Electronic Supplementary Material (ESI) for Dalton Transactions




# Toward Molecular Rotors: Tetra-*N*-Heterocyclic Carbene Ag(I)-Halide Cubane-type Clusters

## Supporting Information

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# Crystallographic Reports

## Crystallographic report for bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (**3a**)

**Data collection.** A suitable prism was selected (0.100, 0.402, 0.554 mm), which was adhered to a fine nylon loop with a tiny bit of fluorocarbon oil; the loop was epoxied to a stout glass fibre mounted on a pin; the pin was placed on a goniometer head. The crystallographic properties and data were collected using MoKα radiation and the charge-coupled area detector (CCD) detector on an Oxford Diffraction Systems Gemini S diffractometer at 101.0 (+/- 1.0) K.[1] A preliminary set of cell constants was calculated from reflections observed on three sets of 5 frames which were oriented approximately in mutually orthogonal directions of reciprocal space. Data collection was carried out using MoKα radiation (graphite monochromator) with 9 runs consisting of 559 frames with a frame time of 10.300 s and a crystal-to-CCD distance of 50.000 mm, and a strategy to achieve a resolution of 0.7 Å. The runs were collected by omega scans of 1.0 ° width, and at detector position of 28.624 -30.343 ° in 2θ. The intensity data were corrected for absorption with an analytical correction.[4] Final cell constants were calculated from 33513 stronger reflections from the actual data collection after integration. See Table S1 for crystal and refinement information.

**Structure solution and refinement**. The crystal belongs to the monoclinic system, space group P2(1)/n (variant of #14, nature's favorite) as determined from the cell geometry, reflections statistics, systematic absences, and successful solution and refinement. The structure was solved with SHELX-97,[2a] and refined with SHELXL-97.[2b] All non-H atoms were refined and with anisotropic vibrational factors. H-atoms were observable in difference electron density maps, and placed in idealized positions; all were refined as riding atoms with relative isotropic displacement parameters of 120% of the U(eq) of the attached atom. All atom positions are ordered, and there is no solvent. The final full-matrix least-squares refinement converged to $R1$ = 0.0189 (12372 reflections, $F^2$, I > 2σ(I)); R1 = 0.0243 and wR2 =0.0463 for all 14474 data, 505 parameters, 0 restraints, goodness-of-fit (S) 1.004, and no extinction. Data were included to 2θ = 61°.

**Structure description.** Molecules are dimers with two ligands embracing an $Ag_4I_4$ core, which is approximately cubical. The NHC's of the five-membered rings are coordinated to the silvers.

**Other Information.** Data collection and structure solution were conducted at the University of Portland Diffraction Facility, 112A Swindells Hall, Department of Chemistry, University of Portland, Portland, OR, 97203. All calculations were performed using Pentium computers using the current SHELX suite of programs.

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Relevant Equations used in this report:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma\, |F_o^2|$$

$$R_1 = \Sigma\, ||F_o| - |F_c|| \,/\, \Sigma\, |F_o|$$

$$wR2 = [\Sigma\, [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

$$\text{where } w = q \,/\, [\sigma^2 (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\Theta)]$$

$$GOF = S = [\Sigma\, [w(F_o^2 - F_c^2)^2] \,/\, (n-p)]^{1/2}$$

**Table S 1.** Crystal data and structure refinement for Bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3a**)

| | |
|---|---|
| Empirical formula | $C_{40}\ H_{52}\ Ag_4\ I_4\ N_8$ |
| Formula weight | 1583.98 |
| Temperature | 101(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, P 1 21/n 1 |
| Unit cell dimensions | a = 14.4126(3) Å α= 90° |
| | b = 19.1785(4) Å β = 96.027(2) ° |
| | c = 17.1627(4) Å γ = 90° |
| Volume | 4717.75(18) $Å^3$ |
| Z, Calculated density | 4, 2.230 $Mg/m^3$ |
| Absorption coefficient | 4.291 $mm^{-1}$ |
| F(000) | 2992 |
| Crystal size | 0.55 x 0.40 x 0.10 mm |
| Theta range for data collection | 3.37 to 30.57° |
| Limiting indices | -20≤h≤17, -27≤k≤27, -24≤l≤24 |
| Reflections collected / unique | 58341 / 14474 [R(int) = 0.0256] |
| Completeness to Θ | 30.57 99.9 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.6736 and 0.2012 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 14474 / 0 / 505 |
| Goodness-of-fit on $F^2$ | 1.004 |
| Final R indices [I>2Σ(I)] | R1 = 0.0189, wR2 = 0.0453 |
| R indices (all data) | R1 = 0.0248, wR2 = 0.0463 |
| Largest diff. peak and hole | 0.812 and -1.126 $e.A^{-3}$ |

Table S 2 Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($A^2$ x $10^3$) Bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3a**)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | -773(1) | 2557(1) | 4360(1) | 13(1) |
| C(2) | -1042(1) | 3218(1) | 4080(1) | 14(1) |
| C(3) | -1398(2) | 3708(1) | 4565(1) | 17(1) |
| C(4) | -1488(2) | 3536(1) | 5340(1) | 18(1) |
| C(5) | -1212(1) | 2887(1) | 5634(1) | 16(1) |
| C(6) | -849(1) | 2405(1) | 5143(1) | 14(1) |
| C(7) | -232(1) | 3234(1) | 2876(1) | 14(1) |
| C(8) | -1362(2) | 3792(1) | 2095(1) | 19(1) |
| C(9) | -1673(2) | 3732(1) | 2807(1) | 19(1) |
| C(10) | 237(2) | 1398(1) | 5333(1) | 15(1) |
| C(11) | -1124(2) | 1330(1) | 5888(1) | 21(1) |
| C(12) | -655(2) | 731(1) | 6049(1) | 22(1) |
| C(13) | 111(2) | 3488(1) | 1514(1) | 15(1) |
| C(14) | 616(2) | 4173(1) | 1465(2) | 30(1) |
| C(15) | 1363(2) | 4127(2) | 895(2) | 34(1) |
| C(16) | 970(2) | 4088(1) | 54(2) | 32(1) |

| | | | | |
|---|---|---|---|---|
| C(17) | 877(2) | 232(1) | 5754(1) | 17(1) |
| C(18) | 1484(2) | 225(1) | 6527(1) | 19(1) |
| C(19) | 2303(2) | -285(1) | 6521(2) | 21(1) |
| C(20) | 2012(2) | -1040(1) | 6365(2) | 23(1) |
| C(21) | 5073(1) | 1761(1) | 3222(1) | 16(1) |
| C(22) | 5555(2) | 2362(1) | 3472(1) | 17(1) |
| C(23) | 6095(2) | 2714(1) | 2973(2) | 24(1) |
| C(24) | 6152(2) | 2468(1) | 2222(2) | 27(1) |
| C(25) | 5666(2) | 1875(1) | 1960(1) | 22(1) |
| C(26) | 5121(2) | 1527(1) | 2461(1) | 16(1) |
| C(27) | 3739(2) | 744(1) | 2341(1) | 15(1) |
| C(28) | 4962(2) | 435(1) | 1673(1) | 22(1) |
| C(29) | 4294(2) | -43(1) | 1514(1) | 22(1) |
| C(30) | 4742(2) | 2708(1) | 4615(1) | 16(1) |
| C(31) | 6034(2) | 2994(1) | 5427(2) | 24(1) |
| C(32) | 6325(2) | 2788(1) | 4740(2) | 24(1) |
| C(33) | 2671(2) | -237(1) | 1899(1) | 21(1) |
| C(34) | 1941(2) | 14(1) | 1261(1) | 22(1) |
| C(35) | 1102(2) | -478(1) | 1139(1) | 23(1) |
| C(36) | 564(2) | -571(1) | 1840(2) | 26(1) |
| C(37) | 4473(2) | 3136(1) | 5944(1) | 20(1) |
| C(38) | 4141(2) | 3884(1) | 5852(1) | 21(1) |
| C(39) | 3490(2) | 4085(1) | 6462(1) | 23(1) |
| C(40) | 3005(2) | 4777(1) | 6258(2) | 33(1) |
| N(1) | -491(1) | 3485(1) | 2153(1) | 14(1) |
| N(2) | -983(1) | 3384(1) | 3277(1) | 14(1) |
| N(3) | -573(1) | 1732(1) | 5446(1) | 15(1) |
| N(4) | 170(1) | 784(1) | 5709(1) | 16(1) |
| N(5) | 3552(1) | 152(1) | 1923(1) | 17(1) |
| N(6) | 4622(1) | 919(1) | 2180(1) | 16(1) |
| N(7) | 5531(1) | 2613(1) | 4251(1) | 17(1) |
| N(8) | 5074(1) | 2939(1) | 5335(1) | 18(1) |
| Ag(1) | 1069(1) | 2726(1) | 3286(1) | 18(1) |
| Ag(2) | 1374(1) | 1754(1) | 4701(1) | 20(1) |
| Ag(3) | 2782(1) | 1273(1) | 3030(1) | 19(1) |
| Ag(4) | 3288(1) | 2512(1) | 4181(1) | 20(1) |
| I(1) | 808(1) | 1210(1) | 3043(1) | 15(1) |
| I(2) | 1759(1) | 3234(1) | 4847(1) | 16(1) |
| I(3) | 2748(1) | 2768(1) | 2552(1) | 16(1) |
| I(4) | 3115(1) | 1060(1) | 4753(1) | 16(1) |

**Table S 3.** Bond lengths [Å] and angles [°] for Bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3a**)

BOND LENGTHS

| | | | |
|---|---|---|---|
| C(1)-C(6) | 1.391(3) | C(8)-C(9) | 1.350(3) |
| C(1)-C(2) | 1.395(3) | C(8)-N(1) | 1.381(3) |
| C(2)-C(3) | 1.390(3) | C(9)-N(2) | 1.384(3) |
| C(2)-N(2) | 1.426(3) | C(10)-N(4) | 1.352(2) |
| C(3)-C(4) | 1.389(3) | C(10)-N(3) | 1.363(3) |
| C(4)-C(5) | 1.387(3) | C(10)-Ag(2) | 2.1684(19) |
| C(5)-C(6) | 1.388(3) | C(11)-C(12) | 1.347(3) |
| C(6)-N(3) | 1.433(3) | C(11)-N(3) | 1.388(2) |
| C(7)-N(1) | 1.346(3) | C(12)-N(4) | 1.382(3) |
| C(7)-N(2) | 1.372(2) | C(13)-N(1) | 1.467(2) |
| C(7)-Ag(1) | 2.164(2) | C(13)-C(14) | 1.510(3) |
| | | C(14)-C(15) | 1.532(3) |
| | | C(15)-C(16) | 1.495(4) |
| | | C(17)-N(4) | 1.465(3) |

| | |
|---|---|
| C(17)-C(18) | 1.510(3) |
| C(18)-C(19) | 1.535(3) |
| C(19)-C(20) | 1.522(3) |
| C(21)-C(22) | 1.390(3) |
| C(21)-C(26) | 1.391(3) |
| C(22)-C(23) | 1.391(3) |
| C(22)-N(7) | 1.425(3) |
| C(23)-C(24) | 1.384(3) |
| C(24)-C(25) | 1.385(3) |
| C(25)-C(26) | 1.394(3) |
| C(26)-N(6) | 1.427(3) |
| C(27)-N(5) | 1.354(3) |
| C(27)-N(6) | 1.371(3) |
| C(27)-Ag(3) | 2.162(2) |
| C(28)-C(29) | 1.336(3) |
| C(28)-N(6) | 1.397(3) |
| C(29)-N(5) | 1.391(3) |
| C(30)-N(8) | 1.352(3) |
| C(30)-N(7) | 1.366(3) |
| C(30)-Ag(4) | 2.181(2) |
| C(31)-C(32) | 1.350(3) |
| C(31)-N(8) | 1.380(3) |
| C(32)-N(7) | 1.389(3) |
| C(33)-N(5) | 1.470(3) |
| C(33)-C(34) | 1.515(3) |
| C(34)-C(35) | 1.532(3) |
| C(35)-C(36) | 1.508(3) |
| C(37)-N(8) | 1.476(3) |
| C(37)-C(38) | 1.516(3) |
| C(38)-C(39) | 1.526(3) |
| C(39)-C(40) | 1.523(3) |
| Ag(1)-I(3) | 2.8447(2) |
| Ag(1)-I(2) | 2.9259(2) |
| Ag(1)-I(1) | 2.9552(2) |
| Ag(1)-Ag(2) | 3.0566(2) |
| Ag(2)-I(4) | 2.8332(2) |
| Ag(2)-I(2) | 2.8976(2) |
| Ag(2)-I(1) | 3.0604(2) |
| Ag(2)-Ag(4) | 3.3215(2) |
| Ag(3)-I(1) | 2.8488(2) |
| Ag(3)-I(4) | 2.9753(2) |
| Ag(3)-I(3) | 2.9814(2) |
| Ag(3)-Ag(4) | 3.1275(2) |
| Ag(4)-I(3) | 2.8652(2) |
| Ag(4)-I(2) | 2.9343(2) |
| Ag(4)-I(4) | 2.9716(2) |

BOND ANGLES

| | |
|---|---|
| C(6)-C(1)-C(2) | 118.47(18) |
| C(3)-C(2)-C(1) | 120.96(19) |
| C(3)-C(2)-N(2) | 119.38(18) |
| C(1)-C(2)-N(2) | 119.63(17) |
| C(4)-C(3)-C(2) | 119.33(19) |
| C(5)-C(4)-C(3) | 120.68(19) |
| C(4)-C(5)-C(6) | 119.22(19) |
| C(5)-C(6)-C(1) | 121.30(18) |
| C(5)-C(6)-N(3) | 119.16(18) |
| C(1)-C(6)-N(3) | 119.51(17) |
| N(1)-C(7)-N(2) | 103.31(17) |
| N(1)-C(7)-Ag(1) | 127.37(14) |
| N(2)-C(7)-Ag(1) | 129.32(15) |
| C(9)-C(8)-N(1) | 106.46(19) |
| C(8)-C(9)-N(2) | 106.35(18) |
| N(4)-C(10)-N(3) | 103.65(16) |
| N(4)-C(10)-Ag(2) | 127.53(15) |
| N(3)-C(10)-Ag(2) | 128.82(14) |
| C(12)-C(11)-N(3) | 106.37(19) |
| C(11)-C(12)-N(4) | 106.68(18) |
| N(1)-C(13)-C(14) | 111.86(17) |
| C(13)-C(14)-C(15) | 111.2(2) |
| C(16)-C(15)-C(14) | 113.5(2) |
| N(4)-C(17)-C(18) | 112.84(17) |
| C(17)-C(18)-C(19) | 111.97(18) |
| C(20)-C(19)-C(18) | 114.20(19) |
| C(22)-C(21)-C(26) | 119.01(19) |
| C(21)-C(22)-C(23) | 120.5(2) |
| C(21)-C(22)-N(7) | 120.56(18) |
| C(23)-C(22)-N(7) | 118.93(19) |
| C(24)-C(23)-C(22) | 120.0(2) |
| C(23)-C(24)-C(25) | 120.3(2) |
| C(24)-C(25)-C(26) | 119.5(2) |
| C(21)-C(26)-C(25) | 120.7(2) |
| C(21)-C(26)-N(6) | 120.52(18) |
| C(25)-C(26)-N(6) | 118.75(19) |
| N(5)-C(27)-N(6) | 103.64(17) |
| N(5)-C(27)-Ag(3) | 125.45(15) |
| N(6)-C(27)-Ag(3) | 130.83(14) |
| C(29)-C(28)-N(6) | 106.87(19) |
| C(28)-C(29)-N(5) | 106.77(19) |
| N(8)-C(30)-N(7) | 103.26(19) |
| N(8)-C(30)-Ag(4) | 127.14(15) |
| N(7)-C(30)-Ag(4) | 129.57(16) |
| C(32)-C(31)-N(8) | 106.1(2) |
| C(31)-C(32)-N(7) | 106.6(2) |
| N(5)-C(33)-C(34) | 113.02(18) |
| C(33)-C(34)-C(35) | 112.45(19) |
| C(36)-C(35)-C(34) | 115.4(2) |
| N(8)-C(37)-C(38) | 111.74(18) |
| C(37)-C(38)-C(39) | 112.20(18) |
| C(40)-C(39)-C(38) | 111.3(2) |
| C(7)-N(1)-C(8) | 112.41(17) |
| C(7)-N(1)-C(13) | 124.18(17) |
| C(8)-N(1)-C(13) | 123.21(18) |
| C(7)-N(2)-C(9) | 111.46(17) |
| C(7)-N(2)-C(2) | 124.59(17) |
| C(9)-N(2)-C(2) | 123.94(17) |
| C(10)-N(3)-C(11) | 111.41(17) |
| C(10)-N(3)-C(6) | 125.50(16) |
| C(11)-N(3)-C(6) | 123.08(17) |
| C(10)-N(4)-C(12) | 111.89(17) |
| C(10)-N(4)-C(17) | 124.78(17) |
| C(12)-N(4)-C(17) | 123.32(17) |

| | | | |
|---|---|---|---|
| C(27)-N(5)-C(29) | 111.82(18) | C(27)-Ag(3)-I(4) | 115.71(6) |
| C(27)-N(5)-C(33) | 124.31(18) | I(1)-Ag(3)-I(4) | 92.497(6) |
| C(29)-N(5)-C(33) | 123.87(18) | C(27)-Ag(3)-I(3) | 107.09(5) |
| C(27)-N(6)-C(28) | 110.90(18) | I(1)-Ag(3)-I(3) | 93.184(6) |
| C(27)-N(6)-C(26) | 125.33(16) | I(4)-Ag(3)-I(3) | 113.684(6) |
| C(28)-N(6)-C(26) | 123.73(18) | C(27)-Ag(3)-Ag(4) | 125.61(6) |
| C(30)-N(7)-C(32) | 111.37(19) | I(1)-Ag(3)-Ag(4) | 101.192(6) |
| C(30)-N(7)-C(22) | 125.30(19) | I(4)-Ag(3)-Ag(4) | 58.213(5) |
| C(32)-N(7)-C(22) | 123.33(18) | I(3)-Ag(3)-Ag(4) | 55.879(5) |
| C(30)-N(8)-C(31) | 112.62(18) | C(30)-Ag(4)-I(3) | 117.12(6) |
| C(30)-N(8)-C(37) | 123.59(19) | C(30)-Ag(4)-I(2) | 121.30(5) |
| C(31)-N(8)-C(37) | 123.75(19) | I(3)-Ag(4)-I(2) | 99.275(7) |
| C(7)-Ag(1)-I(3) | 126.30(5) | C(30)-Ag(4)-I(4) | 99.20(5) |
| C(7)-Ag(1)-I(2) | 110.34(5) | I(3)-Ag(4)-I(4) | 117.371(7) |
| I(3)-Ag(1)-I(2) | 99.950(7) | I(2)-Ag(4)-I(4) | 102.764(6) |
| C(7)-Ag(1)-I(1) | 107.70(5) | C(30)-Ag(4)-Ag(3) | 119.91(5) |
| I(3)-Ag(1)-I(1) | 93.828(6) | I(3)-Ag(4)-Ag(3) | 59.480(5) |
| I(2)-Ag(1)-I(1) | 118.866(7) | I(2)-Ag(4)-Ag(3) | 118.018(7) |
| C(7)-Ag(1)-Ag(2) | 125.47(5) | I(4)-Ag(4)-Ag(3) | 58.329(5) |
| I(3)-Ag(1)-Ag(2) | 108.112(7) | C(30)-Ag(4)-Ag(2) | 141.16(6) |
| I(2)-Ag(1)-Ag(2) | 57.891(5) | I(3)-Ag(4)-Ag(2) | 100.903(7) |
| I(1)-Ag(1)-Ag(2) | 61.174(5) | I(2)-Ag(4)-Ag(2) | 54.764(5) |
| C(10)-Ag(2)-I(4) | 123.32(5) | I(4)-Ag(4)-Ag(2) | 53.161(5) |
| C(10)-Ag(2)-I(2) | 114.39(5) | Ag(3)-Ag(4)-Ag(2) | 72.063(6) |
| I(4)-Ag(2)-I(2) | 107.254(7) | Ag(3)-I(1)-Ag(1) | 81.227(5) |
| C(10)-Ag(2)-Ag(1) | 122.43(6) | Ag(3)-I(1)-Ag(2) | 79.871(6) |
| I(4)-Ag(2)-Ag(1) | 111.407(6) | Ag(1)-I(1)-Ag(2) | 61.047(5) |
| I(2)-Ag(2)-Ag(1) | 58.792(5) | Ag(2)-I(2)-Ag(1) | 63.318(5) |
| C(10)-Ag(2)-I(1) | 102.49(6) | Ag(2)-I(2)-Ag(4) | 69.432(5) |
| I(4)-Ag(2)-I(1) | 91.037(6) | Ag(1)-I(2)-Ag(4) | 71.522(6) |
| I(2)-Ag(2)-I(1) | 116.380(6) | Ag(1)-I(3)-Ag(4) | 73.709(6) |
| Ag(1)-Ag(2)-I(1) | 57.779(5) | Ag(1)-I(3)-Ag(3) | 80.839(5) |
| C(10)-Ag(2)-Ag(4) | 164.72(6) | Ag(4)-I(3)-Ag(3) | 64.641(5) |
| I(4)-Ag(2)-Ag(4) | 57.079(5) | Ag(2)-I(4)-Ag(4) | 69.760(5) |
| I(2)-Ag(2)-Ag(4) | 55.804(5) | Ag(2)-I(4)-Ag(3) | 81.594(6) |
| Ag(1)-Ag(2)-Ag(4) | 64.797(5) | Ag(4)-I(4)-Ag(3) | 63.458(5) |
| I(1)-Ag(2)-Ag(4) | 92.699(6) | | |
| C(27)-Ag(3)-I(1) | 132.79(6) | | |

**Table S 4**. Anisotropic displacement parameters ($A^2$ x $10^3$) ) for Bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3a**).

