Supporting Information

Three's Company: Co-crystallization of a Self-Assembled S_4 Metallacyclophane with Two Diastereomeric Metallacycle Intermediates

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Table of Contents:

S1. Experimental Procedures
S3. X-ray Crystallography
S5. Crystallographic Data: $[As_4\mathbf{L^1}_2Cl_4]\cdot C_2H_2Cl_4$
S7. Crystallographic Data: $[As_4\mathbf{L^1}_2Cl_4]\cdot$*cis*-$[As_2\mathbf{L^1}Cl_2]\cdot$*trans*-$[As_2\mathbf{L^1}Cl_2]\cdot CH_2Cl_2$
S10. NMR Spectra
S14. MALDI data
S15. References

1. Experimental Procedures

General: Commercially available reagents were used as received without further purification. ^{1}H NMR spectra were measured using a Varian INOVA-600 spectrometer. Spectra were referenced using the residual solvent signal as an internal standard.

Preparation of 1,2,4,5-tetrakis(bromomethyl)benzene: This compound was synthesized by modification of the literature procedure from Suzuki *et al*.[1] Durene (5.599g, 41.7 mmol), N-bromosuccimide (33.284g, 187 mmol) and benzoyl peroxide (10 mg, 0.041 mmol) were combined in dry chloroform (300 mL) and irradiated by a 300 W tungsten lamp for 10 h while being heated to reflux. After cooling, succinimide was removed by filtration. After the solvent was evaporated from the filtrate, the crude reaction product was suspended in methanol (100 mL) and then filtered and washed with methanol to give 1,2,4,5-tetrakis(bromomethyl)benzene (7.755 g, 41%) as a white solid. ^{1}H NMR ($CDCl_3$): δ = 7.37 (s, 2H, C*H*), 4.60 (s, 8H, CH_2).

Preparation of 1,2,4,5-tetrakis(mercaptomethyl)benzene: This compound was synthesized by modification of the literature procedure from Tanaka *et al.*[2] 1,2,4,5-tetrakis(bromomethyl)benzene (7.546 g, 16.8 mmol) and thiourea (6.653 g, 87.4 mmol) were heated to reflux in 200 mL anhydrous ethanol under N_2 for 1 h. After the reaction was allowed to cool, the salt product was filtered and washed with ethanol, dried over vacuum overnight, and then placed under N_2. 400 mL of degassed 2M KOH (aq) was transferred via cannula into the reaction vessel containing the salt, and the resulting solution was stirred at 80 °C under N_2 for 3 h. The reaction was cooled to 0 °C, at which point the solution was acidified with degassed 6M HCl (transferred via cannula). The white solid that precipitated out of solution was filtered using air free techniques and allowed to dry overnight under vacuum. 1,2,4,5-tetrakis(mercaptomethyl)benzene (2.12 g, 48%) was stored under argon to prevent disulfide formation. ^{1}H NMR ($CDCl_3$): δ = 7.20 (s, 2H, C*H*), 3.82 (d, 8H, CH_2, J = 7 Hz), 1.87 (t, 4H, S*H*, J = 7 Hz).

Preparation of [$As_4L^1{}_2Cl_4$]·$C_2H_2Cl_4$: 1,2,4,5-tetrakis(mercaptomethyl)benzene ($H_4\mathbf{L^1}$, 8.7 mg, 0.033 mmol) was suspended in 1.3 mL 1,1,2,2-tetrachloroethane-d_2 in a scintillation vial. $AsCl_3$ (5.70 µL, 0.0668 mmol) was added to the vial and the mixture placed in a sonicator for 15 min. The reaction vessel was left overnight at ambient temperature, after which the residual solid (undissolved starting material and a small amount of polymeric byproduct) was filtered off with a Whatman® PURADISC™ 25 TF 0.45 µm PTFE Membrane with Polypropylene Housing filter device. Colorless single crystals suitable for x-ray diffraction were grown out of the filtrate after three days at ambient temperature. Crystal packing is shown in Figures S1 and S2. [$As_4\mathbf{L^1}{}_2Cl_4$] ^{1}H NMR ($C_2D_2Cl_4$): δ = 7.38 (s, 4H, C*H*), 4.57 (d, 4H, CH_2, J = 14.6 Hz), 4.22 (d, 4H, CH_2, J = 13.4 Hz), 4.01 (d, 4H, CH_2, J = 14.6 Hz), 3.96 (d, 4H, CH_2, J = 13.4 Hz). *Cis/trans*-[$As_2\mathbf{L^1}Cl_2$] also present in solution as indicated by ^{1}H spectrum (Figure S6 and Figure S7). *Cis*-[$As_2\mathbf{L^1}Cl_2$] ^{1}H NMR ($C_2D_2Cl_4$): δ = 7.23 (s, 2H, C*H*), 5.10 (d, 4H, CH_2, J = 15.1 Hz), 4.00 (d, 4H, CH_2, J = 15.1 Hz). *Trans*-[$As_2\mathbf{L^1}Cl_2$] ^{1}H NMR ($C_2D_2Cl_4$): δ = 7.23 (s, 2H, C*H*), 5.07 (d, 4H, CH_2, J = 15.1 Hz), 4.00 (d, 4H, CH_2, J = 15.1 Hz).

Preparation of $[As_4L^1{}_2Cl_4]\cdot$*cis*-$[As_2L^1Cl_2]\cdot$*trans*-$[As_2L^1Cl_2]\cdot CH_2Cl_2$: 1,2,4,5-tetrakis(mercaptomethyl)benzene ($H_4\mathbf{L^1}$, 13.3 mg, 0.051 mmol) was suspended in 4 mL dichloromethane in a scintillation vial. $AsCl_3$ (8.65 µL, 0.101 mmol) was added to the vial and the mixture was placed in a sonicator for 15 min. The reaction vessel was left overnight at ambient temperature, after which the residual solid (undissolved starting material and a small amount of polymeric byproduct) was filtered off with a Whatman® PURADISC™ 25 TF 0.45 µm PTFE Membrane with Polypropylene Housing filter device. Colorless single crystals suitable for x-ray diffraction were grown out of the filtrate after two weeks at ambient temperature. Crystal packing is shown in Figures S3, S4, and S5. $[As_4\mathbf{L^1}{}_2Cl_4]$ ^{1}H NMR (CD_2Cl_2): δ = 7.39 (s, 4H, C*H*), 4.58 (d, 4H, CH_2, J = 14.6 Hz), 4.24 (d, 4H, CH_2, J = 13.5 Hz), 4.00 (d, 4H, CH_2), 4.00 (d, 4H, CH_2). *Cis*-$[As_2\mathbf{L^1}Cl_2]$ ^{1}H NMR (CD_2Cl_2): δ = 7.22 (s, 2H, C*H*), 5.09 (d, 4H, CH_2, J = 15.2 Hz), 4.00 (d, 4H, CH_2, J = 15.2 Hz). *Trans*-$[As_2\mathbf{L^1}Cl_2]$ ^{1}H NMR (CD_2Cl_2): δ = 7.23 (s, 2H, C*H*), 5.13 (d, 4H, CH_2, J = 14.6 Hz), 4.00 (d, 4H, CH_2, J = 14.6 Hz).

