Electronic Supplementary Material for CrystEngComm

Extended 3^6 and 6^3 arrays of capsule motifs using ligand tris{4-(3-pyridyl)phenylester}cyclotriguaiacylene

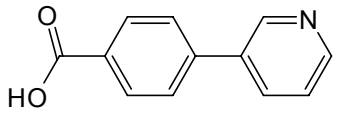
T.K. Ronson and M.J. Hardie

Supplementary Information

Synthesis

All chemicals were obtained from Sigma-Aldrich Chemical Company or Lancaster Synthesis Ltd and were used without further purification. ^{1}H Nuclear Magnetic Resonance spectra were recorded using a Bruker Avance 500 instrument. ^{13}C Nuclear Magnetic Resonance spectra were recorded using a Bruker DPX 300 instrument. ^{1}H spectra are referenced to tetramethylsilane and chemical shifts given in parts per million downfield from TMS. Microanalyses were obtained on a Carlo Erba Elemental Analyser MOD 1106 instrument, found composition is reported to the nearest 0.05 %. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer and samples analysed as solids. Mass spectra were obtained using a micrOTOF spectrometer using time-of-flight electro-spray analysis. EDX analysis was carried out on a Philips/FEI CM200FEGTEM equipped with a UTW Oxford Instruments EDX detector running ISIS software.

Preparation of 4-(3-pyridyl)benzoic acid



Prepared according to literature methods[1] with minor modifications.

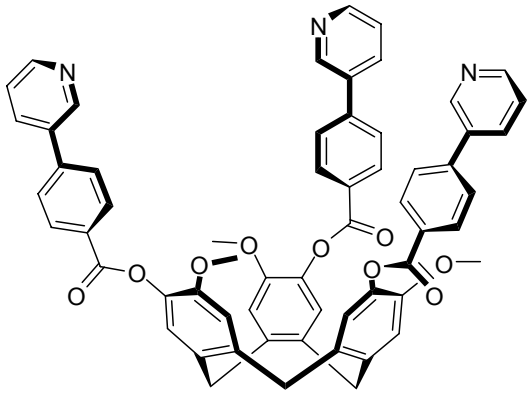
$Pd(PPh_3)_4$ (0.61 g, 0.53 mmol) was added to a degassed solution 4-carboxybenzene boronic acid (1.67 g, 10.1 mmol) and 3-bromopyridine (1.59 g, 10.1 mmol) in 0.4 M Na_2CO_3 solution (50 mL) and acetonitrile (50 mL). The mixture was heated at 90°C under N2 for 16 hours. The hot suspension was filtered. The filtrate was acidified with 1 M HCl and the volume reduced by half *in vacuo*. The white solid was collected by filtration to give 4-(3-pyridyl)benzoic acid as the hydrochloride salt. Yield 2.05 g, 86 %. ^{1}H NMR (500 MHz, d_6-DMSO): δ (ppm) 9.28 (1H, s, pyridyl H^2), 8.90 (1H, d, pyridyl H^6, J = 5.3 Hz), 8.83 (1H, d, pyridyl H^4, J = 8.2 Hz), 8.11 (2H, d, phenyl H^2, J = 8.4 Hz), 8.07 (1H, dd, pyridyl H^5, J = 8.2, 5.3 Hz), 8.01 (2H, d, phenyl H^3, J = 8.4 Hz). ^{13}C NMR (75 MHz, d_6-DMSO): δ (ppm) 167.1, 143.0, 142.2, 142.1, 138.8, 137.5, 131.8,

130.5, 128.0, 127.0. Found C 58.70, H 4.15, N 5.35; $C_{12}H_9NO_2(HCl)(H_2O)_{0.5}$ requires C 58.90, H 4.53, N 5.72 %.

Preparation of 4-(3-pyridyl)benzoyl chloride hydrocloride

4-(3-Pyridyl)benzoic acid hydrochloride (1.98 g, 8.40 mmol) was refluxed under N_2 in thionyl chloride (10 mL) containing a few drops of DMF for 24 hours. The thionyl chloride was removed in vacuo and the off-white solid washed with diethyl ether to give 4-(3-pyridyl)benzoyl chloride hydrochloride as an off-white powder which was dried *in vacuo* for 2 hours and used immediately. Yield 1.87 g, 88 %.

