Self-Assembly of Molecular Cylinders from Polycarbene Ligands and Ag^{I} or Au^{I}

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Supporting Information

Description of synthetic procedures. All manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130 °C prior to use. Solvents were freshly distilled by standard procedures prior to use. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard (CD_3CN, ^{1}H 1.94 ppm and $^{13}C\{^{1}H\}$ 1.32, 118.26 ppm, [d_4]MeOH, ^{1}H 3.31 ppm and $^{13}C\{^{1}H\}$ 49.00 ppm, [d_6]DMSO, ^{1}H 2.50 ppm and $^{13}C\{^{1}H\}$ 39.52 ppm). Coupling constants are expressed in Hertz. Mass spectra were obtained with MicroTof (Bruker Daltonics, Bremen), Quattro LCZ (Waters-Micromass, Manchester, UK) or Varian MAT 212 spectrometers. 1,3,5-Tribromobenzene, 1,2,4,5-Tetrabromobenzene, Ag_2O and [$Au(SMe_2)Cl$)] were purchased from commercial sources and used as received.

Synthesis of 1,2,4,5-Tetra(1-imidazolyl)benzene. 1,2,4,5-Tetrabromobenzene (0.788 g, 2.0 mmol), imidazole (1.09 g, 16.0 mmol), K_2CO_3 (1.52 g, 11.0 mmol) and $CuSO_4$ (0.02 g, 0.08 mmol) were mixed in a 50 mL flask and heated under an argon atmosphere for 24 h to 185 °C. Then the reaction mixture was cooled to ambient temperature, washed three times with water. The remaining solid residue was extracted with methanol (70 mL). The methanol solution was decolorized with activated charcoal and filtered. The filtrate was brought to dryness to give a colorless

solid. Yield: 0.273 g (0.8 mmol, 40 %). ^{1}H NMR (400 MHz, [d_4]MeOH): δ = 8.08 (s, 2H, Ar–H), 7.79 (s, 4H, N–CH–N), 7.22 (s, 4H, imidazole-H5), 7.15 ppm (s, 4H, imidazole-H4). ^{13}C{^{1}H} NMR (100 MHz, [d_4]MeOH): δ = 138.70 (N-C-N), 134.18 (Ar-CN), 130.54 (imidazole-C4), 127.52 (Ar-CH), 121.58 ppm (imidazole-C5). MS (EI, 20 eV): *m/z* (%) = 341 (100) $[M–H]^+$. Anal. Calcd (%): C, 63.14; H, 4.12; N, 32.74. Found: C, 61.64; H, 3.54; N, 32.52.

Synthesis of 1,2,4,5-Tetrakis(3-*n*butyl-1-imidazolium)benzene Tetrabromide H$_4$-1(Br)$_4$. A sample of 1,2,4,5-Tetra(1-imidazolyl)benzene (0.7 g, 2.05 mmol) was dissolved in DMF (10 mL) and *n*butylbromide (2.263 g, 16.4 mmol) was added. The reaction mixture was heated for 40 h to 100 °C. A white precipitate formed during this time. The precipitate was isolated by filtration and washed with diethyl ether. The compound was further purified by precipitation from methanolic solution using diethyl ether to give H$_4$-**1**(Br)$_4$ as a colorless solid. Yield: 1.25 g (1.41 mmol, 69 %). ^{1}H NMR (400 MHz, [d_6]DMSO): δ = 10.24 (s, 4H, N–CH–N), 8.97 (s, 2H, Ar–H), 8.14 (m, 8H, imidazole-H4 and imidazole-H5), 4.31 (t, ^{3}J = 7.18 Hz, 8H, NCH_2), 1.90 (m, 8H, NCH_2CH_2), 1.32 (m, 8H, $NCH_2CH_2CH_2$), 0.94 ppm (t, ^{3}J = 7.35 Hz, 12H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, [d_6]DMSO): δ = 138.40 (N–C–N), 130.40 (Ar-CN), 128.40 (Ar-CH), 123.60 (imidazole-C4), 122.70 (imidazole-C5), 49.40 (NCH_2), 30.80 (NCH_2CH_2), 18.70 ($CH_2CH_2CH_2$), 13.20 ppm (CH_3). MS (ESI, positive ions): *m/z* = 284.1987 (calcd for $[M–4Br–2H]^{2+}$ 284.2001). Anal. Calcd (%): C, 45.86; H, 5.66; N, 12.59. Found: C, 44.25; H, 5.85; N, 11.75.