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [ h^2 a^2 U11 + ... + 2 h k a^* b^* U12 ]$

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 12(1) | 13(1) | 14(1) | -1(1) | 3(1) | -1(1) |
| C(2) | 14(1) | 16(1) | 13(1) | 2(1) | 2(1) | -1(1) |
| C(3) | 18(1) | 13(1) | 19(1) | 0(1) | 2(1) | 1(1) |
| C(4) | 18(1) | 18(1) | 17(1) | -4(1) | 3(1) | 3(1) |
| C(5) | 15(1) | 19(1) | 13(1) | -1(1) | 2(1) | -2(1) |
| C(6) | 12(1) | 15(1) | 15(1) | 2(1) | 1(1) | 1(1) |
| C(7) | 15(1) | 12(1) | 14(1) | 1(1) | 2(1) | 1(1) |
| C(8) | 16(1) | 23(1) | 17(1) | 5(1) | -1(1) | 6(1) |
| C(9) | 16(1) | 22(1) | 19(1) | 3(1) | 2(1) | 6(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(10) | 18(1) | 14(1) | 13(1) | 3(1) | 1(1) | -1(1) |
| C(11) | 23(1) | 21(1) | 22(1) | 4(1) | 11(1) | -2(1) |
| C(12) | 28(1) | 20(1) | 20(1) | 7(1) | 9(1) | -2(1) |
| C(13) | 18(1) | 15(1) | 14(1) | 1(1) | 4(1) | -2(1) |
| C(14) | 43(2) | 25(1) | 23(1) | -4(1) | 8(1) | -17(1) |
| C(15) | 24(1) | 42(2) | 35(2) | 17(1) | -2(1) | -11(1) |
| C(16) | 39(2) | 30(1) | 29(1) | 3(1) | 13(1) | -6(1) |
| C(17) | 22(1) | 14(1) | 15(1) | 2(1) | 1(1) | 1(1) |
| C(18) | 21(1) | 17(1) | 18(1) | -1(1) | 0(1) | 0(1) |
| C(19) | 18(1) | 18(1) | 26(1) | 0(1) | 0(1) | 1(1) |
| C(20) | 25(1) | 18(1) | 27(1) | 2(1) | 4(1) | 0(1) |
| C(21) | 14(1) | 16(1) | 17(1) | 0(1) | 4(1) | 0(1) |
| C(22) | 16(1) | 17(1) | 19(1) | -2(1) | 2(1) | 0(1) |
| C(23) | 22(1) | 26(1) | 25(1) | -2(1) | 7(1) | -8(1) |
| C(24) | 25(1) | 33(1) | 24(1) | 2(1) | 9(1) | -8(1) |
| C(25) | 20(1) | 28(1) | 17(1) | -2(1) | 6(1) | -2(1) |
| C(26) | 14(1) | 18(1) | 16(1) | -1(1) | 2(1) | 3(1) |
| C(27) | 20(1) | 13(1) | 12(1) | 1(1) | 1(1) | 1(1) |
| C(28) | 23(1) | 23(1) | 19(1) | -5(1) | 6(1) | 6(1) |
| C(29) | 29(1) | 20(1) | 18(1) | -5(1) | 4(1) | 5(1) |
| C(30) | 21(1) | 12(1) | 16(1) | -1(1) | 2(1) | -1(1) |
| C(31) | 23(1) | 22(1) | 25(1) | -6(1) | -3(1) | -3(1) |
| C(32) | 19(1) | 25(1) | 27(1) | -5(1) | 0(1) | -5(1) |
| C(33) | 28(1) | 15(1) | 18(1) | 1(1) | 1(1) | -5(1) |
| C(34) | 28(1) | 20(1) | 17(1) | 0(1) | 0(1) | -2(1) |
| C(35) | 28(1) | 21(1) | 20(1) | -5(1) | -1(1) | 0(1) |
| C(36) | 26(1) | 22(1) | 32(1) | -3(1) | 6(1) | -1(1) |
| C(37) | 28(1) | 17(1) | 15(1) | -3(1) | 0(1) | 3(1) |
| C(38) | 28(1) | 16(1) | 19(1) | -3(1) | 2(1) | 1(1) |
| C(39) | 29(1) | 24(1) | 15(1) | -4(1) | -2(1) | 9(1) |
| C(40) | 40(2) | 29(1) | 29(1) | -6(1) | -2(1) | 14(1) |
| N(1) | 14(1) | 15(1) | 13(1) | 2(1) | 2(1) | 2(1) |
| N(2) | 15(1) | 14(1) | 13(1) | 2(1) | 3(1) | 3(1) |
| N(3) | 17(1) | 16(1) | 14(1) | 4(1) | 5(1) | 0(1) |
| N(4) | 21(1) | 13(1) | 14(1) | 2(1) | 2(1) | 0(1) |
| N(5) | 24(1) | 13(1) | 15(1) | 1(1) | 2(1) | 0(1) |
| N(6) | 17(1) | 17(1) | 13(1) | -3(1) | 3(1) | 1(1) |
| N(7) | 17(1) | 16(1) | 17(1) | -3(1) | 2(1) | -3(1) |
| N(8) | 22(1) | 14(1) | 16(1) | -2(1) | 0(1) | -1(1) |
| Ag(1) | 16(1) | 20(1) | 18(1) | 4(1) | 4(1) | 5(1) |
| Ag(2) | 18(1) | 20(1) | 22(1) | 7(1) | 6(1) | 3(1) |
| Ag(3) | 18(1) | 19(1) | 21(1) | -3(1) | 6(1) | 0(1) |
| Ag(4) | 19(1) | 21(1) | 19(1) | -3(1) | 0(1) | 1(1) |
| I(1) | 15(1) | 14(1) | 16(1) | -1(1) | 1(1) | -1(1) |
| I(2) | 16(1) | 17(1) | 16(1) | -2(1) | 3(1) | -1(1) |
| I(3) | 17(1) | 16(1) | 15(1) | 2(1) | 5(1) | 2(1) |
| I(4) | 15(1) | 19(1) | 14(1) | 3(1) | 1(1) | 1(1) |

**Table S 5**. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($A^2$ x $10^3$) for bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra-$μ^3$-iodotetrasilver(I) (**3a**).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | -544 | 2219 | 4024 | 16 |

| | | | | |
|---|---|---|---|---|
| H(3) | -1578 | 4157 | 4368 | 20 |
| H(4) | -1741 | 3867 | 5671 | 21 |
| H(5) | -1271 | 2772 | 6165 | 19 |
| H(8) | -1679 | 4005 | 1643 | 23 |
| H(9) | -2251 | 3896 | 2956 | 23 |
| H(11) | -1714 | 1454 | 6046 | 25 |
| H(12) | -853 | 347 | 6339 | 27 |
| H(13A) | -274 | 3399 | 1012 | 18 |
| H(13B) | 573 | 3107 | 1599 | 18 |
| H(14A) | 913 | 4303 | 1991 | 36 |
| H(14B) | 162 | 4542 | 1288 | 36 |
| H(15A) | 1774 | 4540 | 968 | 41 |
| H(15B) | 1752 | 3708 | 1024 | 41 |
| H(16A) | 544 | 3689 | -20 | 39 |
| H(16B) | 1479 | 4030 | -277 | 39 |
| H(16C) | 629 | 4518 | -92 | 39 |
| H(17A) | 1277 | 297 | 5325 | 21 |
| H(17B) | 562 | -225 | 5676 | 21 |
| H(18A) | 1100 | 92 | 6949 | 22 |
| H(18B) | 1729 | 700 | 6642 | 22 |
| H(19A) | 2699 | -135 | 6114 | 25 |
| H(19B) | 2687 | -260 | 7033 | 25 |
| H(20A) | 1562 | -1177 | 6727 | 28 |
| H(20B) | 2562 | -1342 | 6444 | 28 |
| H(20C) | 1725 | -1086 | 5824 | 28 |
| H(21) | 4716 | 1514 | 3567 | 19 |
| H(23) | 6424 | 3124 | 3148 | 29 |
| H(24) | 6526 | 2706 | 1884 | 32 |
| H(25) | 5703 | 1708 | 1443 | 26 |
| H(28) | 5555 | 443 | 1478 | 26 |
| H(29) | 4321 | -439 | 1185 | 26 |
| H(31) | 6413 | 3146 | 5881 | 29 |
| H(32) | 6952 | 2768 | 4616 | 29 |
| H(33A) | 2421 | -192 | 2412 | 25 |
| H(33B) | 2797 | -737 | 1814 | 25 |
| H(34A) | 2228 | 56 | 764 | 26 |
| H(34B) | 1724 | 483 | 1401 | 26 |
| H(35A) | 670 | -299 | 697 | 28 |
| H(35B) | 1324 | -941 | 984 | 28 |
| H(36A) | 962 | -797 | 2263 | 32 |
| H(36B) | 14 | -862 | 1694 | 32 |
| H(36C) | 365 | -114 | 2017 | 32 |
| H(37A) | 4825 | 3076 | 6467 | 24 |
| H(37B) | 3925 | 2821 | 5913 | 24 |
| H(38A) | 3811 | 3948 | 5322 | 25 |
| H(38B) | 4689 | 4199 | 5903 | 25 |
| H(39A) | 3015 | 3716 | 6490 | 28 |
| H(39B) | 3853 | 4122 | 6983 | 28 |
| H(40A) | 3474 | 5143 | 6228 | 39 |
| H(40B) | 2602 | 4897 | 6664 | 39 |

**Table S 6**. Torsion angles [°] for bis(μ-1,3-bis(3'-butylimidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3a**).

| | | | |
|---|---|---|---|
| | | C(6)-C(1)-C(2)-C(3) | -1.5(3) |

| | | | |
|---|---|---|---|
| C(6)-C(1)-C(2)-N(2) | -179.23(19) | C(5)-C(6)-N(3)-C(11) | 46.6(3) |
| C(1)-C(2)-C(3)-C(4) | -0.1(3) | C(1)-C(6)-N(3)-C(11) | -131.5(2) |
| N(2)-C(2)-C(3)-C(4) | 177.6(2) | N(3)-C(10)-N(4)-C(12) | 0.0(2) |
| C(2)-C(3)-C(4)-C(5) | 1.1(3) | Ag(2)-C(10)-N(4)-C(12) | -179.91(16) |
| C(3)-C(4)-C(5)-C(6) | -0.4(3) | N(3)-C(10)-N(4)-C(17) | 179.71(19) |
| C(4)-C(5)-C(6)-C(1) | -1.3(3) | Ag(2)-C(10)-N(4)-C(17) | -0.2(3) |
| C(4)-C(5)-C(6)-N(3) | -179.37(19) | C(11)-C(12)-N(4)-C(10) | -0.3(3) |
| C(2)-C(1)-C(6)-C(5) | 2.2(3) | C(11)-C(12)-N(4)-C(17) | 179.9(2) |
| C(2)-C(1)-C(6)-N(3) | -179.69(18) | C(18)-C(17)-N(4)-C(10) | 100.8(2) |
| N(1)-C(8)-C(9)-N(2) | -0.4(2) | C(18)-C(17)-N(4)-C(12) | -79.5(3) |
| N(3)-C(11)-C(12)-N(4) | 0.6(3) | N(6)-C(27)-N(5)-C(29) | 0.2(2) |
| N(1)-C(13)-C(14)-C(15) | 170.2(2) | Ag(3)-C(27)-N(5)-C(29) | 177.32(15) |
| C(13)-C(14)-C(15)-C(16) | 71.6(3) | N(6)-C(27)-N(5)-C(33) | -179.45(19) |
| N(4)-C(17)-C(18)-C(19) | -171.95(16) | Ag(3)-C(27)-N(5)-C(33) | -2.4(3) |
| C(17)-C(18)-C(19)-C(20) | -60.1(3) | C(28)-C(29)-N(5)-C(27) | -0.2(3) |
| C(26)-C(21)-C(22)-C(23) | -1.5(3) | C(28)-C(29)-N(5)-C(33) | 179.5(2) |
| C(26)-C(21)-C(22)-N(7) | -179.23(19) | C(34)-C(33)-N(5)-C(27) | 88.5(3) |
| C(21)-C(22)-C(23)-C(24) | 0.2(4) | C(34)-C(33)-N(5)-C(29) | -91.1(2) |
| N(7)-C(22)-C(23)-C(24) | 178.0(2) | N(5)-C(27)-N(6)-C(28) | -0.2(2) |
| C(22)-C(23)-C(24)-C(25) | 0.7(4) | Ag(3)-C(27)-N(6)-C(28) | -177.06(16) |
| C(23)-C(24)-C(25)-C(26) | -0.3(4) | N(5)-C(27)-N(6)-C(26) | 177.30(19) |
| C(22)-C(21)-C(26)-C(25) | 1.9(3) | Ag(3)-C(27)-N(6)-C(26) | 0.4(3) |
| C(22)-C(21)-C(26)-N(6) | -178.82(19) | C(29)-C(28)-N(6)-C(27) | 0.1(3) |
| C(24)-C(25)-C(26)-C(21) | -1.0(3) | C(29)-C(28)-N(6)-C(26) | -177.4(2) |
| C(24)-C(25)-C(26)-N(6) | 179.7(2) | C(21)-C(26)-N(6)-C(27) | 39.5(3) |
| N(6)-C(28)-C(29)-N(5) | 0.1(3) | C(25)-C(26)-N(6)-C(27) | -141.2(2) |
| N(8)-C(31)-C(32)-N(7) | -0.1(3) | C(21)-C(26)-N(6)-C(28) | -143.3(2) |
| N(5)-C(33)-C(34)-C(35) | 169.08(18) | C(25)-C(26)-N(6)-C(28) | 36.0(3) |
| C(33)-C(34)-C(35)-C(36) | 61.3(3) | N(8)-C(30)-N(7)-C(32) | -0.4(2) |
| N(8)-C(37)-C(38)-C(39) | 177.9(2) | Ag(4)-C(30)-N(7)-C(32) | -178.64(16) |
| C(37)-C(38)-C(39)-C(40) | -167.9(2) | N(8)-C(30)-N(7)-C(22) | 179.12(18) |
| N(2)-C(7)-N(1)-C(8) | 0.9(2) | Ag(4)-C(30)-N(7)-C(22) | 0.9(3) |
| Ag(1)-C(7)-N(1)-C(8) | -178.60(15) | C(31)-C(32)-N(7)-C(30) | 0.3(3) |
| N(2)-C(7)-N(1)-C(13) | 175.96(17) | C(31)-C(32)-N(7)-C(22) | -179.22(19) |
| Ag(1)-C(7)-N(1)-C(13) | -3.6(3) | C(21)-C(22)-N(7)-C(30) | -49.6(3) |
| C(9)-C(8)-N(1)-C(7) | -0.3(3) | C(23)-C(22)-N(7)-C(30) | 132.6(2) |
| C(9)-C(8)-N(1)-C(13) | -175.43(19) | C(21)-C(22)-N(7)-C(32) | 129.9(2) |
| C(14)-C(13)-N(1)-C(7) | -94.9(2) | C(23)-C(22)-N(7)-C(32) | -47.9(3) |
| C(14)-C(13)-N(1)-C(8) | 79.6(3) | N(7)-C(30)-N(8)-C(31) | 0.4(2) |
| N(1)-C(7)-N(2)-C(9) | -1.2(2) | Ag(4)-C(30)-N(8)-C(31) | 178.64(15) |
| Ag(1)-C(7)-N(2)-C(9) | 178.33(15) | N(7)-C(30)-N(8)-C(37) | 178.24(18) |
| N(1)-C(7)-N(2)-C(2) | 179.98(18) | Ag(4)-C(30)-N(8)-C(37) | -3.5(3) |
| Ag(1)-C(7)-N(2)-C(2) | -0.5(3) | C(32)-C(31)-N(8)-C(30) | -0.2(3) |
| C(8)-C(9)-N(2)-C(7) | 1.0(3) | C(32)-C(31)-N(8)-C(37) | -178.05(19) |
| C(8)-C(9)-N(2)-C(2) | 179.87(19) | C(38)-C(37)-N(8)-C(30) | -85.0(2) |
| C(3)-C(2)-N(2)-C(7) | 136.9(2) | C(38)-C(37)-N(8)-C(31) | 92.6(3) |
| C(1)-C(2)-N(2)-C(7) | -45.3(3) | N(1)-C(7)-Ag(1)-I(3) | 17.4(2) |
| C(3)-C(2)-N(2)-C(9) | -41.7(3) | N(2)-C(7)-Ag(1)-I(3) | -162.04(15) |
| C(1)-C(2)-N(2)-C(9) | 136.0(2) | N(1)-C(7)-Ag(1)-I(2) | 137.44(16) |
| N(4)-C(10)-N(3)-C(11) | 0.4(2) | N(2)-C(7)-Ag(1)-I(2) | -41.99(19) |
| Ag(2)-C(10)-N(3)-C(11) | -179.74(16) | N(1)-C(7)-Ag(1)-I(1) | -91.36(17) |
| N(4)-C(10)-N(3)-C(6) | -178.53(19) | N(2)-C(7)-Ag(1)-I(1) | 89.21(18) |
| Ag(2)-C(10)-N(3)-C(6) | 1.4(3) | N(1)-C(7)-Ag(1)-Ag(2) | -158.16(14) |
| C(12)-C(11)-N(3)-C(10) | -0.6(3) | N(2)-C(7)-Ag(1)-Ag(2) | 22.4(2) |
| C(12)-C(11)-N(3)-C(6) | 178.3(2) | N(4)-C(10)-Ag(2)-I(4) | -10.4(2) |
| C(5)-C(6)-N(3)-C(10) | -134.6(2) | N(3)-C(10)-Ag(2)-I(4) | 169.70(16) |
| C(1)-C(6)-N(3)-C(10) | 47.3(3) | N(4)-C(10)-Ag(2)-I(2) | -143.90(17) |