Preparation of tris[4-(3-pyridyl)benzoyl]cyclotriguaiacylene, L1

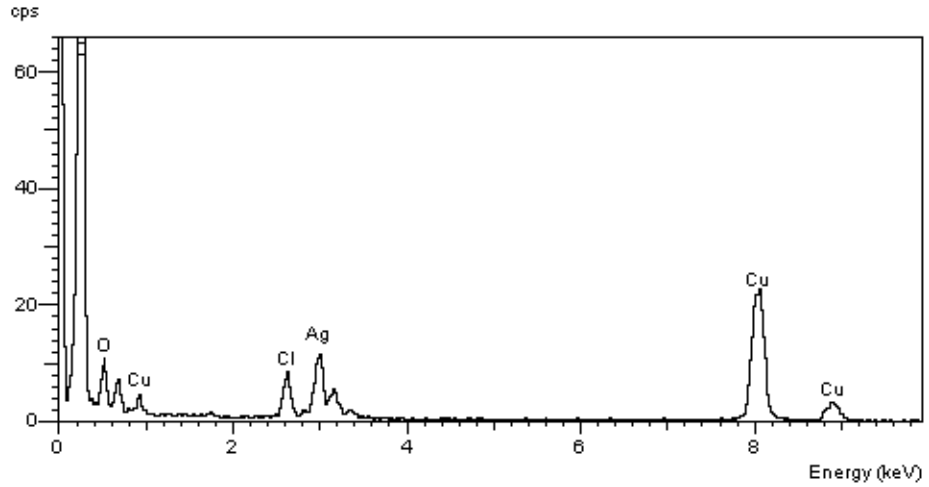


Cyclotriguaiacylene (0.430 g, 1.05 mmol) was dissolved in dry THF (600 mL) under a N_2 atmosphere and cooled to -78°C in an ice bath. Triethylamine (1.8 mL) was added to the reaction, which was stirred for 30 minutes. 4-(3-Pyridyl)benzoyl chloride hydrochloride (1.06 g, 4.17 mmol) was added to the solution which was stirred at -78°C for one hour, and then at room temperature for 4 days. The solution was taken to dryness *in vacuo* and the residue washed with ethanol. The crude product was taken up into $CHCl_3$ and filtered through celite. Evaporation of the filtrate gave tris[4-(3-pyridyl)benzoyl]cyclotriguaiacylene as a white solid. Yield 0.77 g (75 %). HR MS (ES^+): *m*/*z* 952.3254 (MH^+); calc. for $C_{60}H_{46}N_3O_9$ 952.3229. ^{1}H NMR (500 MHz, $CDCl_3$): δ(ppm) 8.92 (3H, s, br, pyridyl H^2), 8.67, (3H, s, br, pyridyl H^6), 8.31 (6H, d, phenyl H^2, J = 8.6 Hz), 7.94 (3H, d, pyridyl H^4, J = 8.2 Hz), 7.72 (6H, d, phenyl H^3, J = 8.6 Hz), 7.42 (3H, dd, pyridyl H^5), 7.21 (3H, s, aryl CH), 6.98 (3H, s, aryl CH), 4.86 (3H, d, CTG CH_2, J = 13.7 Hz), 3.82 (9H, s, CH_3), 3.71 (3H, d, CTG CH_2, J = 13.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ(ppm) 164.8, 150.4, 149.8, 148.8, 143.2, 139.0, 138.5, 136.0, 134.9, 132.0, 131.5, 129.5, 127.6, 124.5, 124.2, 114.7, 56.7, 36.9. IR (solid state): ν (cm^{-1}) 3032 (w), 2933 (w), 2854 (w), 1733 (s), 1609 (s), 1579 (w), 1561 (w), 1508 (s), 1477 (m), 1446 (w), 1427 (w), 1397 (m), 1328 (m), 1266 (s), 1206 (w), 1179 (s), 1140 (m), 1095

(s), 1066 (s), 1018 (w), 1003 (m), 925 (w), 902 (w), 859 (m), 809 (m), 761 (s), 745 (w), 709 (m), 644 (w), 636 (w), 624 (w), 583 (w), 550 (w), 516 (w). Found C 73.70, H 4.95, N 4.30, Cl 0.65; $C_{60}H_{45}N_3O_9(H_2O)(HCl)_{0.2}$ requires C 73.74, H 4.87, N 4.30, Cl 0.73 %.