Synthesis of 1,2,4,5-Tetrakis(3-*n*butyl-1-imidazolium)benzene Tetrakis-(hexafluorophosphate) H$_4$-1(PF$_6$)$_4$. A solution of NH_4PF_6 (0.896 g, 5.5 mmol) in methanol (3 mL) was added slowly to a solution of H$_4$-**1**(Br)$_4$ (0.886 g, 1.0 mmol) in methanol (7 mL). The white hexafluorophosphate salt H$_4$-**1**(PF$_6$)$_4$ precipitated immediately and was collected by filtration, washed with small portions of cold methanol and diethyl ether. Drying *in vacuo* gave H$_4$-**1**(PF$_6$)$_4$ as a colorless solid. Yield: 1.024 g (0.89 mmol, 89 %). ^{1}H NMR (400 MHz, CD_3CN): δ = 9.55 (s, 4H, N–CH–N), 8.64 (s, 2H, Ar–H), 8.13 (s, 4H, imidazole-H5), 7.91 (s, 4H, imidazole-H4), 4.30 (t, ^{3}J = 7.18 Hz, 8H, NCH_2), 1.84 (m, 8H, NCH_2CH_2), 1.31 (m, 8H, $CH_2CH_2CH_2$), 0.94 ppm (t, ^{3}J = 7.36 Hz, 12H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ = 137.68 (N–C–N), 131.00

(Ar-CN), 128.18 (Ar-CH), 124.01 (imidazole-C4), 123.05 (imidazole-C5), 49.59 (NCH_2), 31.03 (NCH_2CH_2), 18.68 ($CH_2CH_2CH_2$), 13.20 ppm (CH_3). MS (ESI, positive ions): *m/z* = 1005.3078 (calcd for $[M-PF_6]^+$ 1005.3075), 430.1710 (calcd for $[M-2PF_6]^{2+}$ 430.1715), 238.4593 (calcd for $[M-3PF_6]^{3+}$ 238.4595). Satisfactory microanalytical data for H_4-**1**$(PF_6)_4$ could not be obtained due to the large amount of fluorine present.

Synthesis of 1,3,5-Tris(1-imidazolyl)benzene.[1] A 100 mL flask was charged with 1,3,5-Tribromobenzene (1.26 g, 4.0 mmol), K_2CO_3 (2.21 g, 16.0 mmol), imidazole (1.63 g, 24.0 mmol), and $CuSO_4$ (0.025 g, 0.10 mmol) and the mixture was heated for 24 h to 150 °C under an argon atmosphere. The mixture was then allowed to cool to ambient temperature. It was washed with water (3 × 20 mL). The residue was extracted with dichloromethane (3 × 50 mL) and the dichloromethane solution was dried over $MgSO_4$. Removal of the solvent gave 1,3,5-Tris(1-imidazolyl)benzene as a colorless solid. Yield: 0.83 g (3.0 mmol, 75%). ^{1}H NMR (400 MHz, [d_6]DMSO): δ = 8.55 (s, 3H), 8.03 (s, 3H), 7.96 (s, 3H), 7.18 ppm (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, [d_6]DMSO): δ = 139.54, 136.57, 130.56, 118.76, 109.76 ppm. MS (EI, 20 eV): *m*/*z* (%) = 276 (100) $[M]^+$. Anal. Calcd (%): C, 65.20; H, 4. 38; N, 30.42. Found: C, 65.27; H, 4.26; N, 30.35. The NMR spectroscopic data match those reported in ref 1.

