with AgNO₃ in THF) in CH₃CN. Peaks at *m/z* 586.98 and 769.34 can be assigned to the complex species of [Ag(**L**)]⁺ and [KAg(**L**)(ACN)₂.NO₃]⁺, respectively.

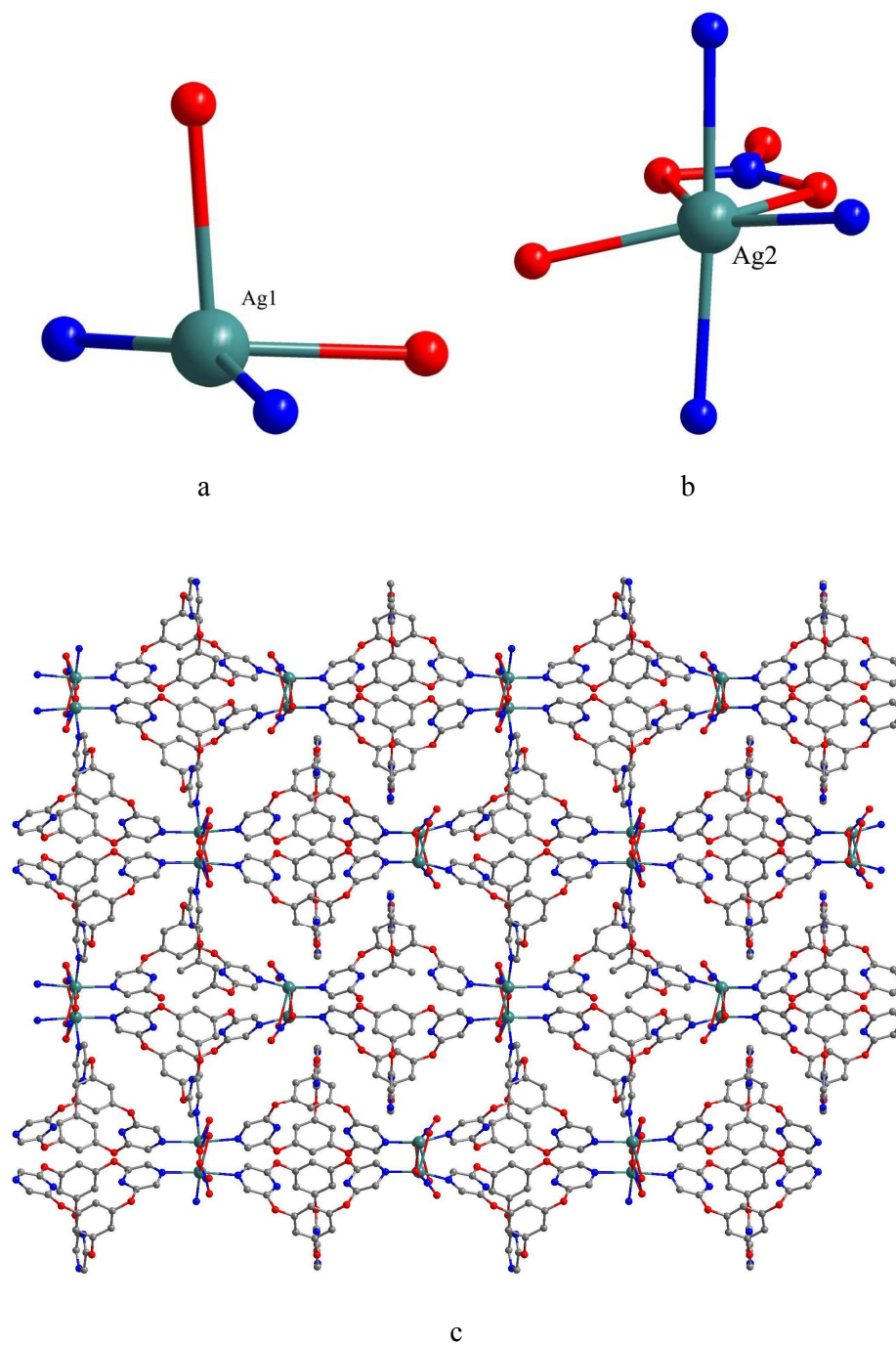


Figure S7: Coordination environments of **Ag1** (a) and **Ag2** (b) in complex **2**, and the three-dimensional network structure of complex **2** (c). Hydrogen atoms and the guest molecule of benzenes in c are omitted for clarity.