$[Ag_3(CH_3CN)_3(L1)_2Cl]\cdot 2(BF_4)\cdot 3(CH_3CN)$ 2 A solution of $Ag(MeCN)_4BF_4$ (19 mg, 0.053 mmol) in MeCN (2 mL) was added to a solution of L1 (30 mg, 0.032 mmol) in MeCN (10 mL). Slow evaporation of the solvent resulted in very small crystals of **2** which were filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 17 mg, 44 %. IR (solid state): ν (cm^{-1}) 1730 (s), 1610 (s), 1581 (w), 1564 (w), 1507 (s), 1468 (m), 1441 (m), 1398 (m), 1330 (m), 1282 (m), 1265 (s), 1206 (m), 1178 (s), 1140 (m), 1093 (s), 1062 (s), 1019 (m), 1008 (m), 940 (w), 909 (w), 861 (m), 813 (m), 764 (s), 746 (w), 701 (m), 666 (w), 640 (w), 630 (w), 624 (m), 584 (w), 555 (w), 526 (w), 503 (w).

The EDX spectrum of **2** is shown below and clearly shows the presence of Cl-.

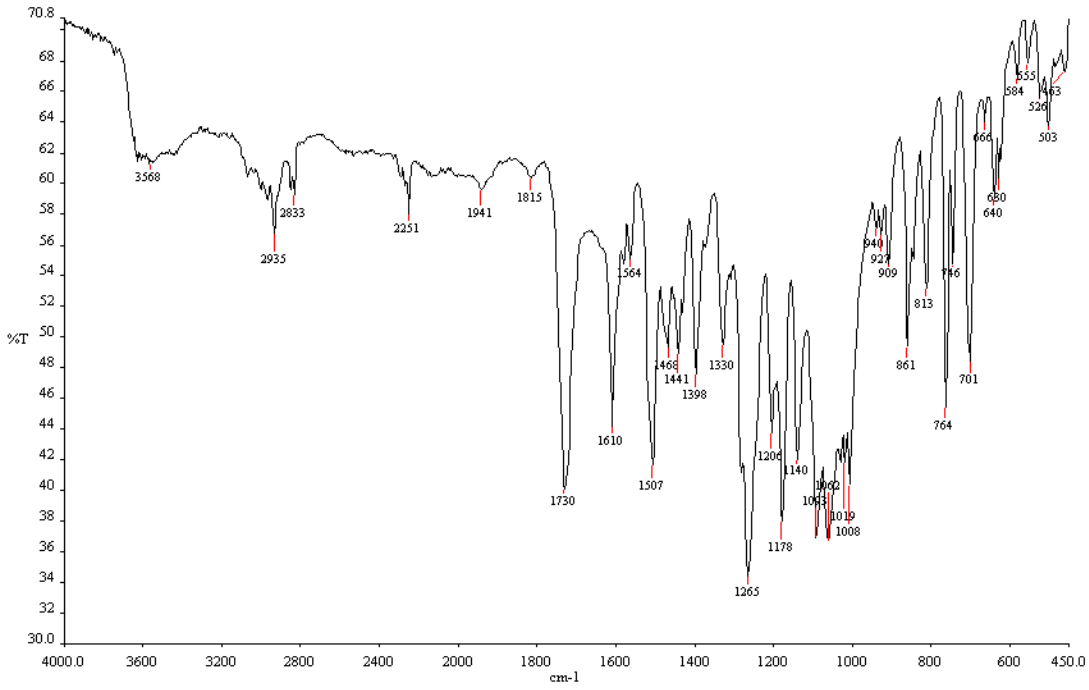


$[Ag_3(CH_3CN)_3(L1)_2Cl]\cdot 2(AsF_6)\cdot n(CH_3CN)$ 3 A solution of $AgAsF_6$ (7 mg, 0.024 mmol) in MeCN (1 mL) was added to a solution of L (15 mg, 0.016 mmol) in MeCN (5 mL). Slow evaporation of the solvent resulted in very small crystals of **3** which were filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 14 mg, 67 %. IR (solid state): ν (cm^{-1}) 1728 (s), 1610 (s), 1580 (w), 1508 (s), 1478 (w), 1468 (w), 1445 (w), 1433 (w), 1398 (m), 1329 (m), 1264 (s), 1205 (m), 1178 (s), 1138 (s), 1093 (s), 1064 (s), 1019 (m), 1007 (m), 949 (w), 929 (w), 916 (w), 861 (m), 810 (m), 763 (s), 746 (w), 703 (m), 660 (s), 623 (m), 584 (w), 555 (w), 527 (w), 509 (w).

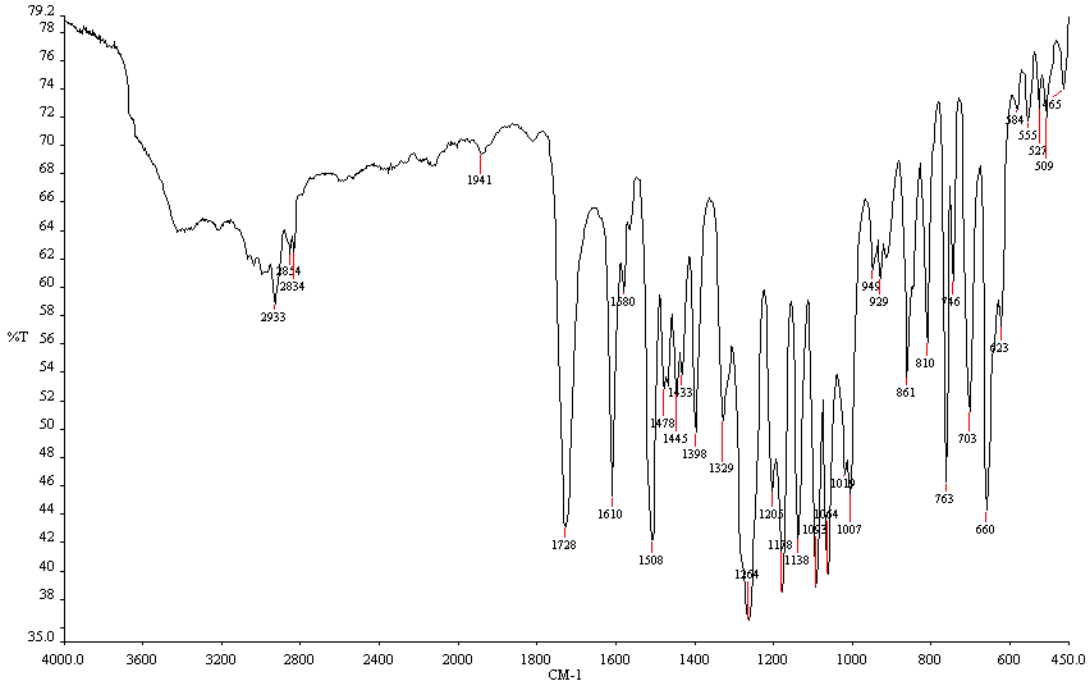
$[Ag_3(CH_3CN)_3(L1)_2Cl]\cdot 2(ClO_4)\cdot n(CH_3CN)$ 4 A solution of $AgClO_4.H_2O$ (12 mg, 0.053 mmol) in MeCN (2 mL) was added to a solution of L1 (30 mg, 0.032 mmol) in MeCN (10 mL). Slow evaporation of the solvent resulted in very small crystals of **4** which were filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 25 mg, 64 %. IR (solid state): ν (cm^{-1}) 1732 (s), 1609 (m), 1580 (w), 1506 (s), 1468 (w), 1442 (w), 1397 (w), 1329 (w), 1264 (s), 1206 (m), 1179 (s), 1140 (m), 1093 (s), 1064 (s), 1019 (w), 1008 (m), 927 (w), 907 (w), 860 (m), 812 (w), 763 (m), 746 (w), 701 (m), 649 (w), 622 (m), 584 (w), 555 (w), 527 (w), 506 (w).