| | | | |
|---|---|---|---|
| N(3)-C(10)-Ag(2)-I(2) | 36.2(2) | C(27)-Ag(3)-Ag(4)-Ag(2) | -157.86(7) |
| N(4)-C(10)-Ag(2)-Ag(1) | 148.81(16) | I(1)-Ag(3)-Ag(4)-Ag(2) | 28.701(6) |
| N(3)-C(10)-Ag(2)-Ag(1) | -31.1(2) | I(4)-Ag(3)-Ag(4)-Ag(2) | -57.264(5) |
| N(4)-C(10)-Ag(2)-I(1) | 89.22(19) | I(3)-Ag(3)-Ag(4)-Ag(2) | 114.936(6) |
| N(3)-C(10)-Ag(2)-I(1) | -90.64(19) | C(10)-Ag(2)-Ag(4)-C(30) | 44.2(2) |
| N(4)-C(10)-Ag(2)-Ag(4) | -96.9(2) | I(4)-Ag(2)-Ag(4)-C(30) | -52.26(8) |
| N(3)-C(10)-Ag(2)-Ag(4) | 83.2(3) | I(2)-Ag(2)-Ag(4)-C(30) | 97.87(8) |
| C(7)-Ag(1)-Ag(2)-C(10) | 7.54(9) | Ag(1)-Ag(2)-Ag(4)-C(30) | 166.00(8) |
| I(3)-Ag(1)-Ag(2)-C(10) | -168.68(6) | I(1)-Ag(2)-Ag(4)-C(30) | -141.75(8) |
| I(2)-Ag(1)-Ag(2)-C(10) | 100.79(6) | C(10)-Ag(2)-Ag(4)-I(3) | -147.4(2) |
| I(1)-Ag(1)-Ag(2)-C(10) | -84.41(6) | I(4)-Ag(2)-Ag(4)-I(3) | 116.149(7) |
| C(7)-Ag(1)-Ag(2)-I(4) | 169.00(7) | I(2)-Ag(2)-Ag(4)-I(3) | -93.721(7) |
| I(3)-Ag(1)-Ag(2)-I(4) | -7.220(10) | Ag(1)-Ag(2)-Ag(4)-I(3) | -25.596(6) |
| I(2)-Ag(1)-Ag(2)-I(4) | -97.758(8) | I(1)-Ag(2)-Ag(4)-I(3) | 26.661(6) |
| I(1)-Ag(1)-Ag(2)-I(4) | 77.050(7) | C(10)-Ag(2)-Ag(4)-I(2) | -53.6(2) |
| C(7)-Ag(1)-Ag(2)-I(2) | -93.25(7) | I(4)-Ag(2)-Ag(4)-I(2) | -150.130(8) |
| I(3)-Ag(1)-Ag(2)-I(2) | 90.537(7) | Ag(1)-Ag(2)-Ag(4)-I(2) | 68.126(6) |
| I(1)-Ag(1)-Ag(2)-I(2) | 174.808(6) | I(1)-Ag(2)-Ag(4)-I(2) | 120.382(7) |
| C(7)-Ag(1)-Ag(2)-I(1) | 91.95(7) | C(10)-Ag(2)-Ag(4)-I(4) | 96.5(2) |
| I(3)-Ag(1)-Ag(2)-I(1) | -84.271(7) | I(2)-Ag(2)-Ag(4)-I(4) | 150.130(8) |
| I(2)-Ag(1)-Ag(2)-I(1) | -174.808(6) | Ag(1)-Ag(2)-Ag(4)-I(4) | -141.745(7) |
| C(7)-Ag(1)-Ag(2)-Ag(4) | -157.07(7) | I(1)-Ag(2)-Ag(4)-I(4) | -89.488(6) |
| I(3)-Ag(1)-Ag(2)-Ag(4) | 26.714(6) | C(10)-Ag(2)-Ag(4)-Ag(3) | 159.9(2) |
| I(2)-Ag(1)-Ag(2)-Ag(4) | -63.823(5) | I(4)-Ag(2)-Ag(4)-Ag(3) | 63.446(6) |
| I(1)-Ag(1)-Ag(2)-Ag(4) | 110.985(6) | I(2)-Ag(2)-Ag(4)-Ag(3) | -146.424(7) |
| N(5)-C(27)-Ag(3)-I(1) | -18.0(2) | Ag(1)-Ag(2)-Ag(4)-Ag(3) | -78.298(6) |
| N(6)-C(27)-Ag(3)-I(1) | 158.26(16) | I(1)-Ag(2)-Ag(4)-Ag(3) | -26.042(5) |
| N(5)-C(27)-Ag(3)-I(4) | 102.76(18) | C(27)-Ag(3)-I(1)-Ag(1) | -141.01(7) |
| N(6)-C(27)-Ag(3)-I(4) | -81.0(2) | I(4)-Ag(3)-I(1)-Ag(1) | 89.790(6) |
| N(5)-C(27)-Ag(3)-I(3) | -129.33(17) | I(3)-Ag(3)-I(1)-Ag(1) | -24.109(6) |
| N(6)-C(27)-Ag(3)-I(3) | 46.9(2) | Ag(4)-Ag(3)-I(1)-Ag(1) | 31.718(6) |
| N(5)-C(27)-Ag(3)-Ag(4) | 170.78(15) | C(27)-Ag(3)-I(1)-Ag(2) | 157.02(7) |
| N(6)-C(27)-Ag(3)-Ag(4) | -13.0(2) | I(4)-Ag(3)-I(1)-Ag(2) | 27.824(5) |
| N(8)-C(30)-Ag(4)-I(3) | 146.89(15) | I(3)-Ag(3)-I(1)-Ag(2) | -86.074(6) |
| N(7)-C(30)-Ag(4)-I(3) | -35.3(2) | Ag(4)-Ag(3)-I(1)-Ag(2) | -30.247(6) |
| N(8)-C(30)-Ag(4)-I(2) | 25.3(2) | C(7)-Ag(1)-I(1)-Ag(3) | 155.47(6) |
| N(7)-C(30)-Ag(4)-I(2) | -156.84(16) | I(3)-Ag(1)-I(1)-Ag(3) | 25.366(6) |
| N(8)-C(30)-Ag(4)-I(4) | -85.80(17) | I(2)-Ag(1)-I(1)-Ag(3) | -78.203(8) |
| N(7)-C(30)-Ag(4)-I(4) | 92.03(18) | Ag(2)-Ag(1)-I(1)-Ag(3) | -83.224(6) |
| N(8)-C(30)-Ag(4)-Ag(3) | -144.43(15) | C(7)-Ag(1)-I(1)-Ag(2) | -121.31(6) |
| N(7)-C(30)-Ag(4)-Ag(3) | 33.4(2) | I(3)-Ag(1)-I(1)-Ag(2) | 108.591(7) |
| N(8)-C(30)-Ag(4)- (2) | -45.9(2) | I(2)-Ag(1)-I(1)-Ag(2) | 5.021(6) |
| N(7)-C(30)-Ag(4)-Ag(2) | 131.91(16) | C(10)-Ag(2)-I(1)-Ag(3) | -153.85(5) |
| C(27)-Ag(3)-Ag(4)-C(30) | -18.54(9) | I(4)-Ag(2)-I(1)-Ag(3) | -29.327(6) |
| I(1)-Ag(3)-Ag(4)-C30) | 168.02(6) | I(2)-Ag(2)-I(1)-Ag(3) | 80.557(7) |
| I(4)-Ag(3)-Ag(4)-C(30) | 82.05(6) | Ag(1)-Ag(2)-I(1)-Ag(3) | 85.513(6) |
| I(3)-Ag(3)-Ag(4)-C(30) | -105.75(6) | Ag(4)-Ag(2)-I(1)-Ag(3) | 27.763(6) |
| C(27)-Ag(3)-Ag(4)-I(3) | 87.21(7) | C(10)-Ag(2)-I(1)-Ag(1) | 120.64(5) |
| I(1)-Ag(3)-Ag(4)-I(3) | -86.235(7) | I(4)-Ag(2)-I(1)-Ag(1) | -114.840(6) |
| I(4)-Ag(3)-Ag(4)-I(3) | -172.200(7) | I(2)-Ag(2)-I(1)-Ag(1) | -4.956(6) |
| C(27)-Ag(3)-Ag(4)-I(2) | 171.37(7) | Ag(4)-Ag(2)-I(1)-Ag(1) | -57.750(5) |
| I(1)-Ag(3)-Ag(4)-I(2) | -2.075(9) | C(10)-Ag(2)-I(2)-Ag(1) | -114.44(6) |
| I(4)-Ag(3)-Ag(4)-I(2) | -88.040(8) | I(4)-Ag(2)-I(2)-Ag(1) | 104.992(7) |
| I(3)-Ag(3)-Ag(4)-I(2) | 84.160(8) | I(1)-Ag(2)-I(2)-Ag(1) | 4.902(6) |
| C(27)-Ag(3)-Ag(4)-I(4) | -100.59(7) | Ag(4)-Ag(2)-I(2)-Ag(1) | 79.031(6) |
| I(1)-Ag(3)-Ag(4)-I(4) | 85.965(6) | C(10)-Ag(2)-I(2)-Ag(4) | 166.53(6) |
| I(3)-Ag(3)-Ag(4)-I(4) | 172.200(7) | I(4)-Ag(2)-I(2)-Ag(4) | 25.961(7) |

| | | | |
|---|---|---|---|
| Ag(1)-Ag(2)-I(2)-Ag(4) | -79.031(6) | Ag(2)-Ag(4)-I(3)-Ag(3) | -61.469(6) |
| I(1)-Ag(2)-I(2)-Ag(4) | -74.129(7) | C(27)-Ag(3)-I(3)-Ag(1) | 161.93(6) |
| C(7)-Ag(1)-I(2)-Ag(2) | 119.87(5) | I(1)-Ag(3)-I(3)-Ag(1) | 25.138(6) |
| I(3)-Ag(1)-I(2)-Ag(2) | -105.220(6) | I(4)-Ag(3)-I(3)-Ag(1) | -68.994(7) |
| I(1)-Ag(1)-I(2)-Ag(2) | -5.194(6) | Ag(4)-Ag(3)-I(3)-Ag(1) | -76.231(6) |
| C(7)-Ag(1)-I(2)-Ag(4) | -164.41(5) | C(27)-Ag(3)-I(3)-Ag(4) | -121.84(6) |
| I(3)-Ag(1)-I(2)-Ag(4) | -29.498(6) | I(1)-Ag(3)-I(3)-Ag(4) | 101.369(6) |
| I(1)-Ag(1)-I(2)-Ag(4) | 70.529(7) | I(4)-Ag(3)-I(3)-Ag(4) | 7.237(6) |
| Ag(2)-Ag(1)-I(2)-Ag(4) | 75.722(6) | C(10)-Ag(2)-I(4)-Ag(4) | -161.74(7) |
| C(30)-Ag(4)-I(2)-Ag(2) | -133.36(6) | I(2)-Ag(2)-I(4)-Ag(4) | -25.553(6) |
| I(3)-Ag(4)-I(2)-Ag(2) | 96.850(7) | Ag(1)-Ag(2)-I(4)-Ag(4) | 36.994(7) |
| I(4)-Ag(4)-I(2)-Ag(2) | -24.123(6) | I(1)-Ag(2)-I(4)-Ag(4) | 92.544(6) |
| Ag(3)-Ag(4)-I(2)-Ag(2) | 36.585(8) | C(10)-Ag(2)-I(4)-Ag(3) | 133.53(7) |
| C(30)-Ag(4)-I(2)-Ag(1) | 158.99(6) | I(2)-Ag(2)-I(4)-Ag(3) | -90.279(7) |
| I(3)-Ag(4)-I(2)-Ag(1) | 29.202(6) | Ag(1)-Ag(2)-I(4)-Ag(3) | -27.731(7) |
| I(4)-Ag(4)-I(2)-Ag(1) | -91.771(7) | I(1)-Ag(2)-I(4)-Ag(3) | 27.818(5) |
| Ag(3)-Ag(4)-I(2)-Ag(1) | -31.063(7) | Ag(4)-Ag(2)-I(4)-Ag(3) | -64.726(5) |
| Ag(2)-Ag(4)-I(2)-Ag(1) | -67.648(6) | C(30)-Ag(4)-I(4)-Ag(2) | 149.84(5) |
| C(7)-Ag(1)-I(3)-Ag(4) | 154.40(7) | I(3)-Ag(4)-I(4)-Ag(2) | -83.009(8) |
| I(2)-Ag(1)-I(3)-Ag(4) | 29.886(6) | I(2)-Ag(4)-I(4)-Ag(2) | 24.652(6) |
| I(1)-Ag(1)-I(3)-Ag(4) | -90.310(6) | Ag(3)-Ag(4)-I(4)-Ag(2) | -90.574(7) |
| Ag(2)-Ag(1)-I(3)-Ag(4) | -29.423(7) | C(30)-Ag(4)-I(4)-Ag(3) | -119.58(5) |
| C(7)-Ag(1)-I(3)-Ag(3) | -139.48(7) | I(3)-Ag(4)-I(4)-Ag(3) | 7.565(6) |
| I(2)-Ag(1)-I(3)-Ag(3) | 96.005(6) | I(2)-Ag(4)-I(4)-Ag(3) | 115.225(7) |
| I(1)-Ag(1)-I(3)-Ag(3) | -24.191(6) | Ag(2)-Ag(4)-I(4)-Ag(3) | 90.574(7) |
| Ag(2)-Ag(1)-I(3)-Ag(3) | 36.696(7) | C(27)-Ag(3)-I(4)-Ag(2) | -170.98(6) |
| C(30)-Ag(4)-I(3)-Ag(1) | -162.19(6) | I(1)-Ag(3)-I(4)-Ag(2) | -30.114(6) |
| I(2)-Ag(4)-I(3)-Ag(1) | -29.726(6) | I(3)-Ag(3)-I(4)-Ag(2) | 64.466(7) |
| I(4)-Ag(4)-I(3)-Ag(1) | 79.945(7) | Ag(4)-Ag(3)-I(4)-Ag(2) | 71.513(6) |
| Ag(3)-Ag(4)-I(3)-Ag(1) | 87.419(6) | C(27)-Ag(3)-I(4)-Ag(4) | 117.51(6) |
| Ag(2)-Ag(4)-I(3)-Ag(1) | 25.949(6) | I(1)-Ag(3)-I(4)-Ag(4) | -101.627(6) |
| C(30)-Ag(4)-I(3)-Ag(3) | 110.39(6) | I(3)-Ag(3)-I(4)-Ag(4) | -7.047(6) |
| I(2)-Ag(4)-I(3)-Ag(3) | -117.145(7) | | |
| I(4)-Ag(4)-I(3)-Ag(3) | -7.473(6) | | |

Crystallographic Report for

**Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (3b)**

Table S7. Crystal data and structure refinement for bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (**3b**)

| | |
|---|---|
| Identification code | Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (3b) |
| Empirical formula | $C_{42}H_{48}Ag_4Cl_4I_4N_8$ |
| Formula weight | 1745.76 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Orthorhombic |
| Space group | P b c n |
| Unit cell dimensions | $a$ = 20.6181(12) Å α = 90° |
| | $b$ = 12.8667(7) Å β = 90° |
| | $c$ = 19.8917(11) Å γ = 90° |
| Volume | 5277.0(5) Å$^3$ |
| Z | 4 |
| Density (calculated) | 2.197 g.cm$^{-3}$ |
| Absorption coefficient (μ) | 4.043 mm$^{-1}$ |
| F(000) | 3296 |
| Crystal color, habit | colorless, block |
| Crystal size | 0.200 × 0.200 × 0.200 mm$^3$ |
| θ range for data collection | 1.866 to 26.433° |
| Index ranges | -20 ≤ h ≤ 24, -16 ≤ k ≤ 10, -24 ≤ l ≤ 15 |
| Reflections collected | 31536 |
| Independent reflections | 5297 [$R_{int}$ = 0.0668] |
| Completeness to θ = 25.242° | 98.2 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7454 and 0.5248 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 5297 / 0 / 280 |
| Goodness-of-fit on F$^2$ | 1.042 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0376, w$R_2$ = 0.0753 |
| R indices (all data) | $R_1$ = 0.0554, w$R_2$ = 0.0835 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.738 and -1.057 e$^-$.Å$^{-3}$ |