Synthesis of 1,3,5-Tris(3-ethyl-1-imidazolium)benzene Tris(hexafluoro-phosphate) H_3-2$(PF_6)_3$. A sample of 1,3,5-Tris(1-imidazolyl)benzene (1.2 g, 4.35 mmol) and ethyl bromide (4.74 g, 43.5 mmol) were dissolved in DMF (15 mL) and heated to 100 °C for 2 d. A white precipitate formed during this time which was isolated by filtration, washed with diethyl ether (3 × 15 mL) and dried *in vacuo* to yield the crude bromide salt H_3-**2**$(Br)_3$ (yield 1.97 g, 75%). The crude bromide salt was converted to H_3-**2**$(PF_6)_3$ by adding a solution of NH_4PF_6 (2.119 g, 13 mmol) in methanol (4 mL) to a methanolic solution (30 mL) of crude H_3-**2**$(Br)_3$ (1.97 g, 3.26 mmol). The white hexafluorophosphate salt precipitated immediately and was collected by filtration, washed with small portions of cold methanol and diethyl ether. Drying *in vacuo* gave H_3-**2**$(PF_6)_3$ as a colorless solid. Yield: 2.08 g (2.61 mmol, 80%). ^{1}H NMR (400 MHz, CD_3CN): δ = 9.15 (s, 3H, N–CH–N), 8.12 (s, 3H, Ar–H), 7.95 (s, 3H, imidazole-H5), 7.73 (s, 3H, imidazole-H4), 4.36 (q, ^3J = 7.33 Hz, 6H, NCH_2),

1.61 ppm (t, ^3J = 7.33 Hz, 9H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 138.25 (Ar-CN), 136.15 (N–C–N), 124.92 (imidazole-C4), 122.87 (imidazole-C5), 119.24 (Ar-CH), 47.10 (NCH_2), 15.20 ppm (CH_3). MS (ESI, positive ions): *m/z* = 653.1566 (calcd for $[M–PF_6]^+$ 653.1575), 254.0961 (calcd for $[M–2PF_6]^{2+}$ = 254.0964). Satisfactory microanalytical data for H_3-**2**$(PF_6)_3$ could not be obtained due to the large amount of fluorine present.

Synthesis of $[Ag_4(\mathbf{1})_2](X)_4$ (X = $AgBr_2^-$ and/or Br^-). A sample of H_4-**1**$(Br)_4$ (0.089 g, 0.1 mmol) was dissolved in methanol (5 mL) and to this solution was added Ag_2O (0.049 g, 0.21 mmol). The resulting suspension was heated to 50 °C for 24 h under exclusion of light. After cooling to ambient temperature, the obtained suspension was filtered. The filtrate was concentrated to 2 mL and diethyl ether (10 mL) was added leading to the formation of a white microcrystalline solid which was collected by filtration, washed with diethyl ether and dried *in vacuo*. Yield: 0.095 g (0.036 mmol, 71%). ^1H NMR (400 MHz, [d_4]MeOH): δ = 8.63 (s, 2H, Ar–H), 7.62 (s, 4H, imidazole-H4), 7.41 (s, br, 4H, imidazole-H5), 4.38 (m, 4H, NC*H*H), 4.21 (m, 4H, NCH*H*), 1.93 (m, 8H, NCH_2CH_2), 1.41 (m, 8H, $CH_2CH_2CH_2$), 1.06 ppm (t, ^3J = 7.36 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, [d_4]MeOH): δ = 182.50 (dd, ^1J(C-Ag^{107}) = 184.3 Hz, ^1J(C-Ag^{109}) = 212.9 Hz, N–C–N), 137.70 (Ar-CN), 130.12 (Ar-CH), 124.70 (imidazole-C5), 124.30 (imidazole-C4), 53.40 (NCH_2), 34.90 (NCH_2CH_2), 21.00 ($CH_2CH_2CH_2$), 14.20 ppm (CH_3). MS (ESI, positive ions): *m/z* = 391.0995 (calcd for $[Ag_4(\mathbf{1})_2]^{4+}$ 391.0969). Consistent microanalytical data for $[Ag_4(\mathbf{1})_2]X_4$ could not be obtained as the relative amounts of anions ($[AgBr_2]^-$ or Br^-) varied.

Synthesis of $[Ag_4(\mathbf{1})_2](PF_6)_4$: A sample of H_4-**1**$(PF_6)_4$ (0.115 g, 0.1 mmol) was dissolved in acetonitrile (7 mL) and to this solution was added Ag_2O (0.051 g, 0.22 mmol). The suspension was heated to 50 °C under exclusion of light until all Ag_2O was used up. After cooling to ambient temperature, the resulting suspension was filtered. The filtrate was concentrated to 3 mL and addition of diethyl ether (15 mL) induced precipitation of a white solid which was collected by filtration, washed with diethyl ether and dried *in vacuo*. Yield: 0.082 g (0.038 mmol, 76%). ^1H NMR (400 MHz, CD_3CN): δ = 7.95 (s, 2H, Ar–H), 7.38 (s, 4H, imidazole-H5), 6.82 (s, br, 4H, imidazole-H4), 4.12–4.16 (m, 8H, NCH_2), 1.79 (m, br, 8H, NCH_2CH_2), 1.28 (m, br,