Complexes **2** – **4** were highly solvated and satisfactory microanalyses could not be obtained. Notably, different batches of each complex showed different levels of Cl^-, which is suggestive of the disordered counter-anion within the crystal lattice being of mixed Cl/X character, where X = BF_4^-, AsF_6^-, ClO_4^- as appropriate. There are clear differences in the IR spectra of complexes **2** – **4** (shown below) indicating that different X counter-anions are present in each case:

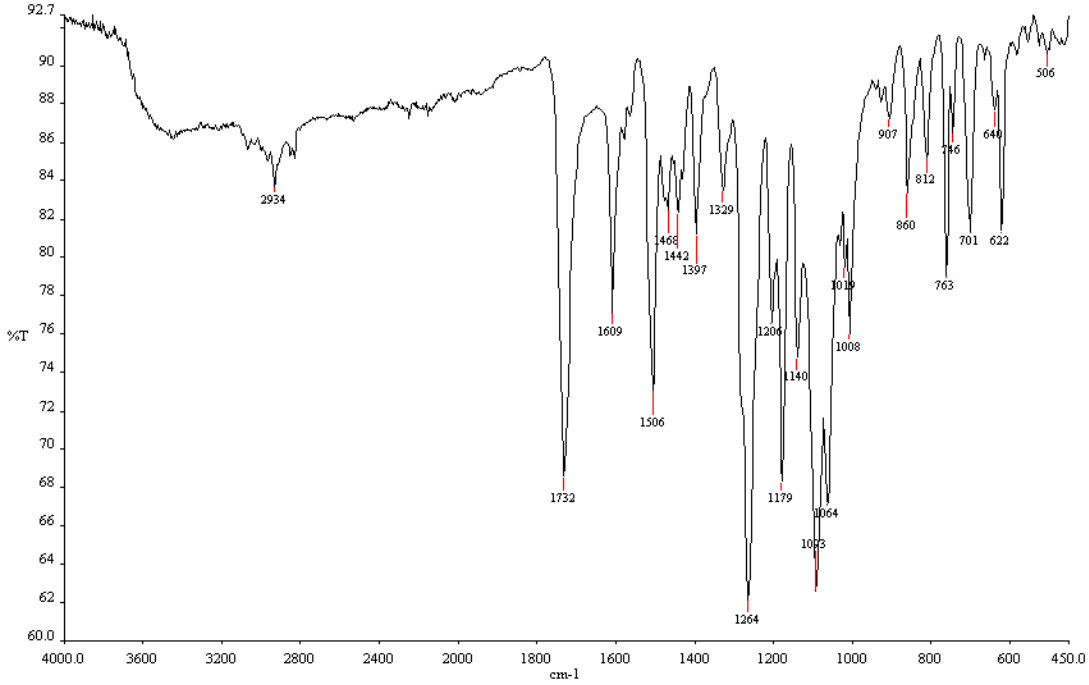
IR Spectrum of $[Ag_3(CH_3CN)_3(L1)_2Cl]\cdot 2(BF_4)\cdot n(CH_3CN)$ 2:



IR Spectrum of $[Ag_3(CH_3CN)_3(L1)_2Cl]\cdot 2(AsF_6)\cdot n(CH_3CN)$ 3:



IR Spectrum of $[Ag_3(CH_3CN)_3(L1)_2Cl]\cdot 2(ClO_4)\cdot n(CH_3CN)$ 4:



X-Ray crystallography

Single crystals of complexes **1 – 4** were mounted on a glass fibre under oil and X-ray diffraction data were collected at 150(1) K on a Bruker X8 diffractometer fitted with an APEX II detector using a rotating anode Mo source ($\lambda = 0.71073$ Å). Data were corrected for Lorentz and polarization effects and absorption corrections were applied using multi-scan methods. The structures were solved by direct methods using *SHELXS-97* [2] and refined by full-matrix least-squares on F^2 using *SHELXL-97*,[3] using the *X-Seed* GUI.[4] All non-hydrogen atoms were refined anisotropically unless otherwise specified and hydrogen atoms were included at geometrically estimated positions, aside from those of CH_3CN groups of complexes **2 – 4** which were excluded as their positions would not converge.