**Table S 8.** Atomic coordinates and equivalent isotropic displacement parameters (Å²) for bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (**3b**). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ag(1) | 0.44702(2) | 0.84640(3) | 0.18789(2) | 0.030(1) |
| I(1) | 0.58418(2) | 0.88582(2) | 0.17498(2) | 0.023(1) |
| N(1) | 0.40111(19) | 0.8988(3) | 0.03585(19) | 0.022(1) |

| | | | | |
|---|---|---|---|---|
| C(1) | 0.4566(2) | 0.8513(4) | 0.0051(2) | 0.021(1) |
| C(1S) | 0.2332(3) | 0.8019(4) | -0.1522(2) | 0.046(2) |
| Cl(1) | 0.26570(7) | 0.92756(11) | -0.15947(7) | 0.045(1) |
| Ag(2) | 0.54241(2) | 0.66738(3) | 0.17890(2) | 0.029(1) |
| I(2) | 0.40166(2) | 0.61048(2) | 0.19424(2) | 0.023(1) |
| N(2) | 0.33242(19) | 0.9563(3) | 0.10809(18) | 0.022(1) |
| C(2) | 0.4843(2) | 0.8995(4) | -0.0506(2) | 0.026(1) |
| Cl(2) | 0.23592(8) | 0.75589(13) | -0.06960(7) | 0.065(1) |
| N(3) | 0.55954(18) | 0.6164(3) | 0.01977(19) | 0.022(1) |
| C(3) | 0.5371(3) | 0.8538(4) | -0.0812(2) | 0.030(1) |
| N(4) | 0.59864(18) | 0.4950(3) | 0.08079(19) | 0.023(1) |
| C(4) | 0.5622(2) | 0.7620(4) | -0.0583(2) | 0.027(1) |
| C(5) | 0.5336(2) | 0.7139(3) | -0.0029(2) | 0.021(1) |
| C(6) | 0.4800(2) | 0.7574(3) | 0.0289(2) | 0.019(1) |
| C(7) | 0.3531(2) | 0.9507(4) | 0.0004(2) | 0.028(1) |
| C(8) | 0.3100(2) | 0.9845(4) | 0.0453(2) | 0.029(1) |
| C(9) | 0.3883(2) | 0.9022(3) | 0.1039(2) | 0.020(1) |
| C(10) | 0.5691(2) | 0.5886(4) | 0.0857(2) | 0.021(1) |
| C(11) | 0.5814(2) | 0.5394(4) | -0.0235(2) | 0.027(1) |
| C(12) | 0.6059(2) | 0.4642(4) | 0.0140(3) | 0.032(1) |
| C(13) | 0.6186(2) | 0.4332(4) | 0.1392(2) | 0.029(1) |
| C(14) | 0.5656(2) | 0.3629(4) | 0.1652(3) | 0.033(1) |
| C(15) | 0.5886(2) | 0.3060(4) | 0.2262(3) | 0.034(1) |
| C(16) | 0.5955(3) | 0.2047(4) | 0.2308(3) | 0.043(2) |
| C(17) | 0.2977(2) | 0.9728(4) | 0.1711(2) | 0.025(1) |
| C(18) | 0.2647(2) | 0.8766(4) | 0.1959(2) | 0.030(1) |
| C(19) | 0.2214(2) | 0.8278(4) | 0.1432(3) | 0.035(1) |
| C(20) | 0.2340(2) | 0.7425(4) | 0.1101(3) | 0.037(1) |
| H(1SA) | 0.1876 | 0.8025 | -0.1678 | 0.055 |
| H(1SB) | 0.2578 | 0.7540 | -0.1817 | 0.055 |
| H(2A) | 0.4671 | 0.9629 | -0.0673 | 0.031 |
| H(3A) | 0.5563 | 0.8868 | -0.1190 | 0.036 |
| H(4A) | 0.5987 | 0.7315 | -0.0798 | 0.033 |
| H(6A) | 0.4600 | 0.7237 | 0.0660 | 0.023 |
| H(7A) | 0.3513 | 0.9602 | -0.0469 | 0.033 |
| H(8A) | 0.2711 | 1.0213 | 0.0359 | 0.035 |
| H(11A) | 0.5792 | 0.5405 | -0.0712 | 0.032 |
| H(12A) | 0.6248 | 0.4013 | -0.0015 | 0.039 |
| H(13A) | 0.6323 | 0.4807 | 0.1757 | 0.034 |

| | | | | |
|---|---|---|---|---|
| H(13B) | 0.6566 | 0.3902 | 0.1267 | 0.034 |
| H(14A) | 0.5269 | 0.4048 | 0.1766 | 0.039 |
| H(14B) | 0.5532 | 0.3124 | 0.1299 | 0.039 |
| H(15A) | 0.5991 | 0.3463 | 0.2648 | 0.041 |
| H(16A) | 0.5855 | 0.1616 | 0.1934 | 0.052 |
| H(16B) | 0.6104 | 0.1745 | 0.2716 | 0.052 |
| H(17A) | 0.2649 | 1.0280 | 0.1645 | 0.031 |
| H(17B) | 0.3287 | 0.9972 | 0.2057 | 0.031 |
| H(18A) | 0.2383 | 0.8941 | 0.2359 | 0.036 |
| H(18B) | 0.2980 | 0.8255 | 0.2098 | 0.036 |
| H(19A) | 0.1817 | 0.8621 | 0.1334 | 0.042 |
| H(20A) | 0.2731 | 0.7057 | 0.1184 | 0.044 |
| H(20B) | 0.2039 | 0.7172 | 0.0778 | 0.044 |

**Table S 9.** Anisotropic displacement parameters ($Å^2$) for bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$μ^3$-iodotetrasilver(I) (**3b**). The anisotropic displacement factor exponent takes the form:

$-2π^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Ag(1) | 0.0280(3) | 0.0380(3) | 0.0234(2) | -0.0002(2) | -0.0021(2) | 0.0082(2) |
| I(1) | 0.0239(2) | 0.0228(2) | 0.0229(2) | 0.0044(1) | -0.0026(1) | -0.0026(2) |
| N(1) | 0.020(3) | 0.022(2) | 0.022(2) | 0.0019(18) | -0.0051(18) | -0.0002(19) |
| C(1) | 0.017(3) | 0.025(3) | 0.020(2) | -0.003(2) | -0.003(2) | 0.001(2) |
| C(1S) | 0.050(4) | 0.052(4) | 0.035(3) | 0.001(3) | -0.010(3) | -0.011(3) |
| Cl(1) | 0.0420(10) | 0.0465(9) | 0.0461(8) | 0.0079(7) | -0.0085(7) | -0.0024(8) |
| Ag(2) | 0.0347(3) | 0.0269(2) | 0.0257(2) | -0.0025(2) | -0.0048(2) | 0.0071(2) |
| I(2) | 0.0254(2) | 0.0215(2) | 0.0218(2) | -0.0008(1) | -0.0014(1) | -0.0017(2) |
| N(2) | 0.020(2) | 0.017(2) | 0.029(2) | -0.0002(18) | 0.0013(18) | 0.0030(19) |
| C(2) | 0.035(4) | 0.020(3) | 0.023(3) | 0.005(2) | -0.002(2) | -0.003(2) |
| Cl(2) | 0.0765(12) | 0.0676(12) | 0.0510(10) | 0.0183(9) | -0.0089(9) | -0.0221(10) |
| N(3) | 0.019(3) | 0.024(2) | 0.025(2) | -0.0014(19) | 0.0007(18) | -0.0027(19) |
| C(3) | 0.042(4) | 0.027(3) | 0.020(3) | 0.003(2) | 0.008(2) | -0.014(3) |
| N(4) | 0.021(3) | 0.014(2) | 0.033(2) | -0.0032(19) | -0.0010(18) | 0.0006(18) |
| C(4) | 0.032(3) | 0.026(3) | 0.025(3) | -0.007(2) | 0.008(2) | -0.007(3) |
| C(5) | 0.020(3) | 0.019(3) | 0.025(3) | -0.005(2) | -0.009(2) | 0.000(2) |
| C(6) | 0.018(3) | 0.022(3) | 0.017(2) | -0.003(2) | -0.002(2) | -0.003(2) |
| C(7) | 0.028(3) | 0.028(3) | 0.027(3) | 0.008(2) | -0.011(2) | 0.000(2) |
| C(8) | 0.029(4) | 0.023(3) | 0.035(3) | 0.003(2) | -0.010(2) | 0.006(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(9) | 0.022(3) | 0.017(3) | 0.022(3) | -0.003(2) | 0.001(2) | -0.007(2) |
| C(10) | 0.013(3) | 0.022(3) | 0.028(3) | 0.001(2) | 0.001(2) | -0.003(2) |
| C(11) | 0.027(3) | 0.028(3) | 0.025(3) | -0.010(2) | 0.007(2) | -0.006(2) |
| C(12) | 0.030(3) | 0.022(3) | 0.044(3) | -0.013(3) | 0.002(3) | -0.007(3) |
| C(13) | 0.018(3) | 0.022(3) | 0.046(3) | -0.001(3) | -0.005(2) | 0.004(2) |
| C(14) | 0.027(4) | 0.032(3) | 0.040(3) | 0.001(3) | -0.008(3) | 0.002(3) |
| C(15) | 0.033(3) | 0.029(3) | 0.040(3) | 0.000(3) | -0.004(3) | 0.005(3) |
| C(16) | 0.047(4) | 0.040(4) | 0.043(3) | 0.010(3) | -0.003(3) | 0.003(3) |
| C(17) | 0.022(3) | 0.025(3) | 0.029(3) | -0.007(2) | -0.001(2) | 0.000(2) |
| C(18) | 0.019(3) | 0.040(3) | 0.031(3) | -0.004(2) | 0.002(2) | -0.003(3) |
| C(19) | 0.016(3) | 0.041(4) | 0.049(3) | 0.002(3) | -0.001(3) | -0.004(3) |
| C(20) | 0.027(3) | 0.032(3) | 0.051(3) | -0.010(3) | -0.006(3) | -0.002(3) |

**Table S 10.** Bond lengths [Å] for Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3b**)

| atom-atom | distance | atom-atom | distance |
|---|---|---|---|
| Ag(1)-C(9) | 2.185(5) | Ag(1)-I(1i) | 2.8482(5) |
| Ag(1)-I(1) | 2.8846(5) | Ag(1)-Ag(2) | 3.0341(6) |
| Ag(1)-I(2) | 3.1789(5) | Ag(1)-Ag(1i) | 3.2985(8) |
| I(1)-Ag(1i) | 2.8481(5) | I(1)-Ag(2) | 2.9406(5) |
| N(1)-C(9) | 1.379(5) | N(1)-C(7) | 1.386(5) |
| N(1)-C(1) | 1.435(6) | C(1)-C(6) | 1.385(6) |
| C(1)-C(2) | 1.391(6) | C(1S)-Cl(2) | 1.748(5) |
| C(1S)-Cl(1) | 1.757(5) | C(1S)-H(1SA) | 0.9900 |
| C(1S)-H(1SB) | 0.9900 | Ag(2)-C(10) | 2.184(5) |
| Ag(2)-I(2i) | 2.8696(5) | Ag(2)-I(2) | 3.0084(5) |
| Ag(2)-Ag(2i) | 3.3254(8) | I(2)-Ag(2i) | 2.8695(5) |
| N(2)-C(9) | 1.349(5) | N(2)-C(8) | 1.381(5) |
| N(2)-C(17) | 1.459(5) | C(2)-C(3) | 1.377(6) |
| C(2)-H(2A) | 0.9500 | N(3)-C(10) | 1.373(5) |
| N(3)-C(11) | 1.388(5) | N(3)-C(5) | 1.437(5) |
| C(3)-C(4) | 1.368(6) | C(3)-H(3A) | 0.9500 |
| N(4)-C(10) | 1.353(5) | N(4)-C(12) | 1.394(6) |
| N(4)-C(13) | 1.467(5) | C(4)-C(5) | 1.395(6) |
| C(4)-H(4A) | 0.9500 | C(5)-C(6) | 1.390(6) |
| C(6)-H(6A) | 0.9500 | C(7)-C(8) | 1.333(6) |
| C(7)-H(7A) | 0.9500 | C(8)-H(8A) | 0.9500 |
| C(11)-C(12) | 1.322(6) | C(11)-H(11A) | 0.9500 |
| C(12)-H(12A) | 0.9500 | C(13)-C(14) | 1.510(6) |
| C(13)-H(13A) | 0.9900 | C(13)-H(13B) | 0.9900 |
| C(14)-C(15) | 1.494(6) | C(14)-H(14A) | 0.9900 |
| C(14)-H(14B) | 0.9900 | C(15)-C(16) | 1.315(7) |
| C(15)-H(15A) | 0.9500 | C(16)-H(16A) | 0.9500 |
| C(16)-H(16B) | 0.9500 | C(17)-C(18) | 1.496(6) |
| C(17)-H(17A) | 0.9900 | C(17)-H(17B) | 0.9900 |
| C(18)-C(19) | 1.513(6) | C(18)-H(18A) | 0.9900 |

| | | | |
|---|---|---|---|
| C(18)-H(18B) | 0.9900 | C(19)-C(20) | 1.305(6) |
| C(19)-H(19A) | 0.9500 | C(20)-H(20A) | 0.9500 |
| C(20)-H(20B) | 0.9500 | | |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

**Table S 11.** Bond angles [°] for Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3b**).

| atom-atom-atom | angle | atom-atom-atom | angle |
|---|---|---|---|
| C(9)-Ag(1)-I(1i) | 123.29(12) | C(9)-Ag(1)-I(1) | 114.65(12) |
| I(1i)-Ag(1)-I(1) | 105.983(15) | C(9)-Ag(1)-Ag(2) | 124.31(12) |
| I(1i)-Ag(1)-Ag(2) | 109.756(15) | I(1)-Ag(1)-Ag(2) | 59.518(13) |
| C(9)-Ag(1)-I(2) | 100.46(11) | I(1i)-Ag(1)-I(2) | 93.758(14) |
| I(1)-Ag(1)-I(2) | 117.378(15) | Ag(2)-Ag(1)-I(2) | 57.865(13) |
| C(9)-Ag(1)-Ag(1i) | 160.03(11) | I(1i)-Ag(1)-Ag(1i) | 55.396(12) |
| I(1)-Ag(1)-Ag(1i) | 54.358(13) | Ag(2)-Ag(1)-Ag(1i) | 67.341(13) |
| I(2)-Ag(1)-Ag(1i) | 99.503(9) | Ag(1i)-I(1)-Ag(1) | 70.248(15) |
| Ag(1i)-I(1)-Ag(2) | 74.825(13) | Ag(1)-I(1)-Ag(2) | 62.769(13) |
| C(9)-N(1)-C(7) | 110.3(4) | C(9)-N(1)-C(1) | 125.8(4) |
| C(7)-N(1)-C(1) | 123.9(4) | C(6)-C(1)-C(2) | 121.2(4) |
| C(6)-C(1)-N(1) | 120.2(4) | C(2)-C(1)-N(1) | 118.5(4) |
| Cl(2)-C(1S)-Cl(1) | 112.1(3) | Cl(2)-C(1S)-H(1SA) | 109.2 |
| Cl(1)-C(1S)-H(1SA) | 109.2 | Cl(2)-C(1S)-H(1SB) | 109.2 |
| Cl(1)-C(1S)-H(1SB) | 109.2 | H(1SA)-C(1S)-H(1SB) | 107.9 |
| C(10)-Ag(2)-I(2i) | 121.80(12) | C(10)-Ag(2)-I(1) | 110.32(12) |
| I(2i)-Ag(2)-I(1) | 98.597(14) | C(10)-Ag(2)-I(2) | 102.49(12) |
| I(2i)-Ag(2)-I(2) | 103.675(15) | I(1)-Ag(2)-I(2) | 121.188(15) |
| C(10)-Ag(2)-Ag(1) | 124.46(12) | I(2i)-Ag(2)-Ag(1) | 113.730(15) |
| I(1)-Ag(2)-Ag(1) | 57.712(13) | I(2)-Ag(2)-Ag(1) | 63.482(14) |
| C(10)-Ag(2)-Ag(2i) | 148.74(12) | I(2i)-Ag(2)-Ag(2i) | 57.542(12) |
| I(1)-Ag(2)-Ag(2i) | 100.171(9) | I(2)-Ag(2)-Ag(2i) | 53.596(13) |
| Ag(1)-Ag(2)-Ag(2i) | 66.986(13) | Ag(2i)-I(2)-Ag(2) | 68.862(15) |
| Ag(2i)-I(2)-Ag(1) | 70.916(12) | Ag(2)-I(2)-Ag(1) | 58.653(12) |
| C(9)-N(2)-C(8) | 111.5(4) | C(9)-N(2)-C(17) | 123.2(4) |
| C(8)-N(2)-C(17) | 125.1(4) | C(3)-C(2)-C(1) | 119.1(4) |
| C(3)-C(2)-H(2A) | 120.5 | C(1)-C(2)-H(2A) | 120.5 |
| C(10)-N(3)-C(11) | 111.1(4) | C(10)-N(3)-C(5) | 125.5(4) |
| C(11)-N(3)-C(5) | 123.4(4) | C(4)-C(3)-C(2) | 121.3(4) |
| C(4)-C(3)-H(3A) | 119.3 | C(2)-C(3)-H(3A) | 119.3 |
| C(10)-N(4)-C(12) | 111.7(4) | C(10)-N(4)-C(13) | 123.5(4) |
| C(12)-N(4)-C(13) | 124.8(4) | C(3)-C(4)-C(5) | 119.1(5) |
| C(3)-C(4)-H(4A) | 120.5 | C(5)-C(4)-H(4A) | 120.5 |
| C(6)-C(5)-C(4) | 121.1(4) | C(6)-C(5)-N(3) | 120.3(4) |
| C(4)-C(5)-N(3) | 118.5(4) | C(1)-C(6)-C(5) | 118.2(4) |
| C(1)-C(6)-H(6A) | 120.9 | C(5)-C(6)-H(6A) | 120.9 |
| C(8)-C(7)-N(1) | 107.0(4) | C(8)-C(7)-H(7A) | 126.5 |
| N(1)-C(7)-H(7A) | 126.5 | C(7)-C(8)-N(2) | 107.2(4) |
| C(7)-C(8)-H(8A) | 126.4 | N(2)-C(8)-H(8A) | 126.4 |
| N(2)-C(9)-N(1) | 103.9(4) | N(2)-C(9)-Ag(1) | 126.5(3) |
| N(1)-C(9)-Ag(1) | 129.4(3) | N(4)-C(10)-N(3) | 103.2(4) |

| | | | |
|---|---|---|---|
| N(4)-C(10)-Ag(2) | 126.0(3) | N(3)-C(10)-Ag(2) | 130.8(3) |
| C(12)-C(11)-N(3) | 107.2(4) | C(12)-C(11)-H(11A) | 126.4 |
| N(3)-C(11)-H(11A) | 126.4 | C(11)-C(12)-N(4) | 106.8(4) |
| C(11)-C(12)-H(12A) | 126.6 | N(4)-C(12)-H(12A) | 126.6 |
| N(4)-C(13)-C(14) | 113.1(4) | N(4)-C(13)-H(13A) | 109.0 |
| C(14)-C(13)-H(13A) | 109.0 | N(4)-C(13)-H(13B) | 109.0 |
| C(14)-C(13)-H(13B) | 109.0 | H(13A)-C(13)-H(13B) | 107.8 |
| C(15)-C(14)-C(13) | 110.0(4) | C(15)-C(14)-H(14A) | 109.7 |
| C(13)-C(14)-H(14A) | 109.7 | C(15)-C(14)-H(14B) | 109.7 |
| C(13)-C(14)-H(14B) | 109.7 | H(14A)-C(14)-H(14B) | 108.2 |
| C(16)-C(15)-C(14) | 125.2(5) | C(16)-C(15)-H(15A) | 117.4 |
| C(14)-C(15)-H(15A) | 117.4 | C(15)-C(16)-H(16A) | 120.0 |
| C(15)-C(16)-H(16B) | 120.0 | H(16A)-C(16)-H(16B) | 120.0 |
| N(2)-C(17)-C(18) | 112.7(4) | N(2)-C(17)-H(17A) | 109.1 |
| C(18)-C(17)-H(17A) | 109.1 | N(2)-C(17)-H(17B) | 109.1 |
| C(18)-C(17)-H(17B) | 109.1 | H(17A)-C(17)-H(17B) | 107.8 |
| C(17)-C(18)-C(19) | 112.6(4) | C(17)-C(18)-H(18A) | 109.1 |
| C(19)-C(18)-H(18A) | 109.1 | C(17)-C(18)-H(18B) | 109.1 |
| C(19)-C(18)-H(18B) | 109.1 | H(18A)-C(18)-H(18B) | 107.8 |
| C(20)-C(19)-C(18) | 125.6(5) | C(20)-C(19)-H(19A) | 117.2 |
| C(18)-C(19)-H(19A) | 117.2 | C(19)-C(20)-H(20A) | 120.0 |
| C(19)-C(20)-H(20B) | 120.0 | H(20A)-C(20)-H(20B) | 120.0 |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