8H, $CH_2CH_2CH_2$), 0.94 ppm (t, ^3J = 7.33 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 181.30 (N–C–N), 136.96 (Ar-CN), 129.71 (Ar-CH), 124.31 (imidazole-C5), 118.50 (imidazole-C4), 53.11 (NCH_2), 34.33 (NCH_2CH_2), 20.54 ($CH_2CH_2CH_2$), 14.11 ppm (CH_3). MS (ESI, positive ions): *m/z* = 927.1598 (calcd for $[M–2PF_6]^{2+}$ 927.1586), 569.7846 (calcd for $[M–3PF_6]^{3+}$ 569.7842), 391.1008 (calcd for $[M–4PF_6]^{4+}$ 391.0969). Satisfactory microanalytical data for $[Ag_4(\mathbf{1})_2](PF_6)_4$ could not be obtained due to the large amount of fluorine present.

Transmetalation of $[Ag_4(1)_2](PF_6)_4$ to $[Au_4(1)_2](PF_6)_4$. A solution of $[Ag_4(\mathbf{1})_2](PF_6)_4$ (0.107 g, 0.05 mmol) in acetonitrile (8 mL) was treated with solid $[AuCl(SMe_2)]$ (0.059 g, 0.2 mmol). During the addition a white and a purple solid precipitated from the reaction mixture. The reaction mixture was stirred at ambient temperature for 12 h and then slowly filtered to get a clear filtrate. The filtrate was added slowly into diethyl ether (20 mL). Upon this addition a white solid precipitated which was collected by filtration, washed with diethyl ether and dried *in vacuo* without heating to give $[Au_4(\mathbf{1})_2](PF_6)_4$ as a colorless solid. Yield: 0.081 g (0.0324 mmol, 65%). ^1H NMR (400 MHz, CD_3CN): δ = 8.00 (s, 2H, Ar–H), 7.41 (s, br, 8H, imidazole-H4 and imidazole-H5), 4.21 (m, br, 8H, NCH_2), 1.83 (m, br, 8H, NCH_2CH_2), 1.31 (m, br, 8H, $CH_2CH_2CH_2$), 0.96 ppm (t, ^3J = 7.23 Hz, 12H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 183.91 (N–C–N), 136.30 (Ar-CN), 130.3 (Ar-CH), 124.60 (imidazole-C4 and imidazole-C5), 52.50 (NCH_2), 34.20 (NCH_2CH_2), 20.50 ($CH_2CH_2CH_2$), 14.10 ppm (CH_3). MS (ESI, positive ions): *m/z* = 688.5323 (calcd for $[M–3PF_6]^{3+}$ 688.5326), 639.8751 (calcd for $[M–4PF_6–H]^{3+}$ 639.8753), 480.1578 (calcd for $[M–4PF_6]^{4+}$ 480.1583). Satisfactory microanalytical data for $[Au_4(\mathbf{1})_2](PF_6)_4$ could not be obtained due to the large amount of fluorine present. The mass spectrometry data and the multiplicity of the N–C–N singnal in the $^{13}C\{^1H\}$ NMR spectrum clearly show the successful transmetallation while the chemical shift data are less informative.

Synthesis of $[Ag_3(2)_2](PF_6)_3$. To a mixture of H_3-$\mathbf{2}(PF_6)_3$ (0.399 g, 0.50 mmol) and Ag_2O (0.179 g, 0.77 mmol) was added acetonitrile (6 mL). The suspension was heated to 60 °C for 24 h under exclusion of light. After cooling to ambient temperature, the obtained suspension was filtered. The filtrate was concentrated to 3 mL and diethyl ether (15 mL) was added. Upon addition of diethyl ether a white solid