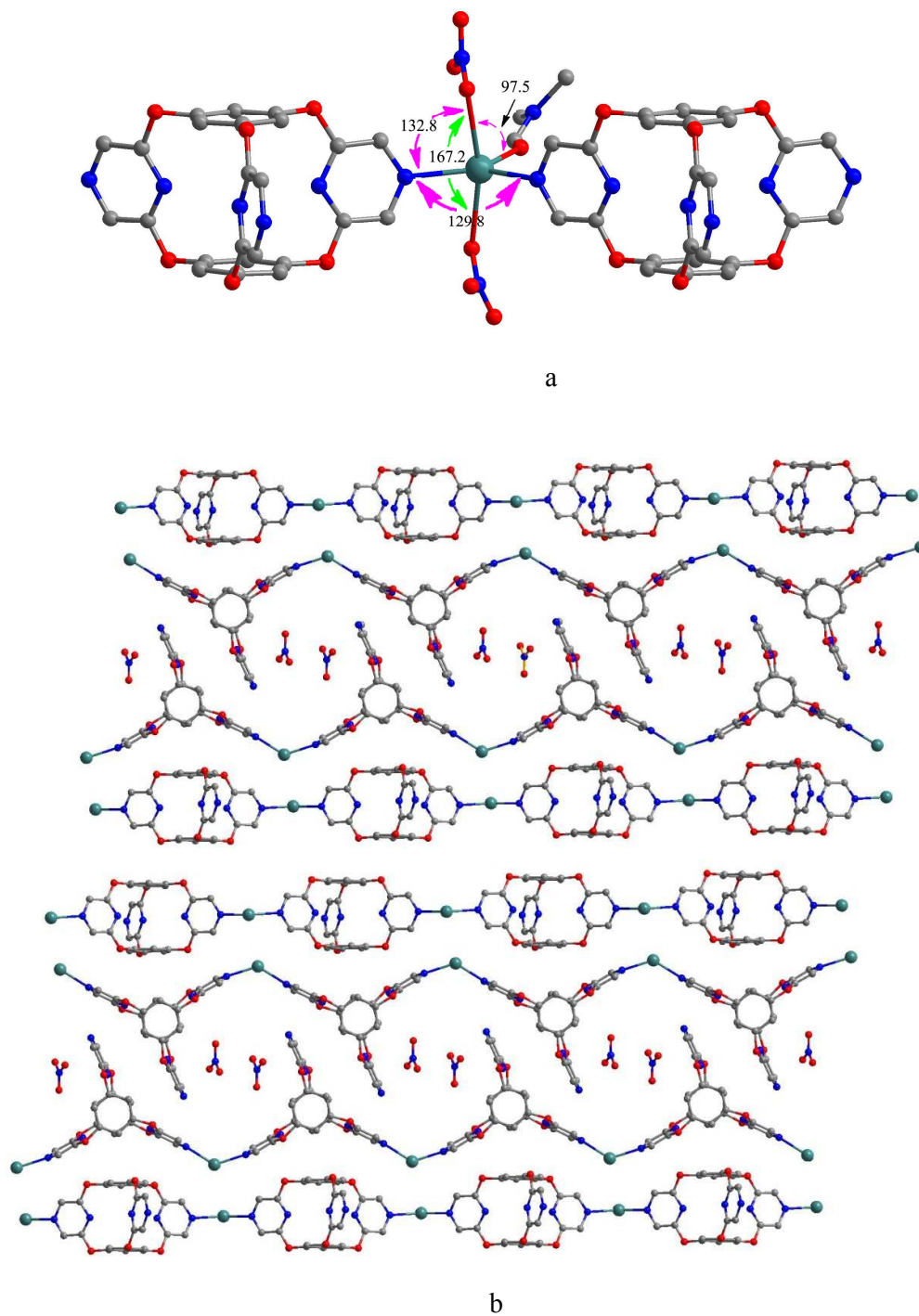


Figure S8: Coordination environment of Ag^+ cation (a) in complex **3**, and the overall layer extension of complex **3** in the crystal lattice (b). Hydrogen atoms, DMFs and nitrate counteranions coordinated to the polymeric chains of **3** in b are omitted for clarity.