Mass Spectrometry Experiments: Laser Desorption Experiments were performed on a Waters Micromass Q-TOF Premier MALDI mass spectrometer (Milford, MA USA) using V-Optics and positive ionization mode. Samples were prepared by spotting the crystallization reaction in 1,1,2,2-tetrachloroethane directly onto the sample plate without a matrix. However, only the $[As_2LCl_2]$ species were observed, with sodium adducts of the species resulting from the direct laser desorption technique: $[As_2\mathbf{L^1}Cl_2 + Na]$, 500.73, calc. 500.74.

X-ray crystallography:

Crystallographic Data for $[As_4\mathbf{L^1}{}_2Cl_4]\cdot C_2H_2Cl_4$ complex: $C_{24}H_{24}As_4Cl_{12}S_8$, M = 1293.99, 0.32 x 0.22 x 0.12 mm, T = 173 K, monoclinic, space group $P2_1/c$, a = 17.9104(11) Å, b = 25.7564(16) Å, c = 18.9947(12) Å, β = 93.086(1)°, V = 8749.7(9) Å^3, Z = 8, Z' = 2, D_c = 1.965 Mg/m^3, μ = 4.166 mm^{-1}, F(000) = 5056, $2\theta_{max}$ = 27.00°, 97922 reflections, 19054 independent reflections [R_{int} = 0.0341], R1 = 0.0476, wR2 = 0.1486 and GOF = 1.286 for 15435 reflections (757 parameters) with I>2σ(I), R1 = 0.0579,

wR2 = 0.1554 and GOF = 1.286 for all reflections, max/min residual electron density +2.710/-1.576 eÅ^3.

Crystallographic Data for $[As_4\mathbf{L^1}_2Cl_4]\cdot$*cis*-$[As_2\mathbf{L^1}Cl_2]\cdot$*trans*-$[As_2\mathbf{L^1}Cl_2]\cdot CH_2Cl_2$ complex: $C_{37}H_{39}As_7Cl_{11}S_{14}$, M = 1846.91, 0.18 x 0.12 x 0.08 mm, T = 173(2) K, triclinic, space group *P*-1, a = 14.3168(10) Å, b = 14.5379(10) Å, c = 16.8865(11) Å, α = 80.564(1)°, β = 80.511(1)°, γ = 61.527(1)°, V = 3032.5(4) Å^3, Z = 2, D_c = 2.023 Mg/m^3, μ = 4.808 mm^{-1}, F(000) = 1806, $2\theta_{max}$ = 27.00°, 34380 reflections, 13158 independent reflections [R_{int} = 0.0280], R1 = 0.0313, wR2 = 0.0721 and GOF = 1.028 for 11084 reflections (649 parameters) with I>2σ(I), R1 = 0.0406, wR2 = 0.0766 and GOF = 1.029 for all reflections, max/min residual electron density +1.166/-1.107 eÅ^3.

Diffraction intensities for $[As_4\mathbf{L^1}_2Cl_4]\cdot C_2H_2Cl_4$ and $[As_4\mathbf{L^1}_2Cl_4]\cdot$*cis*-$[As_2\mathbf{L^1}Cl_2]\cdot$*trans*-$[As_2\mathbf{L^1}Cl_2]\cdot CH_2Cl_2$ were collected at 173(2) K on a Bruker Apex CCD diffractometer using MoKα radiation λ= 0.71073 Å. Space groups were determined based on systematic absences ($[As_4\mathbf{L^1}_2Cl_4]\cdot C_2H_2Cl_4$) and intensity statistics ($[As_4\mathbf{L^1}_2Cl_4]\cdot$*cis*-$[As_2\mathbf{L^1}Cl_2]\cdot$*trans*-$[As_2\mathbf{L^1}Cl_2]\cdot CH_2Cl_2$). Absorption corrections were applied by SADABS.[3] Structures were solved by direct methods and Fourier techniques and refined on F2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms were refined in calculated positions in a rigid group model. In the crystal structure of $[As_4\mathbf{L^1}_2Cl_4]\cdot C_2H_2Cl_4$ there are four solvent molecules, $C_2H_2Cl_4$. Two of them are highly disordered and were treated by SQUEEZE;[4] corrections of the X-ray data by SQUEEZE (645 electron/cell) is close to the required values (656 electron/cell) for eight molecules in the full unit cell. In the crystal structure of $[As_4\mathbf{L^1}_2Cl_4]\cdot$*cis*-$[As_2\mathbf{L^1}Cl_2]\cdot$*trans*-$[As_2\mathbf{L^1}Cl_2]\cdot CH_2Cl_2$ there are two solvent molecules, CH_2Cl_2. One of these molecules is disordered over two positions in ratio 1:1. This disordered solvent molecule was refined with restrictions; the average C—Cl distance of 1.779 Å was used as a target for corresponding C—Cl bonds. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.[5] CCDC 743840 and CCDC 743841 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