precipitated which was collected by filtration, washed with diethyl ether and dried *in vacuo*. Yield: 0.320 g (0.216 mmol, 86%). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.77 (s, 3H, Ar–H), 7.41 (d, ^{3}J = 1.92 Hz, 3H, imidazole-H5), 7.40 (d, ^{3}J = 1.92 Hz, 3H, imidazole-H4), 4.29 (q, ^{3}J = 7.3 Hz, 6H, NCH_2), 1.51 ppm (t, ^{3}J = 7.3 Hz, 9H, CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, CD_3CN): δ = 181.19 (N–C–N), 142.73 (Ar-CN), 123.54 (imidazole-C4), 123.27 (imidazole-C5), 122.42 (Ar-CH), 48.18 (NCH_2), 17.41 ppm (CH_3). MS (ESI, positive ions): *m/z* = 1335.0643 (calcd for $[M–PF_6]^+$ 1335.0551), 595.0459 (calcd for $[M–2PF_6]^{2+}$ 595.0452), 348.3745 (calcd for $[M–3PF_6]^{3+}$ 348.3752). Satisfactory microanalytical data for $[Ag_3(\mathbf{2})_2](PF_6)_3$ could not be obtained due to the large amount of fluorine present.

Transmetalation of $[Ag_3(2)_2](PF_6)_3$ to $[Au_3(2)_2](PF_6)_3$. A sample of $[Ag_3(\mathbf{2})_2](PF_6)_3$ (0.104 g, 0.07 mmol) was dissolved in acetonitrile (8 mL) and to this solution was added solid $[AuCl(SMe_2)]$ (0.062 g, 0.21mmol). A white solid started to precipitate immediately. The mixture was left stirring at ambient temperature for 12 h. The reaction mixture was then filtered until a clear filtrate was obtained. The filtrate was added slowly to diethyl ether (20 mL) to obtain a white microcrystalline solid which was collected by filtration, washed with diethyl ether and dried *in vacuo* without heating. Yield: 0.073 g (0.042 mmol, 60%). ^{1}H NMR (400 MHz, CD_3CN): δ = 7.81 (s, 3H, Ar–H), 7.43 (d, ^{3}J = 1.98 Hz, 3H, imidazole-H5), 7.35 (d, ^{3}J = 1.98 Hz, 3H, imidazole-H4), 4.36 (m, 6H, NCH_2), 1.57 ppm (t, ^{3}J = 7.29 Hz, 9H, CH_3). ^{13}C NMR (100 MHz, CD_3CN): δ = 183.67 (N–C–N), 141.36 (Ar-CN), 124.15 (imidazole-C4), 123.65 (Ar-CH), 123.61 (imidazole-C5), 47.75 (NCH_2), 17.12 ppm (CH_3). MS (ESI, positive ions): *m/z* = 1601.2362 (calcd for $[M–PF_6]^+$ 1601.2405), 728.1372 (calcd for $[M–2PF_6]^{2+}$ 728.1381), 437.1033 (calcd for $[M–3PF_6]^{3+}$ 437.1040). Satisfactory microanalytical data for $[Au_3(\mathbf{2})_2](PF_6)_3$ could not be obtained due to the large amount of fluorine present. The mass spectrometry data clearly show the successful transmetallation.

X-ray Crystallography. Diffraction data were collected at T = 153(2) K with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were

found with the SHELXS-97[2] package using direct methods and were refined with SHELXL-97[2] against $|F^2|$ using first isotropic and later anisotropic thermal parameters (for exceptions see description of the individual molecular structures). Hydrogen atoms were added to the structure models in calculated positions.

$[Ag_4(\mathbf{1})_2](PF_6)_4 \cdot 2CH_3CN$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetonitrile solution of $[Ag_4(\mathbf{1})_2](PF_6)_4$. $C_{72}H_{98}N_{18}Ag_4F_{24}P_4$, M = 2227.04, colorless crystal, 0.18 × 0.05 × 0.03 mm, monoclinc, space group $P2_1/n$, Z = 4, a = 13.6501(6), b = 23.1296(14), c = 20.1054(8) Å, β = 99.1950(10)°, V = 9246.2(7) Å^3, ρ_{calc} = 1.600 g·cm^{-3}, μ = 1.002 mm^{-1}, ω- and ϕ-scans, 94622 measured intensities ($2.4° \le 2\theta \le 56.0°$), λ = 0.71073 Å, semiempirical absorption correction ($0.8403 \le T \le 0.9706$), 22312 independent (R_{int} = 0.0728) and 14468 observed intensities ($I \ge 2\sigma(I)$), refinement of 1108 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0508, wR = 0.1093, R_{all} = 0.0952, wR_{all} = 0.1287. The asymmetric unit contains one formula unit. The terminal carbon atoms of some of the *N-n*butyl substituents exhibit large anisotropic thermal parameters. A potential disorder of these atoms could not be resolved.