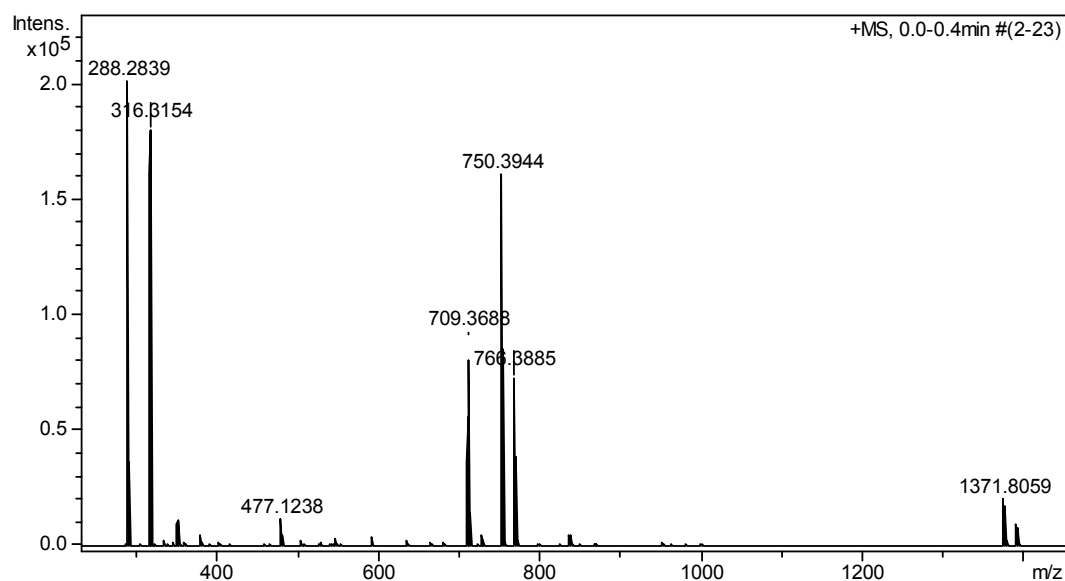


Figure S9: ESI mass spectrum of Cu complexes (obtained by reaction of **L** with $\text{Cu}(\text{NO}_3)_2$ in benzene and acetonitrile or in THF) in CH_3CN . Peaks at m/z 709.37, 750.39 can be assigned to $[\text{HCu}(\text{L})(\text{ACN})\cdot(\text{NO}_3)_2]^+$ and $[\text{HCu}(\text{L})(\text{ACN})_2\cdot(\text{NO}_3)_2]^+$, respectively, peak at m/z 766.39 could not be correctly assigned.