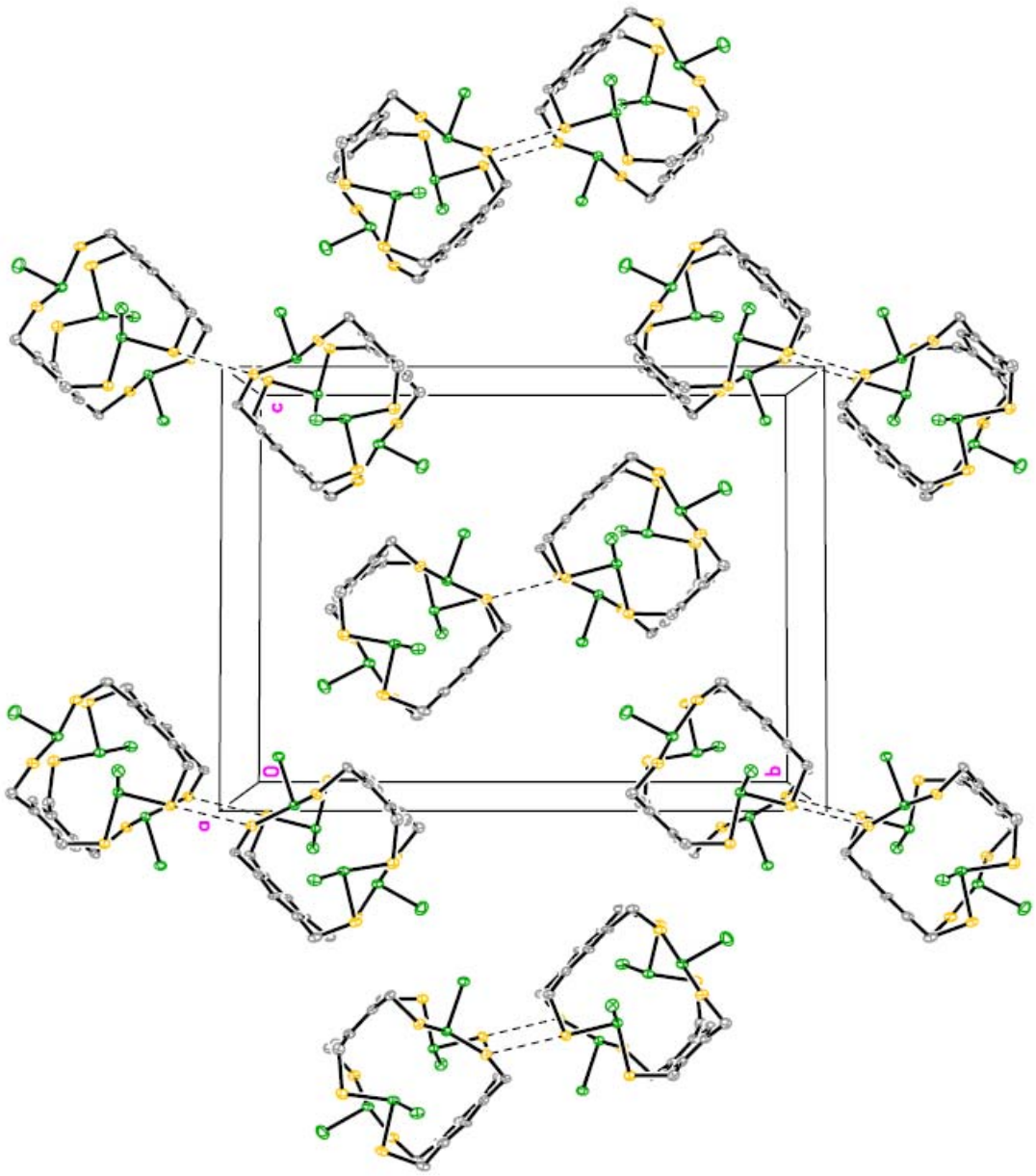

Figure S1. Crystal packing of $[As_4\mathbf{L}^1{}_2Cl_4]\cdot C_2H_2Cl_4$ showing intermolecular close-contacts. Solvent molecules are removed for clarity.