**Table S 12.** Torsion angles [°] for Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3b**)

| atom-atom-atom-atom | angle | atom-atom-atom-atom | angle |
|---|---|---|---|
| C(9)-N(1)-C(1)-C(6) | 40.2(6) | C(7)-N(1)-C(1)-C(6) | -141.6(4) |
| C(9)-N(1)-C(1)-C(2) | -142.5(4) | C(7)-N(1)-C(1)-C(2) | 35.7(6) |
| C(6)-C(1)-C(2)-C(3) | -1.8(7) | N(1)-C(1)-C(2)-C(3) | -179.0(4) |
| C(1)-C(2)-C(3)-C(4) | 0.5(7) | C(2)-C(3)-C(4)-C(5) | 0.2(7) |
| C(3)-C(4)-C(5)-C(6) | 0.3(7) | C(3)-C(4)-C(5)-N(3) | 178.6(4) |
| C(10)-N(3)-C(5)-C(6) | -43.7(6) | C(11)-N(3)-C(5)-C(6) | 139.7(4) |
| C(10)-N(3)-C(5)-C(4) | 138.0(4) | C(11)-N(3)-C(5)-C(4) | -38.6(6) |
| C(2)-C(1)-C(6)-C(5) | 2.2(6) | N(1)-C(1)-C(6)-C(5) | 179.4(4) |
| C(4)-C(5)-C(6)-C(1) | -1.4(6) | N(3)-C(5)-C(6)-C(1) | -179.7(4) |
| C(9)-N(1)-C(7)-C(8) | -1.2(5) | C(1)-N(1)-C(7)-C(8) | -179.7(4) |
| N(1)-C(7)-C(8)-N(2) | 1.7(5) | C(9)-N(2)-C(8)-C(7) | -1.7(5) |
| C(17)-N(2)-C(8)-C(7) | -176.0(4) | C(8)-N(2)-C(9)-N(1) | 1.0(5) |
| C(17)-N(2)-C(9)-N(1) | 175.4(4) | C(8)-N(2)-C(9)-Ag(1) | 176.4(3) |
| C(17)-N(2)-C(9)-Ag(1) | -9.2(6) | C(7)-N(1)-C(9)-N(2) | 0.1(5) |
| C(1)-N(1)-C(9)-N(2) | 178.6(4) | C(7)-N(1)-C(9)-Ag(1) | -175.2(3) |
| C(1)-N(1)-C(9)-Ag(1) | 3.3(6) | C(12)-N(4)-C(10)-N(3) | -1.4(5) |
| C(13)-N(4)-C(10)-N(3) | -179.8(4) | C(12)-N(4)-C(10)-Ag(2) | 176.9(3) |
| C(13)-N(4)-C(10)-Ag(2) | -1.5(6) | C(11)-N(3)-C(10)-N(4) | 1.6(5) |
| C(5)-N(3)-C(10)-N(4) | -175.4(4) | C(11)-N(3)-C(10)-Ag(2) | -176.6(3) |
| C(5)-N(3)-C(10)-Ag(2) | 6.5(7) | C(10)-N(3)-C(11)-C(12) | -1.2(5) |
| C(5)-N(3)-C(11)-C(12) | 175.8(4) | N(3)-C(11)-C(12)-N(4) | 0.3(5) |

| | | | |
|---|---|---|---|
| C(10)-N(4)-C(12)-C(11) | 0.7(5) | C(13)-N(4)-C(12)-C(11) | 179.1(4) |
| C(10)-N(4)-C(13)-C(14) | 87.4(5) | C(12)-N(4)-C(13)-C(14) | -90.7(5) |
| N(4)-C(13)-C(14)-C(15) | -177.6(4) | C(13)-C(14)-C(15)-C(16) | -116.5(6) |
| C(9)-N(2)-C(17)-C(18) | -72.8(5) | C(8)-N(2)-C(17)-C(18) | 100.9(5) |
| N(2)-C(17)-C(18)-C(19) | -52.9(6) | C(17)-C(18)-C(19)-C(20) | 106.7(6) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Experimental

Single crystals of $C_{21}H_{24}Ag_2Cl_2I_2N_4$ [bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3b**)] were [Crystallized via Slow Evaporation of a Saturated Solution of CH2Cl2]. A suitable crystal was selected and [Mounted on a 200 Micron Mitogen Mount] on a Bruker Smart APEX II diffractometer. The crystal was kept at 100K K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. olex2.solve (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011)
3. olex2.refine (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011)

Crystal structure determination of Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (3b).

**Crystal data** for C42 H48 Ag4 Cl4 I4 N8; $M_r$ = 1745.76; Orthorhombic; space group P b c n; *a* = 20.6181(12) Å; *b* = 12.8667(7) Å; *c* = 19.8917(11) Å; α = 90°; β = 90°; γ = 90°; V = 5277.0(5) $Å^3$; Z = 4; T = 100(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 4.043 $mm^{-1}$; $d_{calc}$ = 2.197g.$cm^{-3}$; 31536 reflections collected; 5297 unique ($R_{int}$ = 0.0668); giving $R_1$ = 0.0376, $wR_2$ = 0.0753 for 4069 data with [I>2σ(I)] and $R_1$ = 0.0554, $wR_2$ = 0.0835 for all 5297 data. Residual electron density ($e^-$.$Å^{-3}$) max/min: 0.738/-1.057.

Crystallographic Report forBis(μ-1,3-bis(3'-pent-4"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3c**)

**Figure S 1.** 50% Occupancy of the Pentenyl Chain

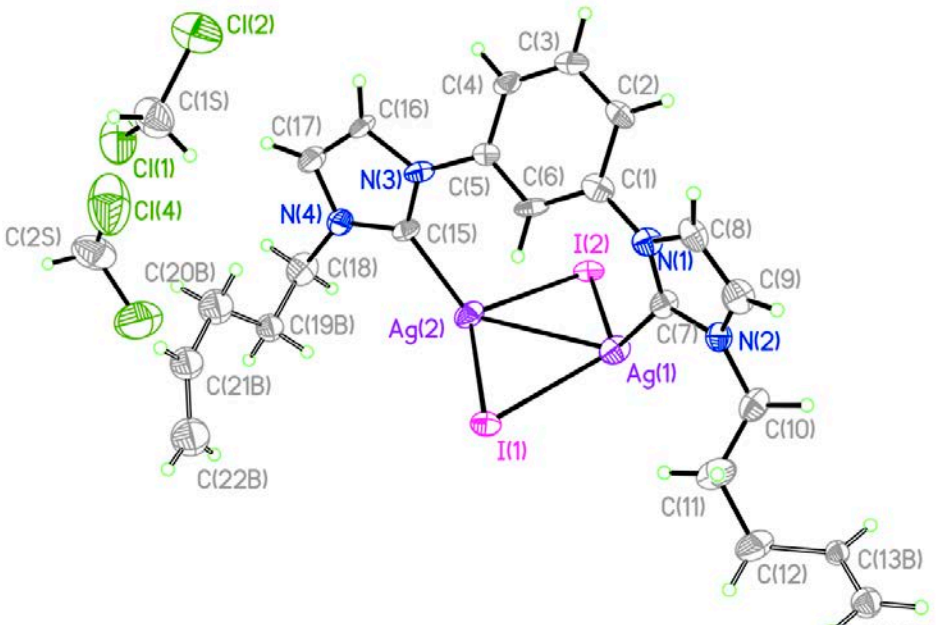


**Figure S 2.** 50% Occupancy of the Pentenyl Chain

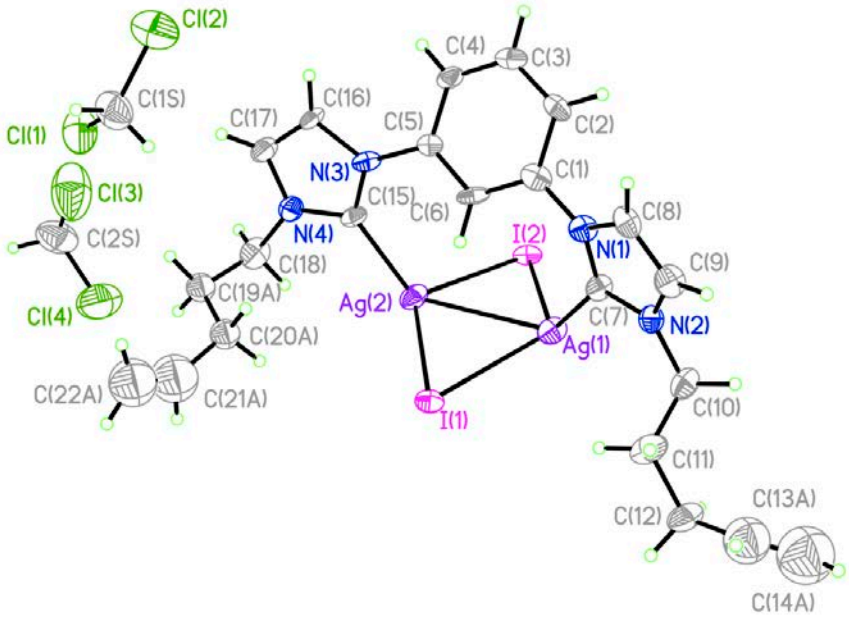

**Table S 13 . Crystal data and structure refinement for Bis(μ-1,3-bis(3'-pent-4''-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (3c) .**

| | |
|---|---|
| Identification code | Bis(μ-1,3-bis(3'-pent-4''-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (**3c**) |
| Empirical formula | $C_{24}H_{30}Ag_2Cl_4I_2N_4$ |
| Formula weight | 985.86 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C 2/c |
| Unit cell dimensions | *a* = 24.593(19) Å α = 90° |
| | *b* = 13.718(10) Å β = 102.384(9)° |
| | *c* = 19.601(15) Å γ = 90° |
| Volume | 6459(8) Å$^3$ |
| Z | 8 |
| Density (calculated) | 2.028 g.cm$^{-3}$ |
| Absorption coefficient (μ) | 3.476 mm$^{-1}$ |
| F(000) | 3760 |
| Crystal color, habit | Colorless, Block |
| Crystal size | 0.20 × 0.20 × 0.20 mm$^3$ |
| θ range for data collection | 1.709 to 26.369° |
| Index ranges | -30 ≤ h ≤ 30, -17 ≤ k ≤ 17, -24 ≤ l ≤ 24 |
| Reflections collected | 31460 |
| Independent reflections | 6584 [$R_{int}$ = 0.0652] |
| Completeness to θ = 25.242° | 99.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 6584 / 0 / 319 |
| Goodness-of-fit on F$^2$ | 1.160 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0605, w$R_2$ = 0.1276 |
| R indices (all data) | $R_1$ = 0.0797, w$R_2$ = 0.1428 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.640 and -1.096 e$^-$.Å$^{-3}$ |

**Table S 14 .** Atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for Bis(μ-1,3-bis(3'-pent-4''-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (**3c**) . U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| I(1) | 0.42230(3) | 0.36651(4) | 0.17018(3) | 0.026(1) |
| I(2) | 0.57327(3) | 0.11114(4) | 0.20259(3) | 0.028(1) |
| Ag(1) | 0.54564(3) | 0.31534(5) | 0.18200(4) | 0.032(1) |
| Ag(2) | 0.45369(3) | 0.15826(5) | 0.16289(4) | 0.032(1) |
| N(1) | 0.5516(3) | 0.3758(6) | 0.0224(4) | 0.027(2) |
| N(2) | 0.5848(3) | 0.4892(5) | 0.0973(4) | 0.026(2) |
| N(3) | 0.4244(3) | 0.0949(5) | -0.0019(4) | 0.025(2) |
| N(4) | 0.3670(3) | 0.0318(6) | 0.0555(4) | 0.028(2) |
| C(1) | 0.5321(4) | 0.2849(7) | -0.0085(5) | 0.028(2) |
| C(2) | 0.5586(4) | 0.2454(7) | -0.0595(5) | 0.027(2) |

| | | | | |
|---|---|---|---|---|
| C(3) | 0.5392(4) | 0.1555(7) | -0.0901(5) | 0.031(2) |
| C(4) | 0.4969(4) | 0.1065(6) | -0.0700(5) | 0.026(2) |
| C(5) | 0.4702(4) | 0.1468(6) | -0.0202(4) | 0.023(2) |
| C(6) | 0.4885(4) | 0.2371(6) | 0.0116(4) | 0.025(2) |
| C(7) | 0.5635(4) | 0.3968(6) | 0.0931(5) | 0.026(2) |
| C(8) | 0.5663(4) | 0.4554(7) | -0.0160(5) | 0.029(2) |
| C(9) | 0.5861(4) | 0.5266(7) | 0.0312(5) | 0.035(2) |
| C(10) | 0.6038(4) | 0.5430(7) | 0.1628(5) | 0.036(2) |
| C(11) | 0.5571(5) | 0.6029(8) | 0.1830(6) | 0.045(3) |
| C(12) | 0.5781(5) | 0.6593(8) | 0.2544(5) | 0.042(3) |
| C(13A) | 0.6044(17) | 0.751(3) | 0.244(2) | 0.082(10) |
| C(14A) | 0.645(2) | 0.791(4) | 0.267(3) | 0.126(17) |
| C(13B) | 0.6273(8) | 0.7259(13) | 0.2548(9) | 0.020(3) |
| C(14B) | 0.6194(9) | 0.8283(15) | 0.2453(10) | 0.030(4) |
| C(15) | 0.4124(4) | 0.0927(6) | 0.0631(4) | 0.024(2) |
| C(16) | 0.3881(4) | 0.0358(7) | -0.0499(5) | 0.030(2) |
| C(17) | 0.3513(4) | -0.0028(8) | -0.0142(5) | 0.034(2) |
| C(18) | 0.3365(5) | 0.0064(8) | 0.1097(5) | 0.039(2) |
| C(19A) | 0.2795(9) | 0.0467(17) | 0.1009(12) | 0.038(5) |
| C(20A) | 0.2824(9) | 0.1560(16) | 0.1078(12) | 0.039(5) |
| C(21A) | 0.2290(18) | 0.204(3) | 0.107(2) | 0.097(12) |
| C(22A) | 0.1909(18) | 0.230(3) | 0.073(3) | 0.093(12) |
| C(19B) | 0.2926(8) | 0.0910(17) | 0.1154(10) | 0.031(4) |
| C(20B) | 0.2468(10) | 0.1082(18) | 0.0516(13) | 0.047(5) |
| C(21B) | 0.2089(10) | 0.1914(17) | 0.0547(12) | 0.040(5) |
| C(22B) | 0.1998(13) | 0.244(2) | 0.1125(16) | 0.055(7) |
| C(1S) | 0.2222(5) | 0.0251(10) | -0.1484(7) | 0.056(3) |
| Cl(1) | 0.20151(15) | -0.0636(3) | -0.0953(2) | 0.068(1) |
| Cl(2) | 0.26764(18) | -0.0205(3) | -0.1990(2) | 0.073(1) |
| C(2S) | 0.1869(7) | -0.2441(10) | 0.1227(9) | 0.072(4) |
| Cl(3) | 0.2013(2) | -0.2008(5) | 0.0468(3) | 0.116(2) |
| Cl(4) | 0.2117(2) | -0.1716(5) | 0.1939(3) | 0.131(3) |
| H(2A) | 0.5886 | 0.2786 | -0.0729 | 0.033 |
| H(3A) | 0.5559 | 0.1284 | -0.1252 | 0.037 |
| H(4A) | 0.4855 | 0.0447 | -0.0899 | 0.031 |
| H(6A) | 0.4713 | 0.2643 | 0.0462 | 0.030 |
| H(8A) | 0.5629 | 0.4584 | -0.0652 | 0.035 |
| H(9A) | 0.5985 | 0.5896 | 0.0212 | 0.042 |
| H(10A) | 0.6346 | 0.5872 | 0.1578 | 0.043 |
| H(10B) | 0.6186 | 0.4963 | 0.2007 | 0.043 |
| H(11A) | 0.5261 | 0.5590 | 0.1874 | 0.055 |
| H(11B) | 0.5427 | 0.6506 | 0.1455 | 0.055 |
| H(12A) | 0.5460 | 0.6718 | 0.2763 | 0.051 |
| H(12B) | 0.6049 | 0.6178 | 0.2866 | 0.051 |
| H(12C) | 0.5469 | 0.6986 | 0.2643 | 0.051 |
| H(12D) | 0.5885 | 0.6109 | 0.2924 | 0.051 |
| H(13A) | 0.5811 | 0.7883 | 0.2091 | 0.098 |
| H(14A) | 0.6723 | 0.7618 | 0.3024 | 0.151 |
| H(14B) | 0.6514 | 0.8536 | 0.2492 | 0.151 |
| H(13B) | 0.6637 | 0.6991 | 0.2614 | 0.024 |
| H(14C) | 0.5831 | 0.8553 | 0.2386 | 0.036 |
| H(14D) | 0.6505 | 0.8696 | 0.2456 | 0.036 |

| | | | | |
|---|---|---|---|---|
| H(16A) | 0.3890 | 0.0250 | -0.0975 | 0.036 |
| H(17A) | 0.3209 | -0.0447 | -0.0325 | 0.041 |
| H(18A) | 0.3586 | 0.0287 | 0.1553 | 0.047 |
| H(18B) | 0.3340 | -0.0656 | 0.1118 | 0.047 |
| H(18C) | 0.3629 | -0.0016 | 0.1552 | 0.047 |
| H(18D) | 0.3166 | -0.0562 | 0.0978 | 0.047 |
| H(19A) | 0.2611 | 0.0191 | 0.1368 | 0.045 |
| H(19B) | 0.2571 | 0.0287 | 0.0544 | 0.045 |
| H(20A) | 0.3086 | 0.1727 | 0.1520 | 0.046 |
| H(20B) | 0.2978 | 0.1827 | 0.0690 | 0.046 |
| H(21A) | 0.2268 | 0.2164 | 0.1542 | 0.116 |
| H(22A) | 0.1859 | 0.2240 | 0.0238 | 0.112 |
| H(22B) | 0.1628 | 0.2601 | 0.0925 | 0.112 |
| H(19C) | 0.2750 | 0.0754 | 0.1551 | 0.037 |
| H(19D) | 0.3134 | 0.1527 | 0.1269 | 0.037 |
| H(20C) | 0.2643 | 0.1183 | 0.0111 | 0.056 |
| H(20D) | 0.2241 | 0.0482 | 0.0425 | 0.056 |
| H(21B) | 0.1875 | 0.2120 | 0.0108 | 0.048 |
| H(22C) | 0.2197 | 0.2278 | 0.1582 | 0.066 |
| H(22D) | 0.1737 | 0.2963 | 0.1060 | 0.066 |
| H(1SA) | 0.2409 | 0.0789 | -0.1187 | 0.067 |
| H(1SB) | 0.1888 | 0.0524 | -0.1800 | 0.067 |
| H(2SA) | 0.2032 | -0.3100 | 0.1318 | 0.087 |
| H(2SB) | 0.1460 | -0.2504 | 0.1167 | 0.087 |

**Table S 15.** Anisotropic displacement parameters (Å²) for Bis(μ-1,3-bis(3'-pent-4''-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ³-iodotetrasilver(I) (**3c**) .

The anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| I(1) | 0.0337(3) | 0.0251(3) | 0.0209(3) | 0.0027(2) | 0.0080(2) | 0.0043(2) |
| I(2) | 0.0377(3) | 0.0254(3) | 0.0221(3) | -0.0026(2) | 0.0076(2) | 0.0068(2) |
| Ag(1) | 0.0448(4) | 0.0283(4) | 0.0221(3) | 0.0037(3) | 0.0087(3) | -0.0052(3) |
| Ag(2) | 0.0433(4) | 0.0318(4) | 0.0214(3) | -0.0026(3) | 0.0058(3) | -0.0086(3) |
| N(1) | 0.034(4) | 0.026(4) | 0.021(4) | 0.005(3) | 0.008(3) | 0.000(3) |
| N(2) | 0.027(4) | 0.025(4) | 0.028(4) | 0.003(3) | 0.008(3) | -0.003(3) |
| N(3) | 0.037(4) | 0.018(3) | 0.020(4) | -0.003(3) | 0.008(3) | 0.001(3) |
| N(4) | 0.030(4) | 0.024(4) | 0.031(4) | -0.002(3) | 0.008(3) | -0.004(3) |
| C(1) | 0.036(5) | 0.031(5) | 0.018(4) | 0.011(4) | 0.009(4) | 0.005(4) |
| C(2) | 0.022(4) | 0.034(5) | 0.027(5) | 0.005(4) | 0.009(4) | 0.007(4) |
| C(3) | 0.038(5) | 0.034(5) | 0.023(4) | -0.005(4) | 0.009(4) | 0.007(4) |
| C(4) | 0.028(5) | 0.018(4) | 0.029(5) | -0.008(4) | 0.003(4) | 0.004(3) |
| C(5) | 0.027(4) | 0.021(4) | 0.020(4) | 0.000(3) | 0.006(3) | 0.003(3) |
| C(6) | 0.044(5) | 0.013(4) | 0.019(4) | -0.003(3) | 0.007(4) | 0.008(4) |
| C(7) | 0.037(5) | 0.019(4) | 0.023(4) | 0.004(3) | 0.010(4) | -0.007(4) |
| C(8) | 0.027(5) | 0.032(5) | 0.029(5) | 0.012(4) | 0.009(4) | 0.002(4) |
| C(9) | 0.042(6) | 0.032(5) | 0.032(5) | 0.009(4) | 0.013(4) | -0.004(4) |
| C(10) | 0.041(6) | 0.028(5) | 0.037(5) | -0.001(4) | 0.004(4) | -0.008(4) |
| C(11) | 0.051(7) | 0.039(6) | 0.042(6) | -0.012(5) | 0.000(5) | 0.005(5) |
| C(12) | 0.061(7) | 0.037(6) | 0.029(5) | -0.007(4) | 0.009(5) | -0.007(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(15) | 0.029(5) | 0.024(4) | 0.017(4) | -0.003(3) | -0.001(3) | 0.003(4) |
| C(16) | 0.029(5) | 0.033(5) | 0.024(4) | -0.015(4) | -0.001(4) | -0.005(4) |
| C(17) | 0.032(5) | 0.036(5) | 0.032(5) | -0.012(4) | 0.000(4) | -0.001(4) |
| C(18) | 0.050(6) | 0.037(6) | 0.030(5) | 0.009(4) | 0.010(5) | -0.012(5) |
| C(1S) | 0.047(7) | 0.058(8) | 0.062(8) | 0.006(6) | 0.010(6) | 0.017(6) |
| Cl(1) | 0.0525(19) | 0.083(3) | 0.065(2) | 0.0131(19) | 0.0062(16) | -0.0095(18) |
| Cl(2) | 0.082(3) | 0.079(3) | 0.064(2) | 0.0045(19) | 0.028(2) | 0.016(2) |
| C(2S) | 0.087(11) | 0.047(8) | 0.094(12) | -0.005(8) | 0.041(9) | 0.010(7) |
| Cl(3) | 0.086(3) | 0.164(6) | 0.095(4) | 0.037(4) | 0.010(3) | -0.029(4) |
| Cl(4) | 0.100(4) | 0.166(6) | 0.116(4) | -0.076(4) | -0.003(3) | 0.029(4) |

**Table S 16.** Bond lengths [Å] for Bis(μ-1,3-bis(3'-pent-4''-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (**3c**) .

| atom-atom | distance | atom-atom | distance |
|---|---|---|---|
| I(1)-Ag(1i) | 2.920(2) | I(1)-Ag(2) | 2.971(2) |
| I(1)-Ag(1) | 3.073(2) | I(2)-Ag(1) | 2.890(2) |
| I(2)-Ag(2i) | 2.926(2) | I(2)-Ag(2) | 2.948(2) |
| Ag(1)-C(7) | 2.192(8) | Ag(1)-I(1i) | 2.921(2) |
| Ag(1)-Ag(2) | 3.088(2) | Ag(2)-C(15) | 2.193(8) |
| Ag(2)-I(2i) | 2.926(2) | N(1)-C(7) | 1.385(11) |
| N(1)-C(8) | 1.416(11) | N(1)-C(1) | 1.423(12) |
| N(2)-C(7) | 1.367(11) | N(2)-C(9) | 1.402(12) |
| N(2)-C(10) | 1.468(12) | N(3)-C(15) | 1.368(11) |
| N(3)-C(16) | 1.407(11) | N(3)-C(5) | 1.442(11) |
| N(4)-C(15) | 1.378(12) | N(4)-C(17) | 1.420(12) |
| N(4)-C(18) | 1.468(12) | C(1)-C(6) | 1.384(13) |
| C(1)-C(2) | 1.413(12) | C(2)-C(3) | 1.409(14) |
| C(3)-C(4) | 1.366(14) | C(4)-C(5) | 1.401(12) |
| C(5)-C(6) | 1.417(12) | C(8)-C(9) | 1.363(14) |
| C(10)-C(11) | 1.532(15) | C(11)-C(12) | 1.585(14) |
| C(12)-C(13A) | 1.44(4) | C(12)-C(13B) | 1.52(2) |
| C(13A)-C(14A) | 1.14(6) | C(13B)-C(14B) | 1.43(3) |
| C(16)-C(17) | 1.364(14) | C(18)-C(19A) | 1.48(2) |
| C(18)-C(19B) | 1.61(2) | C(19A)-C(20A) | 1.50(3) |
| C(20A)-C(21A) | 1.46(5) | C(21A)-C(22A) | 1.09(5) |
| C(19B)-C(20B) | 1.51(3) | C(20B)-C(21B) | 1.48(3) |
| C(21B)-C(22B) | 1.40(4) | C(1S)-Cl(1) | 1.747(14) |
| C(1S)-Cl(2) | 1.759(13) | C(2S)-Cl(3) | 1.709(17) |
| C(2S)-Cl(4) | 1.715(17) | | |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

**Table S 17.** Bond angles [°] for Bis(μ-1,3-bis(3'-pent-4''-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (**3c**) .

| atom-atom-atom | angle | atom-atom-atom | angle |
|---|---|---|---|
| Ag(1i)-I(1)-Ag(2) | 78.40(3) | Ag(1i)-I(1)-Ag(1) | 79.53(3) |
| Ag(2)-I(1)-Ag(1) | 61.42(2) | Ag(1)-I(2)-Ag(2i) | 79.62(3) |
| Ag(1)-I(2)-Ag(2) | 63.85(2) | Ag(2i)-I(2)-Ag(2) | 77.49(4) |
| C(7)-Ag(1)-I(2) | 121.6(2) | C(7)-Ag(1)-I(1i) | 127.5(2) |

| | | | |
|---|---|---|---|
| I(2)-Ag(1)-I(1i) | 95.11(3) | C(7)-Ag(1)-I(1) | 100.7(3) |
| I(2)-Ag(1)-I(1) | 115.50(3) | I(1i)-Ag(1)-I(1) | 94.13(3) |
| C(7)-Ag(1)-Ag(2) | 121.7(2) | I(2)-Ag(1)-Ag(2) | 58.98(5) |
| I(1i)-Ag(1)-Ag(2) | 108.84(3) | I(1)-Ag(1)-Ag(2) | 57.65(5) |
| C(15)-Ag(2)-I(2i) | 124.2(2) | C(15)-Ag(2)-I(2) | 113.0(2) |
| I(2i)-Ag(2)-I(2) | 96.88(4) | C(15)-Ag(2)-I(1) | 111.2(2) |
| I(2i)-Ag(2)-I(1) | 93.31(3) | I(2)-Ag(2)-I(1) | 116.93(3) |
| C(15)-Ag(2)-Ag(1) | 125.5(2) | I(2i)-Ag(2)-Ag(1) | 110.27(4) |
| I(2)-Ag(2)-Ag(1) | 57.17(5) | I(1)-Ag(2)-Ag(1) | 60.93(5) |
| C(7)-N(1)-C(8) | 110.4(8) | C(7)-N(1)-C(1) | 126.0(7) |
| C(8)-N(1)-C(1) | 123.4(8) | C(7)-N(2)-C(9) | 111.7(8) |
| C(7)-N(2)-C(10) | 124.4(8) | C(9)-N(2)-C(10) | 123.9(8) |
| C(15)-N(3)-C(16) | 112.2(8) | C(15)-N(3)-C(5) | 125.4(7) |
| C(16)-N(3)-C(5) | 122.4(7) | C(15)-N(4)-C(17) | 110.7(8) |
| C(15)-N(4)-C(18) | 126.5(8) | C(17)-N(4)-C(18) | 122.8(8) |
| C(6)-C(1)-C(2) | 121.5(9) | C(6)-C(1)-N(1) | 120.3(8) |
| C(2)-C(1)-N(1) | 118.2(8) | C(3)-C(2)-C(1) | 118.2(9) |
| C(4)-C(3)-C(2) | 121.1(8) | C(3)-C(4)-C(5) | 120.5(8) |
| C(4)-C(5)-C(6) | 119.9(8) | C(4)-C(5)-N(3) | 119.1(8) |
| C(6)-C(5)-N(3) | 120.9(8) | C(1)-C(6)-C(5) | 118.8(8) |
| N(2)-C(7)-N(1) | 104.4(7) | N(2)-C(7)-Ag(1) | 124.4(6) |
| N(1)-C(7)-Ag(1) | 130.9(6) | C(9)-C(8)-N(1) | 106.7(8) |
| C(8)-C(9)-N(2) | 106.8(8) | N(2)-C(10)-C(11) | 112.3(8) |
| C(10)-C(11)-C(12) | 111.7(9) | C(13A)-C(12)-C(11) | 112.0(18) |
| C(13B)-C(12)-C(11) | 114.0(11) | C(14A)-C(13A)-C(12) | 139(5) |
| C(14B)-C(13B)-C(12) | 120.4(18) | N(3)-C(15)-N(4) | 104.1(7) |
| N(3)-C(15)-Ag(2) | 132.1(7) | N(4)-C(15)-Ag(2) | 123.7(6) |
| C(17)-C(16)-N(3) | 106.0(8) | C(16)-C(17)-N(4) | 106.9(8) |
| N(4)-C(18)-C(19A) | 116.4(12) | N(4)-C(18)-C(19B) | 109.6(10) |
| C(18)-C(19A)-C(20A) | 109.6(18) | C(21A)-C(20A)-C(19A) | 115(2) |
| C(22A)-C(21A)-C(20A) | 144(6) | C(20B)-C(19B)-C(18) | 116.6(17) |
| C(21B)-C(20B)-C(19B) | 117(2) | C(22B)-C(21B)-C(20B) | 130(3) |
| Cl(1)-C(1S)-Cl(2) | 112.9(7) | Cl(3)-C(2S)-Cl(4) | 113.8(9) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

**Table S 18 .** Torsion angles [°] for Bis(μ-1,3-bis(3'-pent-4"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3c**) .

| atom-atom-atom-atom | angle | atom-atom-atom-atom | angle |
|---|---|---|---|
| C(7)-N(1)-C(1)-C(6) | 47.4(13) | C(8)-N(1)-C(1)-C(6) | -138.6(9) |
| C(7)-N(1)-C(1)-C(2) | -132.3(10) | C(8)-N(1)-C(1)-C(2) | 41.6(13) |
| C(6)-C(1)-C(2)-C(3) | 0.3(13) | N(1)-C(1)-C(2)-C(3) | -179.9(8) |
| C(1)-C(2)-C(3)-C(4) | -1.4(14) | C(2)-C(3)-C(4)-C(5) | 2.5(14) |
| C(3)-C(4)-C(5)-C(6) | -2.5(13) | C(3)-C(4)-C(5)-N(3) | 177.9(8) |
| C(15)-N(3)-C(5)-C(4) | 145.1(9) | C(16)-N(3)-C(5)-C(4) | -31.6(12) |
| C(15)-N(3)-C(5)-C(6) | -34.5(13) | C(16)-N(3)-C(5)-C(6) | 148.9(9) |
| C(2)-C(1)-C(6)-C(5) | -0.3(13) | N(1)-C(1)-C(6)-C(5) | 179.9(8) |
| C(4)-C(5)-C(6)-C(1) | 1.4(13) | N(3)-C(5)-C(6)-C(1) | -179.0(8) |
| C(9)-N(2)-C(7)-N(1) | 0.5(10) | C(10)-N(2)-C(7)-N(1) | -179.7(8) |
| C(9)-N(2)-C(7)-Ag(1) | -173.5(7) | C(10)-N(2)-C(7)-Ag(1) | 6.3(13) |
| C(8)-N(1)-C(7)-N(2) | 0.6(10) | C(1)-N(1)-C(7)-N(2) | 175.2(8) |
| C(8)-N(1)-C(7)-Ag(1) | 174.0(7) | C(1)-N(1)-C(7)-Ag(1) | -11.4(14) |
| C(7)-N(1)-C(8)-C(9) | -1.4(11) | C(1)-N(1)-C(8)-C(9) | -176.2(9) |
| N(1)-C(8)-C(9)-N(2) | 1.6(11) | C(7)-N(2)-C(9)-C(8) | -1.3(11) |
| C(10)-N(2)-C(9)-C(8) | 178.9(9) | C(7)-N(2)-C(10)-C(11) | -89.9(12) |
| C(9)-N(2)-C(10)-C(11) | 89.8(12) | N(2)-C(10)-C(11)-C(12) | 179.1(9) |
| C(10)-C(11)-C(12)-C(13A) | 84(2) | C(10)-C(11)-C(12)-C(13B) | 56.5(15) |
| C(13B)-C(12)-C(13A)-C(14A) | -29(5) | C(11)-C(12)-C(13A)-C(14A) | -129(6) |
| C(13A)-C(12)-C(13B)-C(14B) | 10(4) | C(11)-C(12)-C(13B)-C(14B) | 101.0(17) |
| C(16)-N(3)-C(15)-N(4) | -0.9(10) | C(5)-N(3)-C(15)-N(4) | -177.8(8) |
| C(16)-N(3)-C(15)-Ag(2) | 175.8(7) | C(5)-N(3)-C(15)-Ag(2) | -1.1(13) |
| C(17)-N(4)-C(15)-N(3) | -0.2(10) | C(18)-N(4)-C(15)-N(3) | -178.2(9) |
| C(17)-N(4)-C(15)-Ag(2) | -177.2(6) | C(18)-N(4)-C(15)-Ag(2) | 4.8(13) |
| C(15)-N(3)-C(16)-C(17) | 1.6(11) | C(5)-N(3)-C(16)-C(17) | 178.6(8) |
| N(3)-C(16)-C(17)-N(4) | -1.6(11) | C(15)-N(4)-C(17)-C(16) | 1.2(11) |
| C(18)-N(4)-C(17)-C(16) | 179.3(9) | C(15)-N(4)-C(18)-C(19A) | 110.0(15) |
| C(17)-N(4)-C(18)-C(19A) | -67.8(16) | C(15)-N(4)-C(18)-C(19B) | 82.1(14) |
| C(17)-N(4)-C(18)-C(19B) | -95.7(13) | N(4)-C(18)-C(19A)-C(20A) | -66(2) |
| C(19B)-C(18)-C(19A)-C(20A) | 15(2) | C(18)-C(19A)-C(20A)-C(21A) | -174(2) |
| C(19A)-C(20A)-C(21A)-C(22A) | -82(8) | N(4)-C(18)-C(19B)-C(20B) | 63(2) |
| C(19A)-C(18)-C(19B)-C(20B) | -47(3) | C(18)-C(19B)-C(20B)-C(21B) | -175.3(18) |
| C(19B)-C(20B)-C(21B)-C(22B) | -17(4) | | |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

## Experimental

Single crystals of $C_{24}H_{27}Ag_2Cl_4I_2N_4$ [bis(μ-1,3-bis(3-but-3-enyl-imidazol-2-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3b**)] were [Crystallized via Vapor Diffussion of Et2O into a Saturated Solution of CH2Cl2]. A suitable crystal was selected and [Mounted on a 100um Mitogen Mount] on a Bruker Smart APEX II diffractometer. The crystal was kept at 100K K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. olex2.solve (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011)
3. olex2.refine (L.J. Bourhis, O.V. Dolomanov, R.J. Gildea, J.A.K. Howard, H. Puschmann, in preparation, 2011)

**Crystal data** for C24 H30 Ag2 Cl4 I2 N4; $M_r$ = 985.86; Monoclinic; space group C 2/c; *a* = 24.593(19) Å; *b* = 13.718(10) Å; *c* = 19.601(15) Å; α = 90°; β = 102.384(9)°; γ = 90°; V = 6459(8) $Å^3$; Z = 8; T = 100(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 3.476 $mm^{-1}$; $d_{calc}$ = 2.028g.$cm^{-3}$; 31460 reflections collected; 6584 unique ($R_{int}$ = 0.0652); giving $R_1$ = 0.0605, $wR_2$ = 0.1276 for 5253 data with [I>2σ(I)] and $R_1$ = 0.0797, $wR_2$ = 0.1428 for all 6584 data. Residual electron density ($e^-$.$Å^{-3}$) max/min: 1.640/-1.096.

This report has been created with Olex2, compiled on 2012.11.06 svn.r2526. Please let us know if there are any errors or if you would like to have additional featrues.