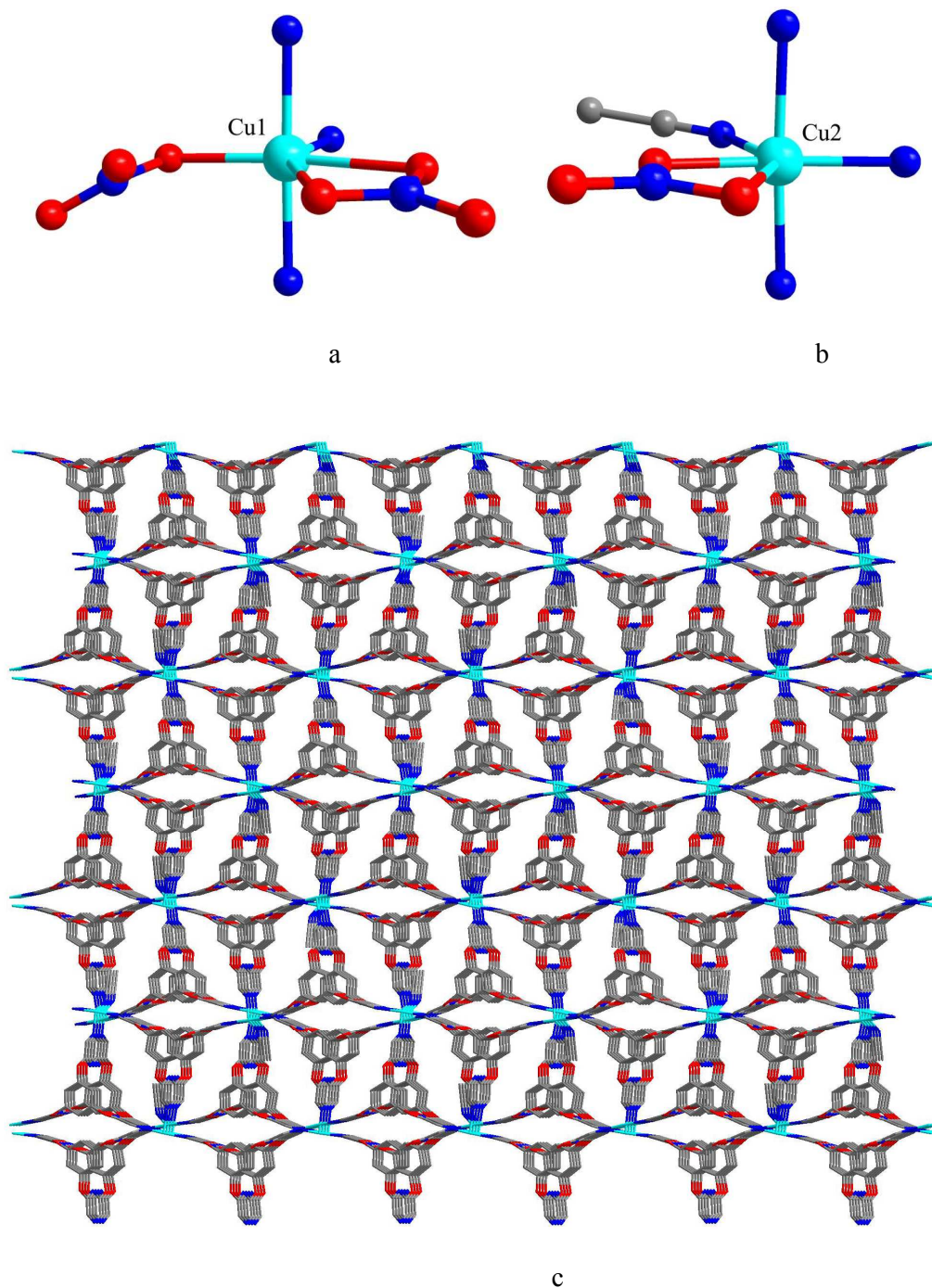


Figure S10: Coordination environments of **Cu1** (a) and **Cu2** (b) in complex **4**, and the staggered layers of complex **4** with an ABAB... sequence in the crystal lattice (c). Hydrogen atoms, nitrate counteranions, coordinated acetonitriles and guest molecules in c are omitted for clarity.

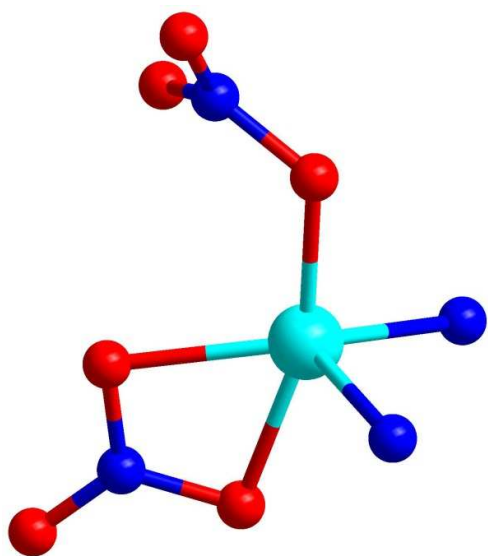
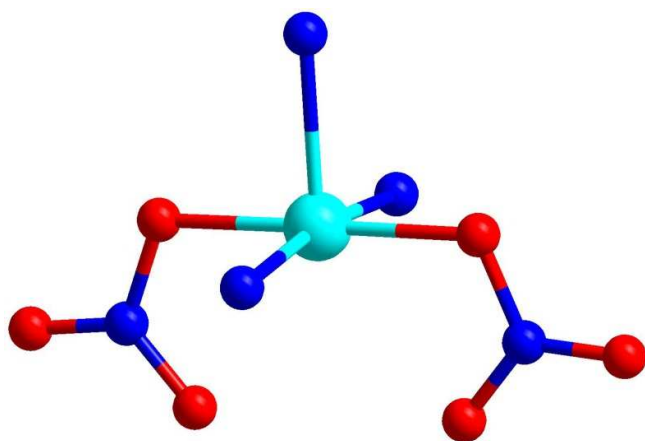
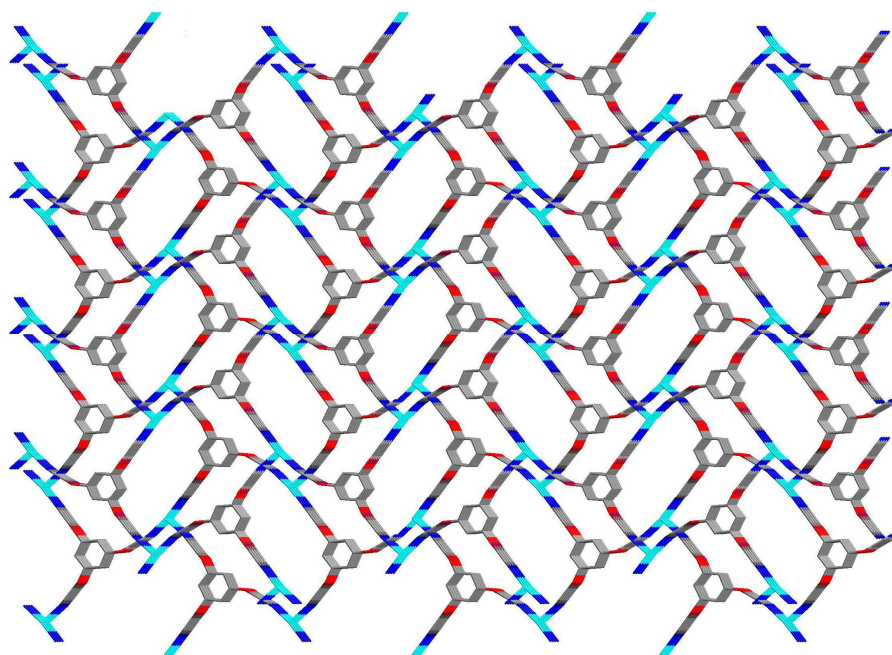


Figure S11: Coordination environment of **Cu** cation in complex **5**.