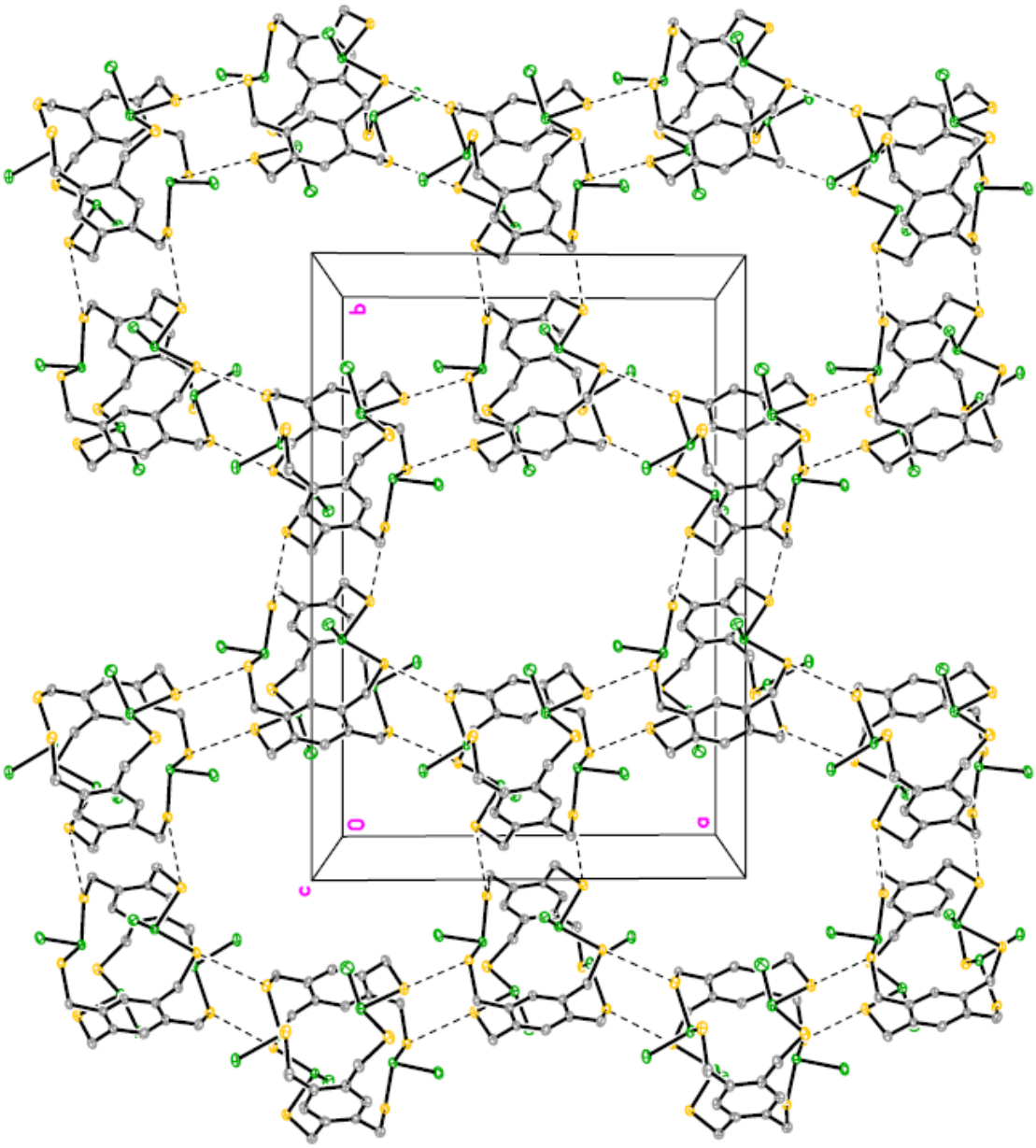

Figure S2. Crystal packing of $[As_4\mathbf{L}^1{}_2Cl_4]\cdot C_2H_2Cl_4$ showing intermolecular close-contacts. Solvent molecules are removed for clarity.

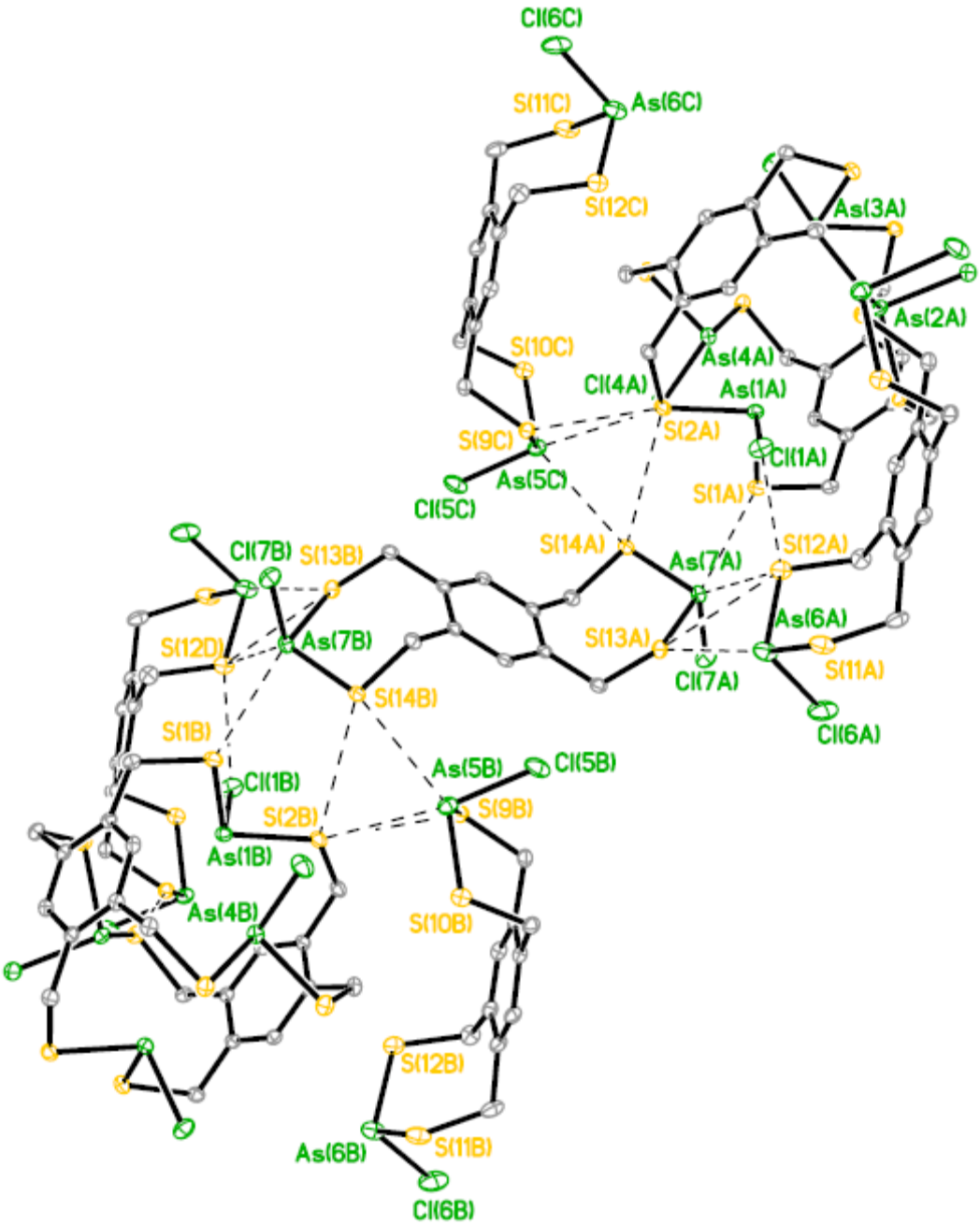

Figure S3. Crystal packing of $[As_4\mathbf{L}^1{}_2Cl_4]\cdot$*cis*-$[As_2\mathbf{L}^1Cl_2]\cdot$*trans*-$[As_2\mathbf{L}^1Cl_2]\cdot CH_2Cl_2$ showing intermolecular close-contacts. Solvent molecules are removed for clarity.