$[Au_3(\mathbf{2})_2](PF_6)_3 \cdot 0.5Et_2O \cdot 1.5CH_3CN \cdot 0.5(CH_3)_2CO$. Crystals suitable for an X-ray diffraction study were obtained by diffusion of diethyl ether into a saturated acetone/acetonitrile solution of $[Au_3(\mathbf{2})_2](PF_6)_3$. $C_{48.5}H_{60.5}N_{13.5}Au_3F_{18}OP_3$, M = 1874.41, colorless crystal, 0.27 × 0.13 × 0.03 mm, monoclinc, space group $P2_1/c$, Z = 4, a = 15.020(2), b = 21.071(3), c = 22.150(3) Å, β = 90.546(2)°, V = 7010(2) Å^3, ρ_{calc} = 1.776 g·cm^{-3}, μ = 6.422 mm^{-1}, ω- and ϕ-scans, 81172 measured intensities ($2.7° \le 2\theta \le 60.0°$), λ = 0.71073 Å, semiempirical absorption correction ($0.2760 \le T \le 0.8307$), 20444 independent (R_{int} = 0.0386) and 15487 observed intensities ($I \ge 2\sigma(I)$), refinement of 781 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0392, wR = 0.1019, R_{all} = 0.0605, wR_{all} = 0.1135. The asymmetric unit contains one formula unit. Positional parameters for the atoms of solvent molecules in the asymmetric unit (3 × ½ CH_3CN, ½ $(CH_3)_2CO$ and ½ Et_2O, SOF = 1/2 for all solvent atoms) have been refined with

isotropic thermal parameters and no hydrogen positions have been calculated for the solvent molecules.

References

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(2) *SHELXS-97*, *SHELXL-97*, G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