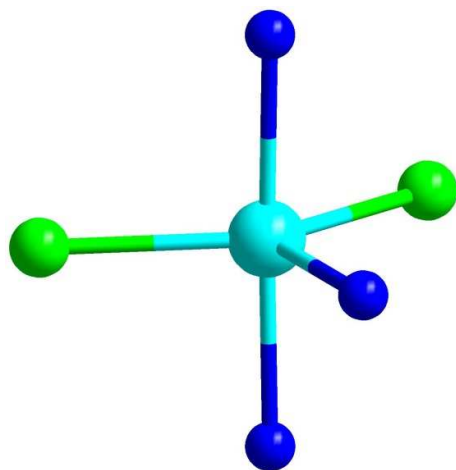


a

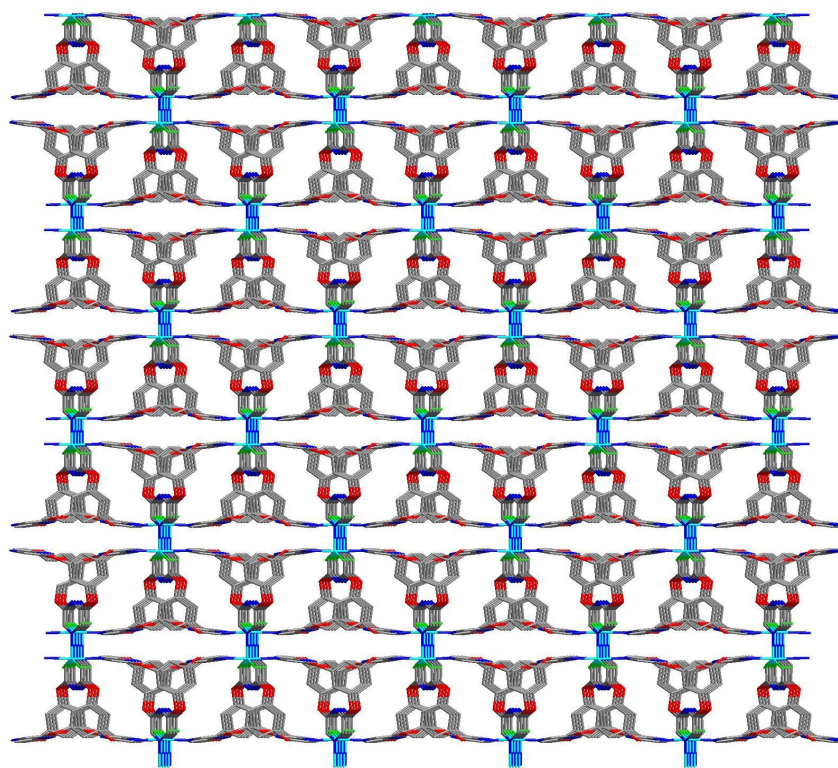


b

Figure S12: Coordination environment of Cu cation (a) in complex **6**, and the staggered layers of complex **6** with an ABAB... sequence in the crystal lattice (c). Hydrogen atoms, counteranions, and guest molecules of THF in b are omitted for clarity.



a



b

Figure S13: Coordination environment of **Cu** cation (a) in complex **7**, and the staggered layers of complex **7** with an ABAB... sequence in the crystal lattice (c). Hydrogen atoms, chlorides, and guest molecules of THF in b are omitted for clarity.