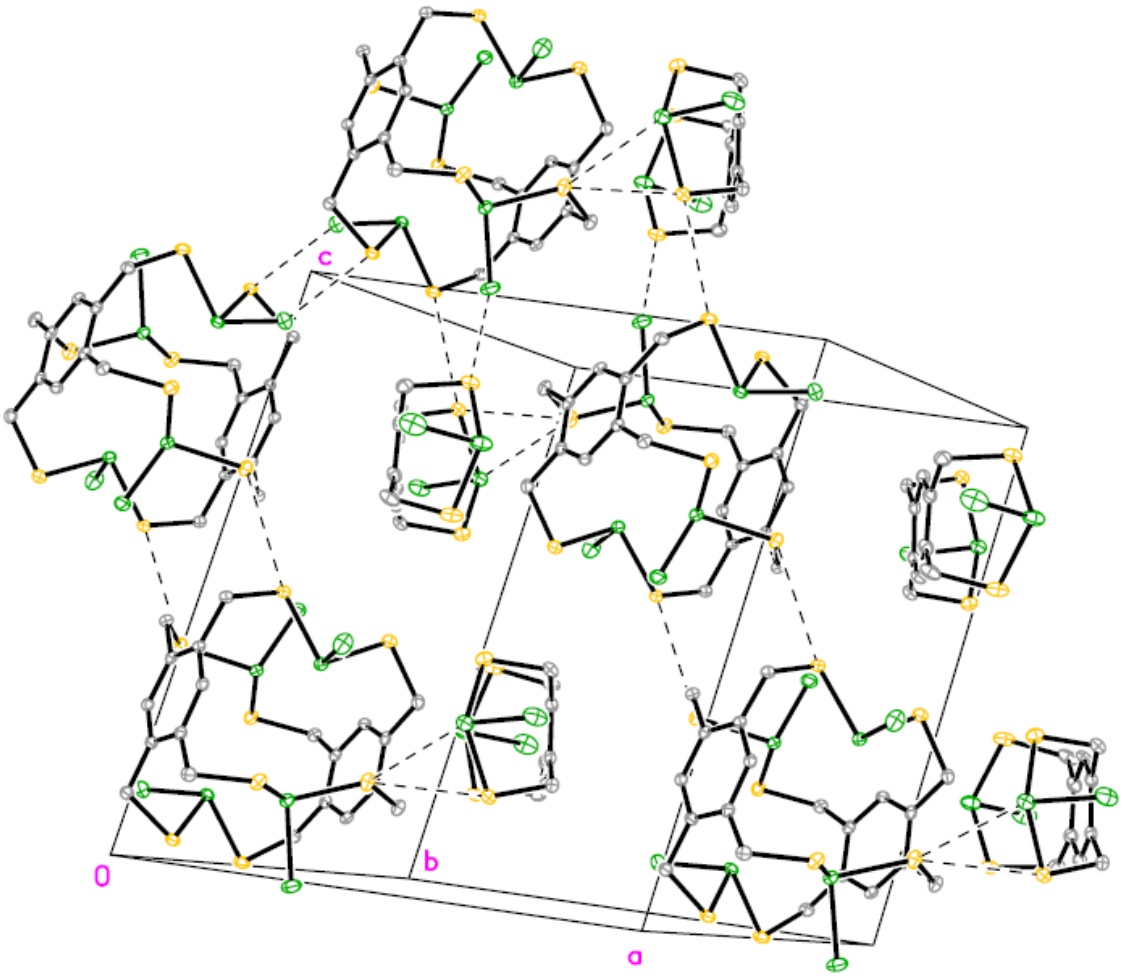

Figure S4. Crystal packing of $[As_4\mathbf{L}^1{}_2Cl_4]\cdot$*cis*-$[As_2\mathbf{L}^1Cl_2]\cdot$*trans*-$[As_2\mathbf{L}^1Cl_2]\cdot CH_2Cl_2$ showing intermolecular close-contacts. Solvent molecules are removed for clarity.