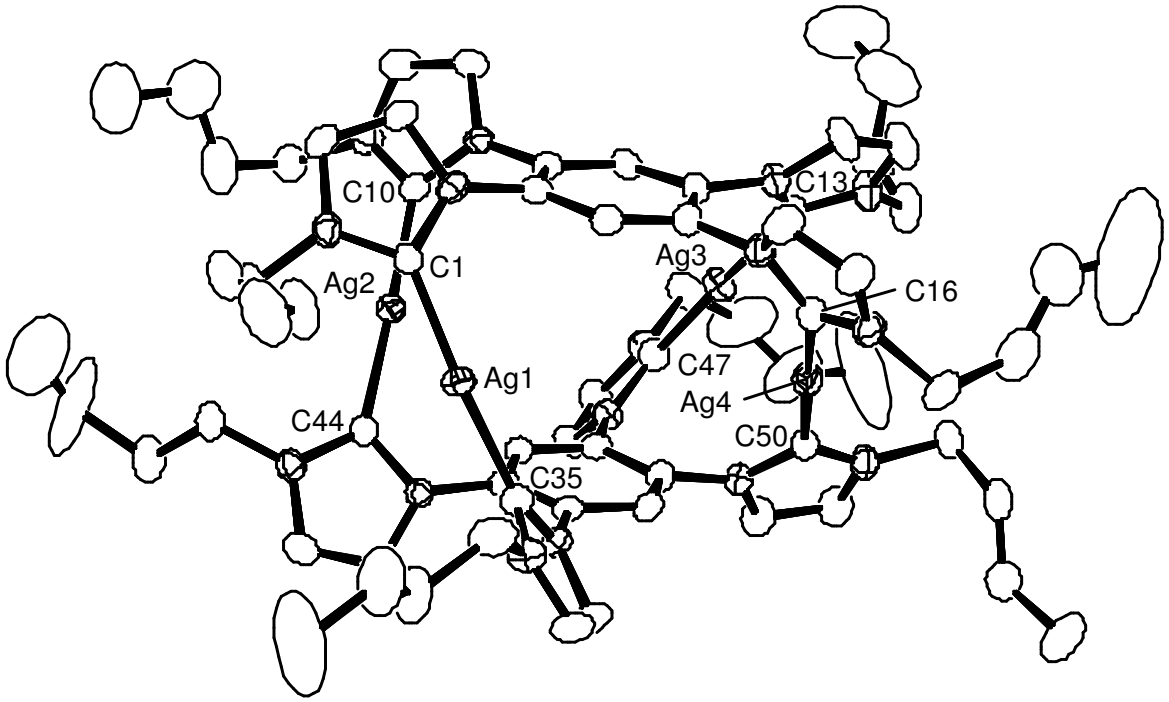

Figure S1. Molecular structure of the tetracation $[Ag_4(\mathbf{1})_2]^{4+}$ in $[Ag_4(\mathbf{1})_2](PF_6)_4 \cdot 2CH_3CN$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability limit. Selected bond lengths (Å) and bond angles (°): Ag1–C1 2.073(4), Ag1–C35 2.078(4), Ag2–C10 2.081(4), Ag2–C44 2.089(4), Ag3–C13 2.083(5), Ag3–C47 2.086(5), Ag4–C16 2.083(5), Ag4–C50 2.086(5); C1–Ag1–C35 175.2(2), C10–Ag2–C44 178.5(2), C13–Ag3–C47 177.9(2), C16–Ag4–C50 177.4(2).

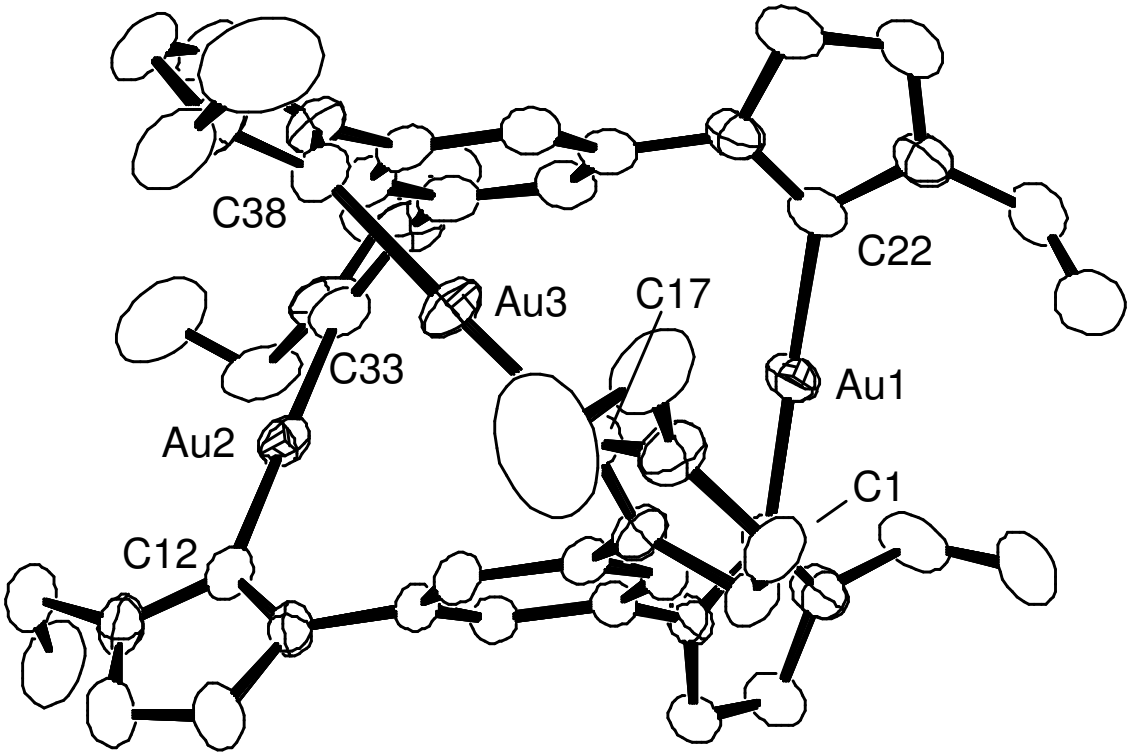

Figure S2. Molecular structure of the trication $[Au_3(\mathbf{2})_2]^{3+}$ in $[Au_3(\mathbf{3})_2](PF_6)_3 \cdot 0.5Et_2O \cdot 1.5CH_3CN \cdot 0.5(CH_3)_2CO$. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability limit. Selected bond lengths (Å) and bond angles (°): Au1–C1 2.010(5), Au1–C22 2.017(5), Au2–C12 2.014(6), Au2–C33 2.018(6), Au3–C17 2.009(5), Au3–C38 2.011(5); C1–Au1–C22 176.2(2), C12–Au2–C33 177.2(2), C17–Au3–C38 176.4(2).