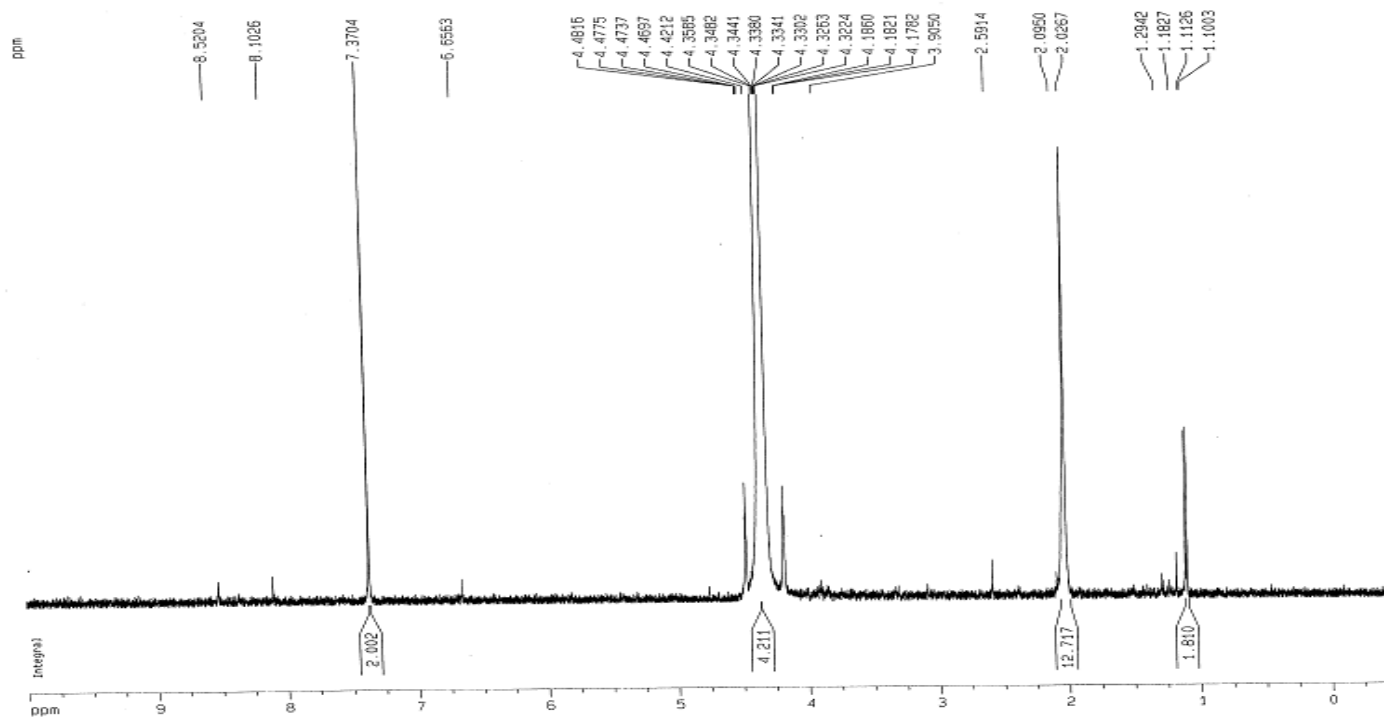


Figure S14: ¹H NMR spectrum of complex **8** [obtained by reaction of **L** with Zn(NO₃)₂ in benzene and acetonitrile] in CD₃NO₂.

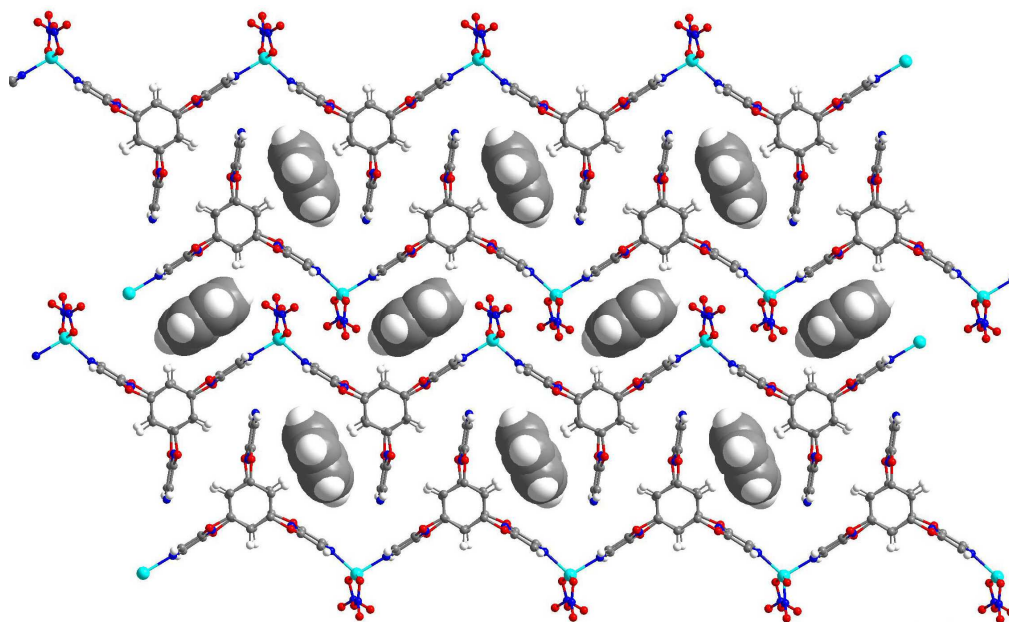


Figure S15: The anti-parallel arrangement of the polymeric chains of complexes **8** and their interactions with guest molecules of benzene in the solid state (crystallographically isostructural and isomorphous to the structure of complex **5**). Color code: Zn (green), O (red), N (blue), C (gray), H (white).