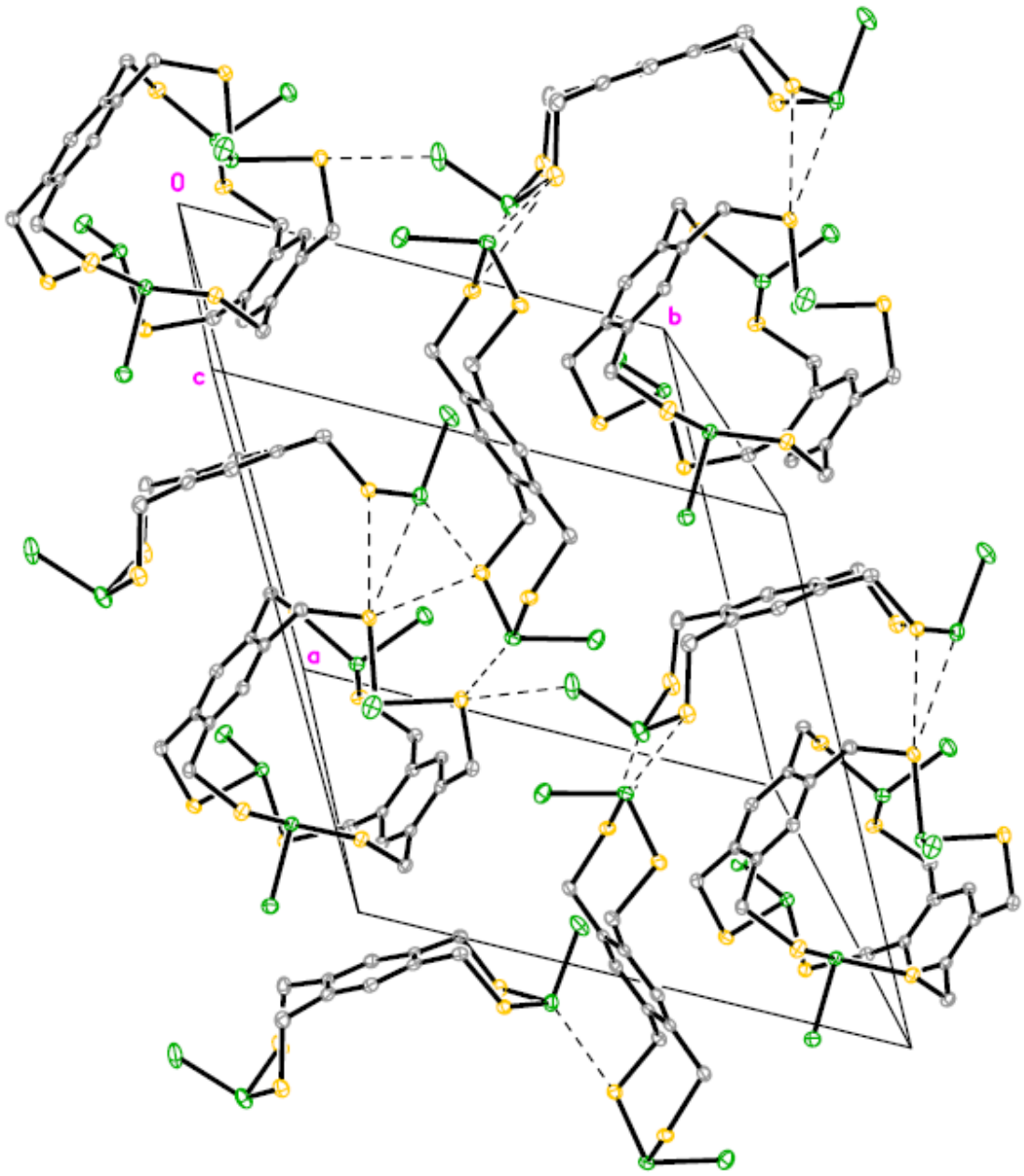

Figure S5. Crystal packing of $[As_4\mathbf{L}^1{}_2Cl_4]\cdot$*cis*-$[As_2\mathbf{L}^1Cl_2]\cdot$*trans*-$[As_2\mathbf{L}^1Cl_2]\cdot CH_2Cl_2$ showing intermolecular close-contacts. Solvent molecules are removed for clarity.

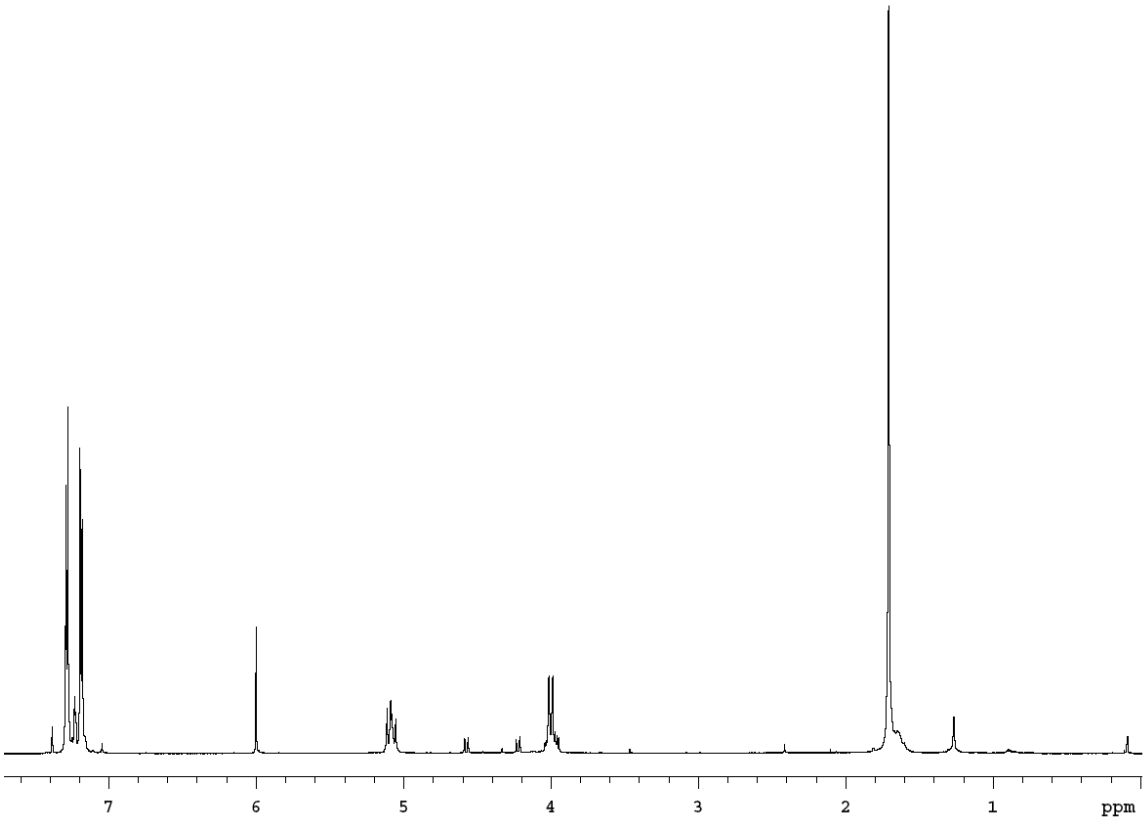

Figure S6. ^{1}H NMR spectra of Scheme 1 in 1,1,2,2-tetrachloroethane. Peaks indicative of [As_4**L**$^{1}{}_2Cl_4$], *cis*-[As_2**L**$^{1}Cl_2$], and *trans*-[As_2**L**$^{1}Cl_2$] are all present following this workup.