Crystallographic Report for Bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**)

**Table S 19**

Crystal data and structure refinement for Bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**)

| | |
|---|---|
| Identification code | Bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**) |
| Empirical formula | $C_{36}H_{48}Ag_4I_4N_{12}$ |
| Formula weight | 1587.94 |
| Temperature/K | 100K |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 12.1183(2) |
| b/Å | 17.1196(3) |
| c/Å | 23.9166(4) |
| α/° | 90.00 |
| β/° | 102.4310(10) |
| γ/° | 90.00 |
| Volume/Å$^3$ | 4845.43(14) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 2.177 |
| m/mm$^{-1}$ | 33.099 |
| F(000) | 2992.0 |
| Crystal size/mm$^3$ | 0.35 × 0.25 × 0.11 |
| 2Θ range for data collection | 6.4 to 134.8° |
| Index ranges | $-13 \leq h \leq 10$, $-19 \leq k \leq 19$, $-28 \leq l \leq 26$ |
| Reflections collected | 37413 |
| Independent reflections | 7895[R(int) = 0.0723] |
| Data/restraints/parameters | 7895/30/510 |
| Goodness-of-fit on $F^2$ | 1.020 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0480, $wR_2$ = 0.1225 |
| Final R indexes [all data] | $R_1$ = 0.0627, $wR_2$ = 0.1325 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.31/-1.04 |

**Table S 20**

Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for Bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**).
$U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *Y* | *z* | U(eq) |
|---|---|---|---|---|
| C1 | 9751(7) | 6080(5) | -258(4) | 43.5(19) |
| C2 | 6135(9) | 7563(6) | 3451(4) | 63(3) |
| C3 | 7553(8) | 6642(6) | 3179(4) | 67(3) |
| C4 | 8739(9) | 6920(8) | 3314(7) | 112(5) |
| C5 | 9610(15) | 6306(16) | 3537(10) | 214(13) |
| C6 | 9930(30) | 5909(19) | 3090(10) | 340(30) |
| C7 | 6082(6) | 5999(4) | -382(3) | 33.3(16) |
| C8 | 4996(7) | 8727(5) | 2311(3) | 42.6(19) |
| C9 | 3859(8) | 8798(6) | 2307(4) | 61(3) |
| C10 | 10457(6) | 6693(5) | 698(4) | 44(2) |
| C11 | 4829(7) | 9663(5) | 1572(3) | 44(2) |
| C12 | 3680(8) | 9732(6) | 1553(4) | 62(3) |
| C13 | 8170(8) | 5769(6) | -1247(4) | 62(3) |
| C14 | 5315(9) | 11016(5) | 605(4) | 64(3) |
| C15 | 6817(7) | 10546(5) | 96(4) | 52(2) |
| C16 | 7903(12) | 10894(15) | 354(7) | 201(13) |
| C17 | 8778(16) | 10829(14) | -30(11) | 320(30) |
| C18 | 8530(19) | 11468(14) | -390(10) | 212(12) |
| C19 | 5503(7) | 9163(5) | 1945(3) | 40.5(18) |
| C20 | 5094(7) | 5162(5) | -996(4) | 49(2) |
| C21 | 4032(6) | 5902(5) | -365(3) | 45(2) |
| C22 | 3415(7) | 6576(5) | -690(3) | 54(2) |
| C23 | 2812(8) | 6398(6) | -1289(4) | 71(3) |
| C24 | 2168(12) | 7052(9) | -1582(6) | 119(6) |
| C25 | 8639(6) | 5948(4) | -225(3) | 36.7(18) |
| C26 | 7863(6) | 5795(4) | -725(3) | 37.6(18) |
| C27 | 6070(7) | 9875(5) | 875(3) | 42.7(19) |
| C28 | 9281(9) | 5870(8) | -1258(4) | 84(4) |
| C29 | 10076(8) | 6045(7) | -774(4) | 77(3) |
| C30 | 6420(7) | 7685(5) | 2571(3) | 44(2) |
| C31 | 3221(9) | 9299(7) | 1939(5) | 73(3) |
| C32 | 12221(7) | 6365(5) | 724(5) | 56(2) |
| C33 | 11892(8) | 7150(7) | 1554(5) | 69(3) |
| C34 | 11892(15) | 6624(11) | 2055(6) | 156(8) |
| C35 | 12780(18) | 6013(9) | 2213(7) | 148(7) |
| C36 | 13926(16) | 6347(11) | 2375(10) | 173(9) |
| N1 | 6083(6) | 10473(4) | 518(3) | 46.4(17) |
| N2 | 4813(7) | 10816(4) | 996(3) | 62(2) |
| N3 | 5290(6) | 10101(4) | 1160(3) | 43.6(16) |
| N4 | 5668(6) | 8185(4) | 2690(3) | 45.1(17) |
| N5 | 5464(7) | 8115(4) | 3237(3) | 57(2) |

| | | | | |
|---|---|---|---|---|
| N6 | 6718(6) | 7288(4) | 3068(3) | 51.6(18) |
| N7 | 6702(5) | 5654(4) | -705(3) | 37.0(15) |
| N8 | 5056(5) | 5673(4) | -569(3) | 38.1(15) |
| N9 | 6113(5) | 5125(4) | -1105(3) | 50.3(18) |
| N10 | 10583(5) | 6273(4) | 241(3) | 40.3(16) |
| N11 | 11530(5) | 6745(4) | 1009(3) | 48.5(17) |
| N12 | 11710(6) | 6065(4) | 256(3) | 53.2(19) |
| Ag1 | 6549.3(5) | 6861.9(4) | 301.4(3) | 56.7(2) |
| Ag2 | 8991.1(5) | 7259.3(4) | 923.6(3) | 60.2(2) |
| Ag3 | 7003.8(7) | 8776.9(4) | 901.5(3) | 66.7(2) |
| Ag4 | 6958.6(7) | 7449.1(4) | 1770.3(3) | 62.3(2) |
| I1 | 7795.8(4) | 8177.6(3) | -56.4(2) | 45.70(17) |
| I2 | 7755.5(4) | 6023.4(3) | 1391.0(2) | 46.98(17) |
| I3 | 4940.6(4) | 7630.3(3) | 820.9(2) | 40.68(17) |
| I4 | 8983.4(5) | 8458.1(3) | 1779.5(2) | 54.35(19) |

**Table S 21**

Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| C1 | 28(5) | 53(5) | 53(5) | -11(4) | 16(4) | -1(4) |
| C2 | 72(7) | 80(7) | 39(5) | 12(5) | 19(5) | -3(6) |
| C3 | 73(7) | 65(6) | 61(6) | 18(5) | 10(5) | 11(5) |
| C4 | 59(9) | 137(12) | 140(13) | 56(11) | 21(8) | 19(8) |
| C5 | 65(12) | 350(40) | 220(30) | 70(30) | 3(13) | 54(17) |
| C6 | 570(80) | 270(40) | 130(20) | 40(30) | -40(30) | 140(40) |
| C7 | 25(4) | 40(4) | 34(4) | -3(3) | 6(3) | -3(3) |
| C8 | 48(5) | 55(5) | 28(4) | -6(4) | 15(4) | 7(4) |
| C9 | 53(6) | 83(7) | 55(5) | 6(5) | 31(5) | 17(5) |
| C10 | 19(4) | 51(5) | 58(5) | 1(4) | 2(4) | -9(3) |
| C11 | 49(5) | 52(5) | 30(4) | -2(4) | 9(3) | 17(4) |
| C12 | 54(6) | 72(6) | 63(6) | 6(5) | 18(5) | 22(5) |
| C13 | 37(5) | 97(7) | 54(5) | -25(6) | 15(4) | -12(5) |
| C14 | 84(8) | 48(5) | 59(6) | 17(5) | 16(5) | 19(5) |
| C15 | 62(6) | 52(5) | 42(5) | 12(4) | 10(4) | -3(4) |
| C16 | 68(11) | 420(40) | 123(13) | -47(18) | 45(10) | -107(17) |
| C17 | 120(20) | 240(30) | 540(70) | 140(40) | -90(30) | -60(20) |
| C18 | 160(20) | 190(20) | 260(30) | 90(20) | -24(19) | -21(18) |
| C19 | 39(5) | 54(5) | 31(4) | 2(4) | 13(3) | 7(4) |
| C20 | 36(5) | 47(5) | 61(5) | -9(5) | 2(4) | -10(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C21 | 27(4) | 66(5) | 49(5) | 3(4) | 19(4) | -8(4) |
| C22 | 36(5) | 74(6) | 55(5) | 8(5) | 21(4) | 2(4) |
| C23 | 56(6) | 104(8) | 64(6) | 15(6) | 35(5) | 19(6) |
| C24 | 115(12) | 147(13) | 98(10) | 70(10) | 28(8) | 60(10) |
| C25 | 29(4) | 42(4) | 44(4) | -11(4) | 19(3) | -7(3) |
| C26 | 21(4) | 45(4) | 48(5) | -10(4) | 9(3) | -6(3) |
| C27 | 46(5) | 48(5) | 32(4) | 10(4) | 3(3) | 9(4) |
| C28 | 50(7) | 159(12) | 50(6) | -26(7) | 27(5) | -18(7) |
| C29 | 37(6) | 134(10) | 68(6) | -26(7) | 31(5) | -20(6) |
| C30 | 45(5) | 48(5) | 39(5) | 6(4) | 7(4) | 8(4) |
| C31 | 61(7) | 94(8) | 73(7) | 11(6) | 31(6) | 33(6) |
| C32 | 17(4) | 65(6) | 87(7) | -15(6) | 12(4) | 2(4) |
| C33 | 41(6) | 85(7) | 75(7) | -18(6) | -1(5) | 6(5) |
| C34 | 145(17) | 210(20) | 97(12) | -89(15) | -6(11) | 1(15) |
| C35 | 210(30) | 121(14) | 113(13) | -28(12) | 35(14) | -4(15) |
| C36 | 134(18) | 124(14) | 230(20) | -9(16) | -19(16) | -3(13) |
| N1 | 56(5) | 42(4) | 40(4) | 9(3) | 9(3) | 4(3) |
| N2 | 79(6) | 52(4) | 58(5) | 20(4) | 23(4) | 33(4) |
| N3 | 57(5) | 36(3) | 37(4) | 8(3) | 8(3) | 15(3) |
| N4 | 57(5) | 55(4) | 26(3) | 9(3) | 16(3) | 4(3) |
| N5 | 72(6) | 64(5) | 39(4) | 12(4) | 24(4) | 9(4) |
| N6 | 55(5) | 55(4) | 45(4) | 12(4) | 11(4) | 3(4) |
| N7 | 25(3) | 45(4) | 40(3) | -13(3) | 5(3) | -4(3) |
| N8 | 27(4) | 45(4) | 42(4) | -1(3) | 6(3) | -3(3) |
| N9 | 27(4) | 60(4) | 62(4) | -23(4) | 4(3) | -4(3) |
| N10 | 18(3) | 56(4) | 51(4) | -7(4) | 16(3) | -3(3) |
| N11 | 26(4) | 48(4) | 67(5) | -11(4) | 3(3) | -3(3) |
| N12 | 22(4) | 66(5) | 78(5) | -12(4) | 25(4) | 0(3) |
| Ag1 | 35.9(4) | 74.0(5) | 62.7(4) | -25.1(4) | 16.2(3) | -3.5(3) |
| Ag2 | 34.4(4) | 76.1(5) | 70.5(5) | -18.5(4) | 12.5(3) | 6.0(3) |
| Ag3 | 79.0(6) | 66.0(4) | 64.4(5) | 17.0(4) | 36.2(4) | 30.5(4) |
| Ag4 | 73.7(5) | 68.4(4) | 49.1(4) | 2.9(3) | 22.4(3) | 21.1(4) |
| I1 | 43.6(3) | 54.6(3) | 41.8(3) | -2.3(3) | 15.8(2) | -0.8(2) |
| I2 | 39.8(3) | 47.4(3) | 54.5(3) | -4.2(3) | 11.7(2) | 0.4(2) |
| I3 | 32.2(3) | 51.5(3) | 40.5(3) | -3.0(2) | 12.5(2) | 3.7(2) |
| I4 | 48.8(4) | 60.2(4) | 53.0(3) | -12.7(3) | 8.7(3) | -1.8(3) |

**Table S 22**

Bond Lengths for Bis(μ-1,3-bis(4’-butyl-1’,2’,4’-triazol-2’-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**).

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | N10 | 1.426(10) | C27 | N1 | 1.334(10) |
| C2 | N5 | 1.279(12) | C27 | N3 | 1.337(10) |
| C2 | N6 | 1.356(12) | C28 | C29 | 1.371(14) |
| C3 | C4 | 1.482(12) | C29 | C1 | 1.374(12) |
| C3 | N6 | 1.483(12) | C30 | N4 | 1.325(10) |
| C4 | C5 | 1.504(16) | C30 | N6 | 1.351(10) |
| C5 | C6 | 1.393(18) | C31 | C12 | 1.392(14) |
| C7 | N7 | 1.326(9) | C32 | N11 | 1.355(11) |
| C7 | N8 | 1.349(9) | C32 | N12 | 1.265(12) |
| C8 | C9 | 1.382(12) | C33 | C34 | 1.497(14) |
| C8 | N4 | 1.424(10) | C33 | N11 | 1.458(12) |
| C9 | C31 | 1.347(14) | C34 | C35 | 1.490(16) |
| C10 | N10 | 1.344(10) | C35 | C36 | 1.475(16) |
| C10 | N11 | 1.355(10) | N2 | N3 | 1.374(9) |
| C11 | C12 | 1.389(12) | N4 | N5 | 1.389(9) |
| C11 | N3 | 1.443(10) | N7 | N9 | 1.396(9) |
| C13 | C28 | 1.363(13) | N10 | N12 | 1.404(9) |
| C14 | N1 | 1.362(12) | Ag1 | C7 | 2.185(7) |
| C14 | N2 | 1.267(12) | Ag1 | Ag2 | 3.0882(10) |
| C15 | C16 | 1.456(13) | Ag1 | I1 | 2.9400(9) |
| C15 | N1 | 1.486(11) | Ag1 | I2 | 3.0575(9) |
| C16 | C17 | 1.548(18) | Ag1 | I3 | 2.8492(7) |
| C17 | C18 | 1.385(17) | Ag2 | C10 | 2.190(8) |
| C19 | C8 | 1.389(11) | Ag2 | I1 | 2.9326(9) |
| C19 | C11 | 1.372(11) | Ag2 | I2 | 2.9479(9) |
| C20 | N8 | 1.354(10) | Ag2 | I4 | 2.9001(9) |
| C20 | N9 | 1.317(10) | Ag3 | C27 | 2.189(8) |
| C21 | C22 | 1.498(10) | Ag3 | Ag4 | 3.0883(10) |
| C21 | N8 | 1.480(9) | Ag3 | I1 | 2.8580(8) |
| C22 | C23 | 1.492(12) | Ag3 | I3 | 3.1519(10) |
| C23 | C24 | 1.457(13) | Ag3 | I4 | 2.8799(10) |
| C25 | C1 | 1.385(11) | Ag4 | C30 | 2.189(8) |
| C25 | C26 | 1.377(11) | Ag4 | I2 | 2.8443(8) |
| C26 | C13 | 1.379(11) | Ag4 | I3 | 2.9735(9) |
| C26 | N7 | 1.438(9) | Ag4 | I4 | 2.9970(10) |

**Table S 23**

Bond Angles for Bis(μ-1,3-bis(4’-butyl-1’,2’,4’-triazol-2’-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**).

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C25 | C1 | N10 | 120.8(7) | N9 | N7 | C26 | 116.4(6) |
| C29 | C1 | C25 | 120.9(8) | C7 | N8 | C20 | 109.8(6) |
| C29 | C1 | N10 | 118.3(7) | C7 | N8 | C21 | 124.1(6) |
| N5 | C2 | N6 | 111.5(8) | C20 | N8 | C21 | 126.0(6) |
| C4 | C3 | N6 | 113.1(9) | C20 | N9 | N7 | 101.3(6) |
| C3 | C4 | C5 | 115.3(13) | C10 | N10 | C1 | 128.4(6) |
| C6 | C5 | C4 | 111.1(18) | C10 | N10 | N12 | 113.2(6) |
| N7 | C7 | N8 | 102.7(6) | N12 | N10 | C1 | 118.1(6) |
| N7 | C7 | Ag1 | 130.4(5) | C10 | N11 | C32 | 108.4(8) |
| N8 | C7 | Ag1 | 126.8(5) | C10 | N11 | C33 | 126.2(7) |
| C9 | C8 | C19 | 121.7(8) | C32 | N11 | C33 | 125.3(8) |
| C9 | C8 | N4 | 119.6(7) | C32 | N12 | N10 | 102.1(7) |
| C19 | C8 | N4 | 118.7(7) | C7 | Ag1 | Ag2 | 125.19(19) |
| C31 | C9 | C8 | 119.4(9) | C7 | Ag1 | I1 | 111.54(19) |
| N10 | C10 | N11 | 102.6(7) | C7 | Ag1 | I2 | 108.61(19) |
| N10 | C10 | Ag2 | 132.6(5) | C7 | Ag1 | I3 | 123.15(19) |
| N11 | C10 | Ag2 | 124.7(6) | I1 | Ag1 | Ag2 | 58.16(2) |
| C12 | C11 | N3 | 117.7(7) | I1 | Ag1 | I2 | 115.24(2) |
| C19 | C11 | C12 | 121.8(8) | I2 | Ag1 | Ag2 | 57.32(2) |
| C19 | C11 | N3 | 120.3(7) | I3 | Ag1 | Ag2 | 111.27(3) |
| C11 | C12 | C31 | 118.3(9) | I3 | Ag1 | I1 | 102.47(3) |
| C28 | C13 | C26 | 118.3(8) | I3 | Ag1 | I2 | 95.25(2) |
| N2 | C14 | N1 | 112.4(8) | C10 | Ag2 | Ag1 | 121.8(2) |
| C16 | C15 | N1 | 111.5(8) | C10 | Ag2 | I1 | 109.1(2) |
| C15 | C16 | C17 | 113.1(14) | C10 | Ag2 | I2 | 106.3(2) |
| C18 | C17 | C16 | 103.2(18) | C10 | Ag2 | I4 | 127.8(2) |
| C11 | C19 | C8 | 117.5(8) | I1 | Ag2 | Ag1 | 58.39(2) |
| N9 | C20 | N8 | 111.5(7) | I1 | Ag2 | I2 | 118.95(3) |
| N8 | C21 | C22 | 113.1(6) | I2 | Ag2 | Ag1 | 60.81(2) |
| C23 | C22 | C21 | 115.3(8) | I4 | Ag2 | Ag1 | 110.35(2) |
| C24 | C23 | C22 | 114.0(10) | I4 | Ag2 | I1 | 96.24(3) |
| C26 | C25 | C1 | 118.3(7) | I4 | Ag2 | I2 | 99.27(3) |
| C13 | C26 | N7 | 118.8(7) | C27 | Ag3 | Ag4 | 124.6(2) |
| C25 | C26 | C13 | 121.7(7) | C27 | Ag3 | I1 | 123.1(2) |
| C25 | C26 | N7 | 119.5(6) | C27 | Ag3 | I3 | 97.8(2) |
| N1 | C27 | N3 | 102.2(6) | C27 | Ag3 | I4 | 121.9(2) |
| N1 | C27 | Ag3 | 126.9(6) | Ag4 | Ag3 | I3 | 56.91(2) |
| N3 | C27 | Ag3 | 130.6(6) | I1 | Ag3 | Ag4 | 109.44(3) |
| C13 | C28 | C29 | 121.9(9) | I1 | Ag3 | I3 | 97.25(3) |
| C28 | C29 | C1 | 118.9(8) | I1 | Ag3 | I4 | 98.38(3) |
| N4 | C30 | N6 | 101.7(7) | I4 | Ag3 | Ag4 | 60.17(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N4 | C30 | Ag4 | 131.0(6) | I4 | Ag3 | I3 | 116.86(3) |
| N6 | C30 | Ag4 | 127.1(6) | C30 | Ag4 | Ag3 | 120.3(2) |
| C9 | C31 | C12 | 121.2(10) | C30 | Ag4 | I2 | 128.5(2) |
| N12 | C32 | N11 | 113.7(8) | C30 | Ag4 | I3 | 107.3(2) |
| N11 | C33 | C34 | 112.2(9) | C30 | Ag4 | I4 | 106.6(2) |
| C35 | C34 | C33 | 120.1(14) | I2 | Ag4 | Ag3 | 111.14(3) |
| C36 | C35 | C34 | 112.4(14) | I2 | Ag4 | I3 | 97.23(3) |
| C14 | N1 | C15 | 125.1(7) | I2 | Ag4 | I4 | 99.40(3) |
| C27 | N1 | C14 | 108.8(7) | I3 | Ag4 | Ag3 | 62.63(2) |
| C27 | N1 | C15 | 126.1(7) | I3 | Ag4 | I4 | 118.88(3) |
| C14 | N2 | N3 | 102.2(7) | I4 | Ag4 | Ag3 | 56.47(2) |
| C27 | N3 | C11 | 128.2(6) | Ag2 | I1 | Ag1 | 63.45(2) |
| C27 | N3 | N2 | 114.3(7) | Ag3 | I1 | Ag1 | 76.09(2) |
| N2 | N3 | C11 | 117.2(6) | Ag3 | I1 | Ag2 | 75.24(2) |
| C30 | N4 | C8 | 127.5(6) | Ag2 | I2 | Ag1 | 61.86(2) |
| C30 | N4 | N5 | 114.7(7) | Ag4 | I2 | Ag1 | 74.70(2) |
| N5 | N4 | C8 | 117.6(6) | Ag4 | I2 | Ag2 | 74.93(2) |
| C2 | N5 | N4 | 102.3(7) | Ag1 | I3 | Ag3 | 72.90(2) |
| C2 | N6 | C3 | 125.0(8) | Ag1 | I3 | Ag4 | 75.96(2) |
| C30 | N6 | C2 | 109.8(7) | Ag4 | I3 | Ag3 | 60.47(2) |
| C30 | N6 | C3 | 125.2(7) | Ag2 | I4 | Ag4 | 73.38(2) |
| C7 | N7 | C26 | 128.7(6) | Ag3 | I4 | Ag2 | 75.41(2) |
| C7 | N7 | N9 | 114.7(6) | Ag3 | I4 | Ag4 | 63.37(2) |

**Table S 24**

Torsion Angles for Bis(μ-1,3-bis(4’-butyl-1’,2’,4’-triazol-2’-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**).