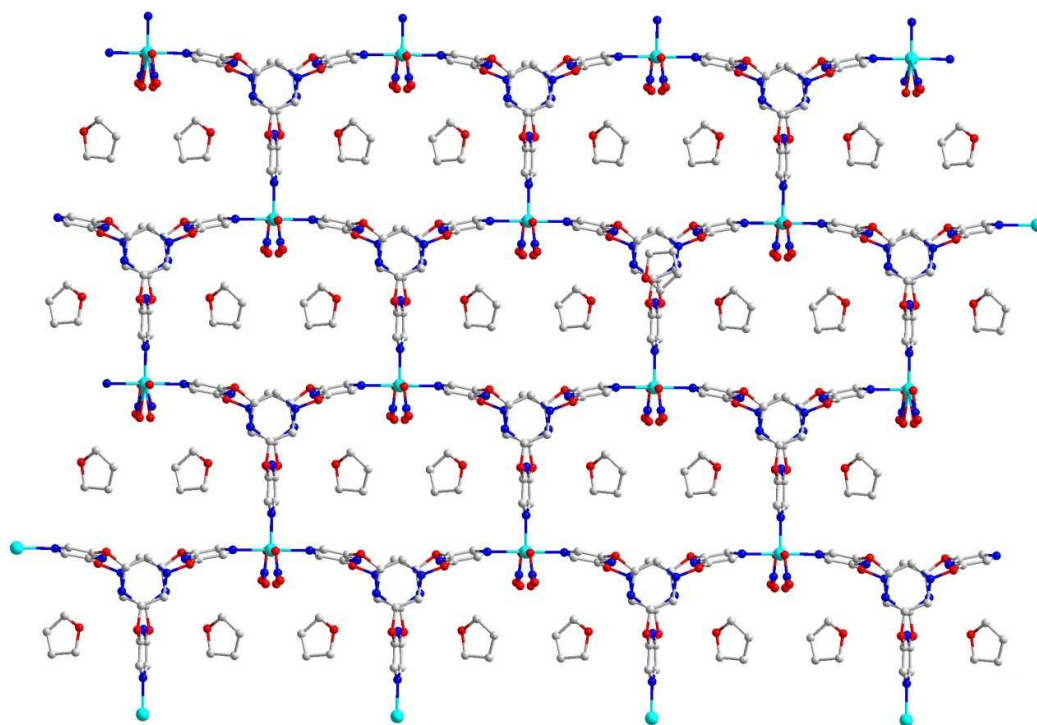
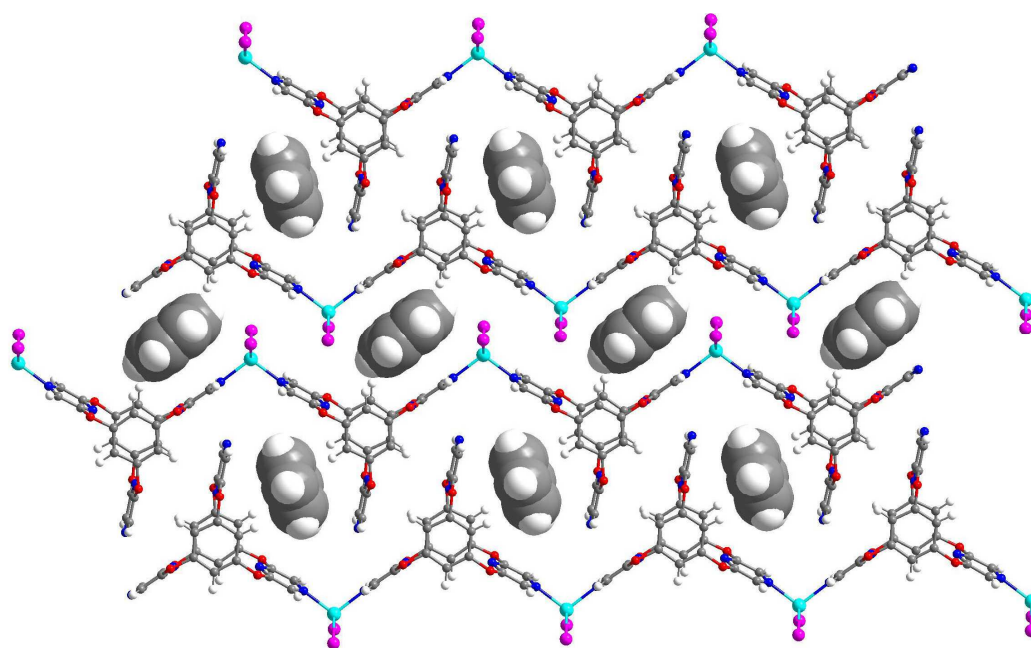
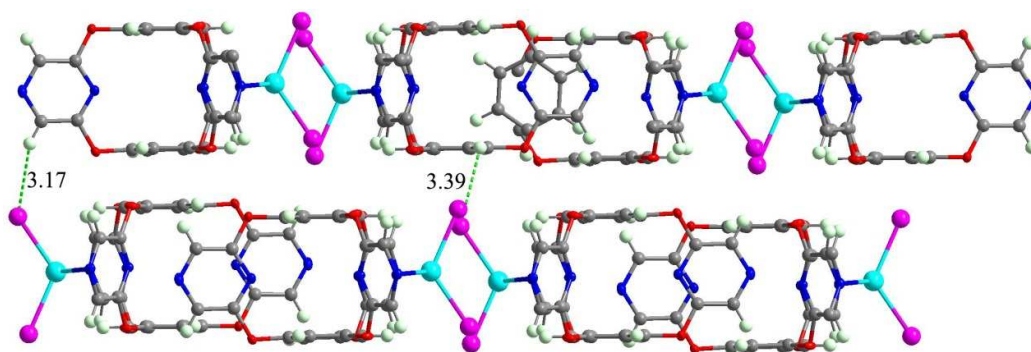