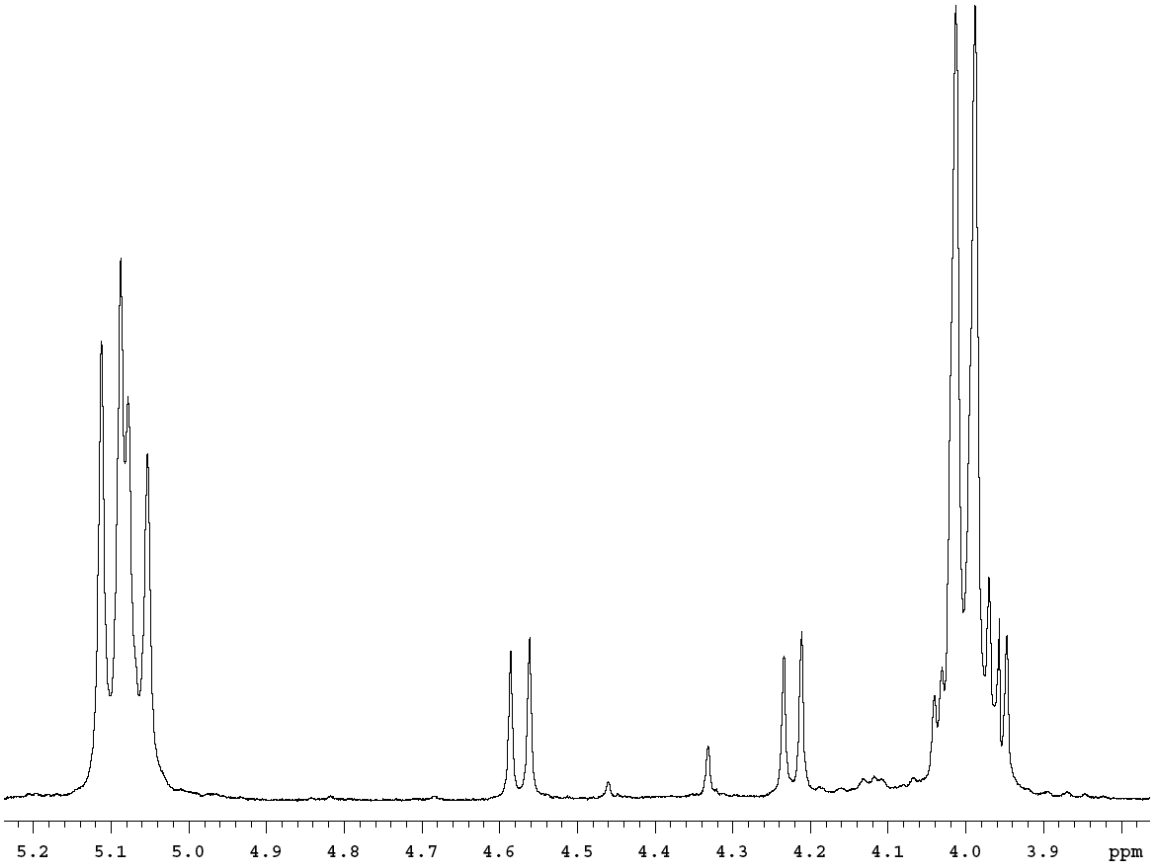

Figure S7. Inset of the methylene region of Figure S6.

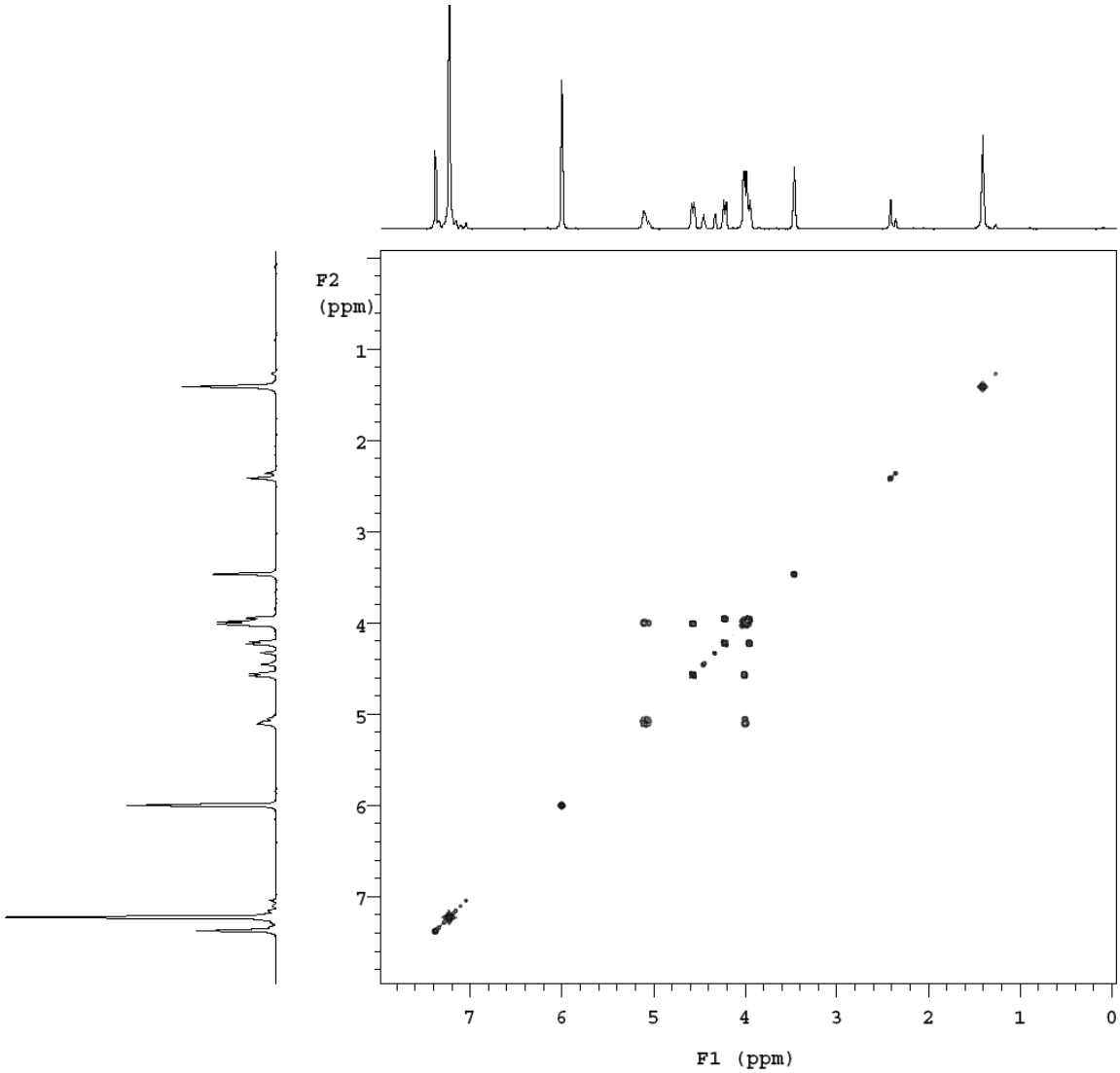

Figure S8. *g*COSY spectrum of Scheme 1 in 1,1,2,2-tetrachloroethane. Cross-peaks confirm geminal coupling of protons in $[As_4\mathbf{L^1}_2Cl_4]$, *cis*-$[As_2\mathbf{L^1}Cl_2]$, and *trans*-$[As_2\mathbf{L^1}Cl_2]$ assemblies.