For complex **1,** two of the $CHCl_3$ molecules showed symmetry-imposed disorder disordered with one modelled with three positions for the central C atom, and the other modelled over two positions for the central C atom and with partially occupied Cl positions in all four tetrahedral sites around the central C atom. The hydrogen atom was excluded from the latter disordered $CHCl_3$ and it was given an isotropic refinement.

In complex **2** the BF_4^- counter-anions could not be located in the difference map, presumably due to severe disorder, and their presence was included in the formula. Solvent CH_3CN had symmetry imposed disorder and were refined isotropically with some restraints on C-C bond lengths.

For both complexes **3** and **4** the anions could be partially located. As the structure model contained significant voids and diffuse residual electron density could not be adequately modelled as either solvent or as anion positions, the SQUEEZE procedure of PLATON [5] was employed for both complexes. In complex **3** one As position was clearly defined although the surrounding F atoms were severely disordered. F positions were visible in the difference map but attempts to refine these F sites were not successful with non-convergence of the refinement. The three largest peaks in the difference map were refined (isotropically) as further disordered As positions with occupancies set so that overall charge balance was achieved. The F atoms associated with both AsF_6^- were not refined but were included in the formula. No solvent CH_3CN molecules were reliably located and these were excluded from the given molecular formula.

Complex **3** is isomorphic with complex **2** with the same positioning of the coordination polymer within the unit cell but differing anion positions. Crystal data for **3**: $C_{126}H_{99}Ag_3As_2ClF_{12}N_9O_{18}$, *Mr* = 2764.04, hexagonal, $P6_3/m$, $a = 15.7496(2)$, $c = 35.0891(11)$ Å, $V = 7537.7(3)$ Å^3, $Z = 2$, ρ_{calc} =

1.218 g cm^{-3}, μ = 0.910 mm^{-1}, θ_{max} = 22.5°, 85656 reflections collected, 3336 unique (R_{int} = 0.0862), 248 parameters, R_1 = 0.0959 (for 2570 reflections $I > 2\sigma(I)$), wR_2 = 0.2816 (all reflections), S = 1.115.

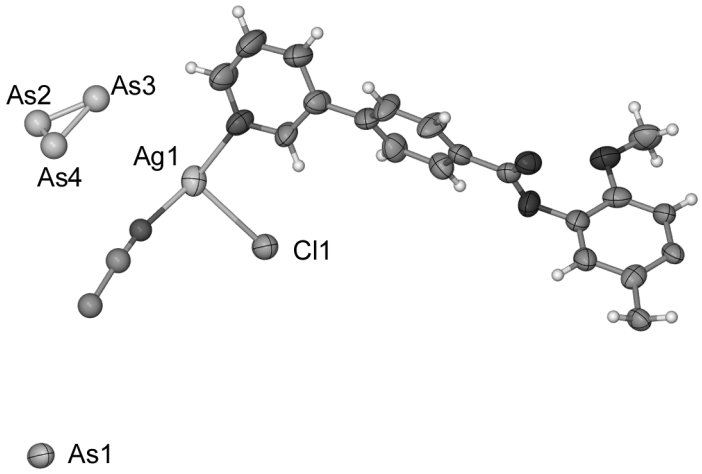


*Figure S1: Asymmetric unit of the crystal structure of complex **3**. Ellipsoids are shown at 50% probability level aside from for isotropically refined atoms.*

Complex **4** is structurally very similar to complexes **2** and **3**, with slightly different positioning of the coordination network within the unit cell. In complex **4** the terminal CH_3CN ligand was modelled with an isotropic refinement and as being disordered over two positions, with one position refined with a group U_{iso} value. The solvent CH_3CN showed symmetry imposed disorder and was refined isotropically. The ClO_4^- was refined isotropically at overall half occupancy. Further ClO_4^- anions required for charge balance were not located but have been included in the molecular formula. Some restraints were placed on bond lengths and displacement parameters.