Figure S16: The 2D polymeric network structure of complex **9** with a “brick wall” like topology comprised of highly symmetrical rectangular cage motif $[\text{Zn}_3(\text{L}^3)_3]$ (crystallographically isomorphous to the structure of complex **7**). Hydrogen atoms are omitted for clarity. Color code: Zn (green), O (red), N (blue), C (gray).



a



b

Figure S17: The anti-parallel arrangement of the polymeric chains of complexes **10** (crystallographically isomorphous to the structures of complexes **5** and **8**) and their interactions with guest molecules of benzene in the solid state (a), intermolecular hydrogen bonds between the pyrazinyl protons and iodine atoms in the neighboring layers (b). Color code: Zn (green), O (red), N (blue), C (gray), I (purple), H (white).

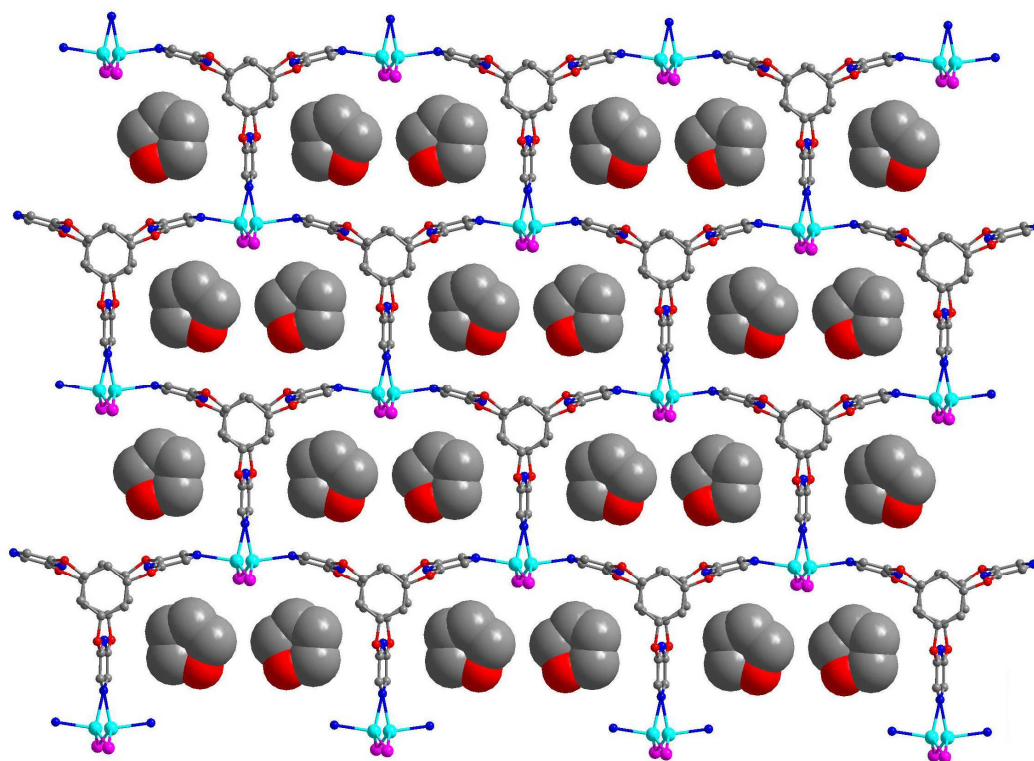


Figure S18: The 2D polymeric network structure of complex **11** with a “brick wall” like topology comprised of symmetrical rectangular cage motif $[\text{Zn}_3(\text{L}^3)_3 \cdot 2\text{THF}]$ (crystallographically isostructural and isomorphous to the structure of complex **7**). The vibrational nature of the zinc atoms is indicated. Hydrogen atoms are omitted for clarity. Color code: Zn (green), O (red), N (blue), C (gray), I (purple).