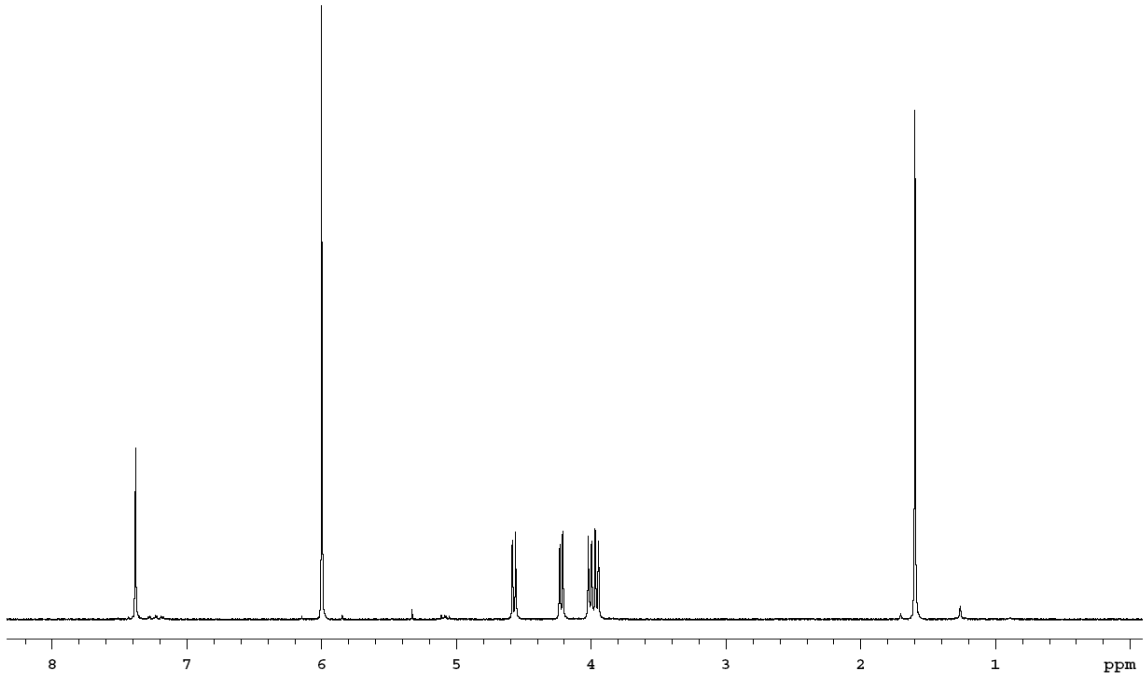

Figure S9. ^{1}H NMR of redissolved $[As_4\mathbf{L^1}_2Cl_4]\cdot C_2H_2Cl_4$ single crystals in 1,1,2,2-tetrachloroethane-d_2.

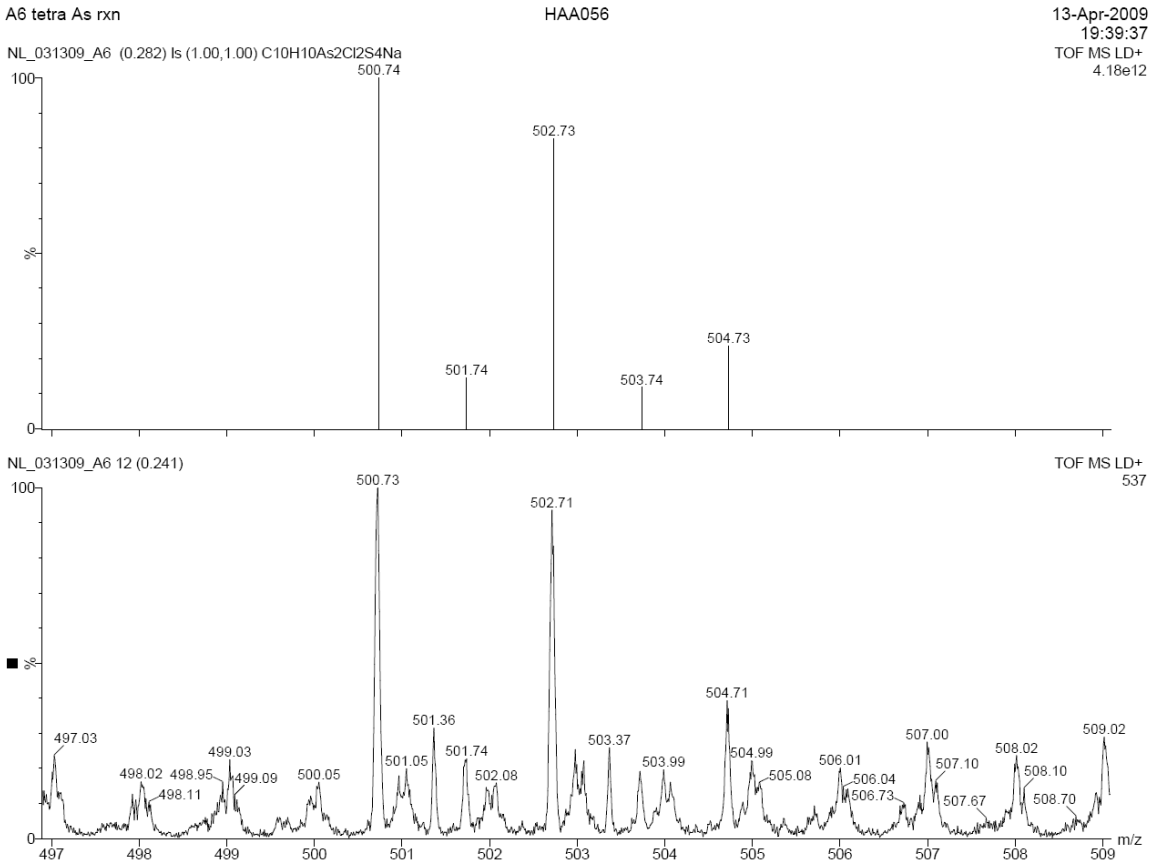

Figure S10. MALDI spectra for [As_2**L**^{1}Cl_2] metallacycles: [As_2**L**^{1}Cl_2 + Na], 500.73, calc. 500.74.

References:

[1] H. Kawai, T. Umehara, K. Fujiwara, T. Tsuji and T. Suzuki, *Angew. Chem., Int. Ed. Engl.,* 2006, **45**, 4281-4286.
[2] T. Otsubo, Y. Aso, F. Ogura, S. Misumi, A. Kawamoto and J. Tanaka, *Bull. Chem. Soc. Jpn.,* 1989, **62**, 164-170.
[3] G. M. Sheldrick, *Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, 1998.
[4] P. Van der Sluis and A. L. Spek, *Acta Cryst., Sect. A,* 1990, **A46**, 194-201.
[5] SHELXTL-6.10 "Program for Structure Solution, Refinement, and Presentation" BRUKER AXS Inc., 5464 East Cheryl Parkway, Madison, WI 53711-5373 USA.