Crystal data for **4**: $C_{128}H_{102}Ag_3Cl_3N_{10}O_{26}$, Mr = 2626.16, hexagonal, $P6_3/m$, a = 16.2470(6), c = 34.382(3) Å, V = 7859.8(7) Å^3, Z = 2, ρ_{calc} = 1.110 g cm^{-3}, μ = 0.481 mm^{-1}, θ_{max} = 26.04°, 92000 reflections collected, 5245 unique (R_{int} = 0.0710), 256 parameters, R_1 = 0.0641 (for 3614 reflections $I > 2\sigma(I)$), wR_2 = 0.1986 (all reflections), S = 1.087.

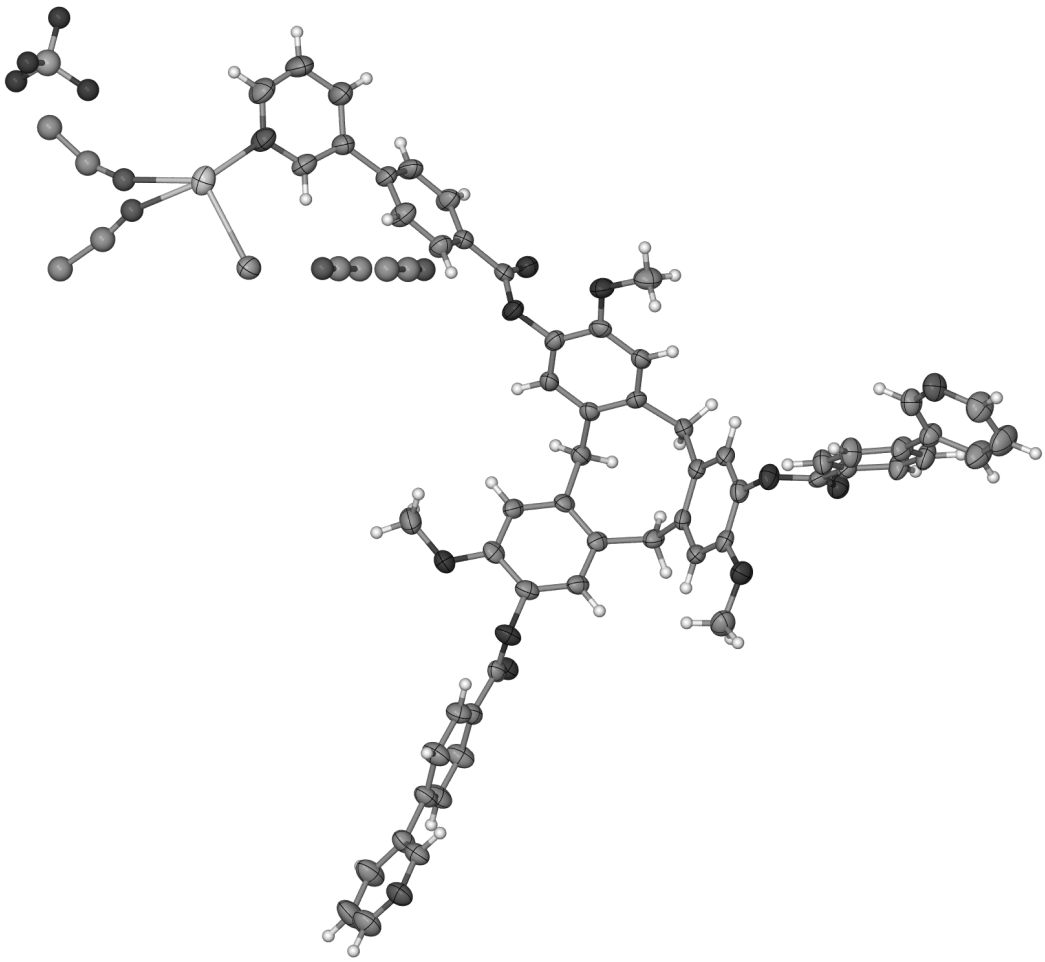


*Figure S2: From the crystal structure of complex **4** showing one complete L1 (H atoms excluded), the ClO_4^- anion and positions of disordered CH_3CN molecules. Ellipsoids are shown at 50% probability level, aside from isotropically refined atoms.*

1. Y. Gong and H. W. Pauls, *Synlett*., 2000, 829.
2. G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany, **1990.**
3. G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany, **1997.**
4. L. J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189.
5. A. Spek, P. can der Sluis, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 194.