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| C1 | C25 | C26 | C13 | 0.1(12) | Ag1 | Ag2 | I1 | Ag3 | 81.59(2) |
| C1 | C25 | C26 | N7 | 179.8(7) | Ag1 | Ag2 | I2 | Ag4 | -80.45(2) |
| C1 | N10 | N12 | C32 | 175.3(8) | Ag1 | Ag2 | I4 | Ag3 | -30.31(3) |
| C3 | C4 | C5 | C6 | 86(3) | Ag1 | Ag2 | I4 | Ag4 | 35.75(3) |
| C4 | C3 | N6 | C2 | -100.6(12) | Ag2 | C10 | N10 | C1 | 1.4(12) |
| C4 | C3 | N6 | C30 | 79.8(12) | Ag2 | C10 | N10 | N12 | 175.7(6) |
| C7 | N7 | N9 | C20 | -1.0(9) | Ag2 | C10 | N11 | C32 | -176.1(6) |
| C7 | Ag1 | Ag2 | C10 | 1.2(3) | Ag2 | C10 | N11 | C33 | 2.9(12) |
| C7 | Ag1 | Ag2 | I1 | 95.2(2) | Ag2 | Ag1 | C7 | N7 | -15.7(8) |
| C7 | Ag1 | Ag2 | I2 | -90.7(2) | Ag2 | Ag1 | C7 | N8 | 162.9(5) |
| C7 | Ag1 | Ag2 | I4 | 179.9(2) | Ag2 | Ag1 | I1 | Ag3 | -80.23(2) |
| C7 | Ag1 | I1 | Ag2 | -119.0(2) | Ag2 | Ag1 | I2 | Ag4 | 80.83(2) |

| | | | | |
|---|---|---|---|---|
| C7 | Ag1 | I1 | Ag3 | 160.8(2) |
| C7 | Ag1 | I2 | Ag2 | 120.43(19) |
| C7 | Ag1 | I2 | Ag4 | -158.73(19) |
| C7 | Ag1 | I3 | Ag3 | -151.3(2) |
| C7 | Ag1 | I3 | Ag4 | 145.7(2) |
| C8 | C9 | C31 | C12 | 1.6(16) |
| C8 | C19 | C11 | C12 | -0.5(12) |
| C8 | C19 | C11 | N3 | -176.6(7) |
| C8 | N4 | N5 | C2 | 176.0(8) |
| C9 | C8 | N4 | C30 | 134.7(9) |
| C9 | C8 | N4 | N5 | -39.4(11) |
| C9 | C31 | C12 | C11 | -2.9(16) |
| C10 | N10 | N12 | C32 | 0.4(9) |
| C10 | Ag2 | I1 | Ag1 | 116.2(2) |
| C10 | Ag2 | I1 | Ag3 | -162.2(2) |
| C10 | Ag2 | I2 | Ag1 | -117.8(2) |
| C10 | Ag2 | I2 | Ag4 | 161.8(2) |
| C10 | Ag2 | I4 | Ag3 | 148.4(3) |
| C10 | Ag2 | I4 | Ag4 | -145.6(3) |
| C11 | C19 | C8 | C9 | -0.9(12) |
| C11 | C19 | C8 | N4 | 178.0(7) |
| C12 | C11 | N3 | C27 | -140.2(9) |
| C12 | C11 | N3 | N2 | 33.6(11) |
| C13 | C26 | N7 | C7 | -141.9(9) |
| C13 | C26 | N7 | N9 | 33.0(11) |
| C13 | C28 | C29 | C1 | 3(2) |
| C14 | N2 | N3 | C11 | -174.3(8) |
| C14 | N2 | N3 | C27 | 0.3(11) |
| C15 | C16 | C17 | C18 | 85(2) |
| C16 | C15 | N1 | C14 | 92.4(16) |
| C16 | C15 | N1 | C27 | -87.2(15) |
| C19 | C8 | C9 | C31 | 0.3(14) |
| C19 | C8 | N4 | C30 | -44.2(12) |
| C19 | C8 | N4 | N5 | 141.6(8) |
| C19 | C11 | C12 | C31 | 2.3(14) |
| C19 | C11 | N3 | C27 | 36.1(12) |
| C19 | C11 | N3 | N2 | -150.1(8) |
| C21 | C22 | C23 | C24 | 176.7(9) |
| C22 | C21 | N8 | C7 | 86.7(9) |
| C22 | C21 | N8 | C20 | -87.7(10) |
| C25 | C1 | N10 | C10 | -33.9(12) |
| C25 | C1 | N10 | N12 | 152.0(7) |
| Ag2 | Ag1 | I3 | Ag3 | 35.49(3) |
| Ag2 | Ag1 | I3 | Ag4 | -27.47(3) |
| Ag3 | C27 | N1 | C14 | 174.7(7) |
| Ag3 | C27 | N1 | C15 | -5.7(11) |
| Ag3 | C27 | N3 | C11 | -0.8(13) |
| Ag3 | C27 | N3 | N2 | -174.8(6) |
| Ag3 | Ag4 | C30 | N4 | 32.7(9) |
| Ag3 | Ag4 | C30 | N6 | -154.1(7) |
| Ag3 | Ag4 | I2 | Ag1 | -33.59(3) |
| Ag3 | Ag4 | I2 | Ag2 | 30.78(3) |
| Ag3 | Ag4 | I3 | Ag1 | 78.07(2) |
| Ag3 | Ag4 | I4 | Ag2 | -81.70(3) |
| Ag4 | C30 | N4 | C8 | -0.7(13) |
| Ag4 | C30 | N4 | N5 | 173.6(6) |
| Ag4 | C30 | N6 | C2 | -174.5(7) |
| Ag4 | C30 | N6 | C3 | 5.1(13) |
| Ag4 | Ag3 | C27 | N1 | 178.2(6) |
| Ag4 | Ag3 | C27 | N3 | -8.1(9) |
| Ag4 | Ag3 | I1 | Ag1 | 33.38(3) |
| Ag4 | Ag3 | I1 | Ag2 | -32.36(3) |
| Ag4 | Ag3 | I3 | Ag1 | -83.25(2) |
| Ag4 | Ag3 | I4 | Ag2 | 78.46(2) |
| I1 | Ag1 | C7 | N7 | 49.7(7) |
| I1 | Ag1 | C7 | N8 | -131.6(6) |
| I1 | Ag1 | Ag2 | C10 | -94.1(3) |
| I1 | Ag1 | Ag2 | I2 | 174.13(3) |
| I1 | Ag1 | Ag2 | I4 | 84.72(3) |
| I1 | Ag1 | I2 | Ag2 | -5.51(2) |
| I1 | Ag1 | I2 | Ag4 | 75.32(3) |
| I1 | Ag1 | I3 | Ag3 | -24.92(2) |
| I1 | Ag1 | I3 | Ag4 | -87.88(3) |
| I1 | Ag2 | C10 | N10 | -48.4(8) |
| I1 | Ag2 | C10 | N11 | 127.0(6) |
| I1 | Ag2 | I2 | Ag1 | 5.71(3) |
| I1 | Ag2 | I2 | Ag4 | -74.73(3) |
| I1 | Ag2 | I4 | Ag3 | 28.24(2) |
| I1 | Ag2 | I4 | Ag4 | 94.30(2) |
| I1 | Ag3 | C27 | N1 | -23.0(8) |
| I1 | Ag3 | C27 | N3 | 150.7(7) |
| I1 | Ag3 | Ag4 | C30 | 179.1(3) |
| I1 | Ag3 | Ag4 | I2 | 1.26(5) |
| I1 | Ag3 | Ag4 | I3 | -85.98(3) |

| | | | | |
|---|---|---|---|---|
| C25 | C26 | C13 | C28 | 2.5(15) |
| C25 | C26 | N7 | C7 | 38.4(12) |
| C25 | C26 | N7 | N9 | -146.7(7) |
| C26 | C13 | C28 | C29 | -4.3(19) |
| C26 | C25 | C1 | C29 | -1.0(13) |
| C26 | C25 | C1 | N10 | 177.4(7) |
| C26 | N7 | N9 | C20 | -176.7(7) |
| C27 | Ag3 | Ag4 | C30 | -19.6(4) |
| C27 | Ag3 | Ag4 | I2 | 162.5(3) |
| C27 | Ag3 | Ag4 | I3 | 75.3(3) |
| C27 | Ag3 | Ag4 | I4 | -110.2(3) |
| C27 | Ag3 | I1 | Ag1 | -128.2(3) |
| C27 | Ag3 | I1 | Ag2 | 166.0(3) |
| C27 | Ag3 | I3 | Ag1 | 150.2(2) |
| C27 | Ag3 | I3 | Ag4 | -126.6(2) |
| C27 | Ag3 | I4 | Ag2 | -167.1(2) |
| C27 | Ag3 | I4 | Ag4 | 114.5(2) |
| C28 | C29 | C1 | C25 | -0.7(17) |
| C28 | C29 | C1 | N10 | -179.2(10) |
| C29 | C1 | N10 | C10 | 144.6(9) |
| C29 | C1 | N10 | N12 | -29.5(12) |
| C30 | N4 | N5 | C2 | 1.1(10) |
| C30 | Ag4 | I2 | Ag1 | 148.8(3) |
| C30 | Ag4 | I2 | Ag2 | -146.9(3) |
| C30 | Ag4 | I3 | Ag1 | -166.2(2) |
| C30 | Ag4 | I3 | Ag3 | 115.7(2) |
| C30 | Ag4 | I4 | Ag2 | 162.6(2) |
| C30 | Ag4 | I4 | Ag3 | -115.7(2) |
| C33 | C34 | C35 | C36 | 62(2) |
| C34 | C33 | N11 | C10 | 90.9(12) |
| C34 | C33 | N11 | C32 | -90.1(13) |
| N1 | C14 | N2 | N3 | -0.6(11) |
| N1 | C15 | C16 | C17 | 168.4(15) |
| N1 | C27 | N3 | C11 | 174.0(7) |
| N1 | C27 | N3 | N2 | 0.1(9) |
| N2 | C14 | N1 | C15 | -178.9(8) |
| N2 | C14 | N1 | C27 | 0.7(12) |
| N3 | C11 | C12 | C31 | 178.5(8) |
| N3 | C27 | N1 | C14 | -0.4(9) |
| N3 | C27 | N1 | C15 | 179.2(8) |
| N4 | C8 | C9 | C31 | -178.6(9) |
| N4 | C30 | N6 | C2 | 0.3(10) |
| I1 | Ag3 | Ag4 | I4 | 88.61(3) |
| I1 | Ag3 | I3 | Ag1 | 25.25(2) |
| I1 | Ag3 | I3 | Ag4 | 108.51(3) |
| I1 | Ag3 | I4 | Ag2 | -29.20(3) |
| I1 | Ag3 | I4 | Ag4 | -107.65(3) |
| I2 | Ag1 | C7 | N7 | -78.3(7) |
| I2 | Ag1 | C7 | N8 | 100.3(6) |
| I2 | Ag1 | Ag2 | C10 | 91.8(3) |
| I2 | Ag1 | Ag2 | I1 | -174.13(3) |
| I2 | Ag1 | Ag2 | I4 | -89.41(3) |
| I2 | Ag1 | I1 | Ag2 | 5.46(2) |
| I2 | Ag1 | I1 | Ag3 | -74.77(3) |
| I2 | Ag1 | I3 | Ag3 | 92.40(2) |
| I2 | Ag1 | I3 | Ag4 | 29.44(2) |
| I2 | Ag2 | C10 | N10 | 81.0(8) |
| I2 | Ag2 | C10 | N11 | -103.5(7) |
| I2 | Ag2 | I1 | Ag1 | -5.86(3) |
| I2 | Ag2 | I1 | Ag3 | 75.73(3) |
| I2 | Ag2 | I4 | Ag3 | -92.51(3) |
| I2 | Ag2 | I4 | Ag4 | -26.44(2) |
| I2 | Ag4 | C30 | N4 | -149.9(7) |
| I2 | Ag4 | C30 | N6 | 23.4(9) |
| I2 | Ag4 | I3 | Ag1 | -32.03(2) |
| I2 | Ag4 | I3 | Ag3 | -110.10(3) |
| I2 | Ag4 | I4 | Ag2 | 27.50(3) |
| I2 | Ag4 | I4 | Ag3 | 109.20(3) |
| I3 | Ag1 | C7 | N7 | 172.1(6) |
| I3 | Ag1 | C7 | N8 | -9.3(7) |
| I3 | Ag1 | Ag2 | C10 | 174.2(3) |
| I3 | Ag1 | Ag2 | I1 | -91.77(3) |
| I3 | Ag1 | Ag2 | I2 | 82.36(3) |
| I3 | Ag1 | Ag2 | I4 | -7.05(4) |
| I3 | Ag1 | I1 | Ag2 | 107.46(3) |
| I3 | Ag1 | I1 | Ag3 | 27.23(3) |
| I3 | Ag1 | I2 | Ag2 | -111.95(3) |
| I3 | Ag1 | I2 | Ag4 | -31.12(2) |
| I3 | Ag3 | C27 | N1 | -127.0(7) |
| I3 | Ag3 | C27 | N3 | 46.7(8) |
| I3 | Ag3 | Ag4 | C30 | -94.9(3) |
| I3 | Ag3 | Ag4 | I2 | 87.23(3) |
| I3 | Ag3 | Ag4 | I4 | 174.59(3) |
| I3 | Ag3 | I1 | Ag1 | -24.02(2) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| N4 | C30 | N6 | C3 | 179.9(8) | I3 | Ag3 | I1 | Ag2 | -89.76(2) |
| N5 | C2 | N6 | C3 | -179.3(8) | I3 | Ag3 | I4 | Ag2 | 73.38(3) |
| N5 | C2 | N6 | C30 | 0.4(12) | I3 | Ag3 | I4 | Ag4 | -5.08(2) |
| N6 | C2 | N5 | N4 | -0.8(11) | I3 | Ag4 | C30 | N4 | -35.3(9) |
| N6 | C3 | C4 | C5 | 169.0(13) | I3 | Ag4 | C30 | N6 | 138.0(7) |
| N6 | C30 | N4 | C8 | -175.2(8) | I3 | Ag4 | I2 | Ag1 | 29.81(2) |
| N6 | C30 | N4 | N5 | -0.9(10) | I3 | Ag4 | I2 | Ag2 | 94.17(2) |
| N7 | C7 | N8 | C20 | -0.8(8) | I3 | Ag4 | I4 | Ag2 | -76.21(3) |
| N7 | C7 | N8 | C21 | -176.0(7) | I3 | Ag4 | I4 | Ag3 | 5.49(3) |
| N7 | C26 | C13 | C28 | -177.2(10) | I4 | Ag2 | C10 | N10 | -162.9(6) |
| N8 | C7 | N7 | C26 | 176.2(7) | I4 | Ag2 | C10 | N11 | 12.5(8) |
| N8 | C7 | N7 | N9 | 1.2(8) | I4 | Ag2 | I1 | Ag1 | -110.08(3) |
| N8 | C20 | N9 | N7 | 0.4(9) | I4 | Ag2 | I1 | Ag3 | -28.50(3) |
| N8 | C21 | C22 | C23 | 71.4(9) | I4 | Ag2 | I2 | Ag1 | 108.20(3) |
| N9 | C20 | N8 | C7 | 0.2(9) | I4 | Ag2 | I2 | Ag4 | 27.75(3) |
| N9 | C20 | N8 | C21 | 175.3(7) | I4 | Ag3 | C27 | N1 | 104.6(6) |
| N10 | C10 | N11 | C32 | 0.4(9) | I4 | Ag3 | C27 | N3 | -81.7(8) |
| N10 | C10 | N11 | C33 | 179.5(8) | I4 | Ag3 | Ag4 | C30 | 90.5(3) |
| N11 | C10 | N10 | C1 | -174.8(7) | I4 | Ag3 | Ag4 | I2 | -87.35(3) |
| N11 | C10 | N10 | N12 | -0.5(9) | I4 | Ag3 | Ag4 | I3 | -174.59(3) |
| N11 | C32 | N12 | N10 | -0.1(10) | I4 | Ag3 | I1 | Ag1 | 94.61(3) |
| N11 | C33 | C34 | C35 | 73.0(16) | I4 | Ag3 | I1 | Ag2 | 28.87(3) |
| N12 | C32 | N11 | C10 | -0.2(11) | I4 | Ag3 | I3 | Ag1 | -77.99(3) |
| N12 | C32 | N11 | C33 | -179.3(9) | I4 | Ag3 | I3 | Ag4 | 5.26(2) |
| Ag1 | C7 | N7 | C26 | -5.0(12) | I4 | Ag4 | C30 | N4 | 93.1(8) |
| Ag1 | C7 | N7 | N9 | -180.0(5) | I4 | Ag4 | C30 | N6 | -93.7(7) |
| Ag1 | C7 | N8 | C20 | -179.8(6) | I4 | Ag4 | I2 | Ag1 | -91.15(2) |
| Ag1 | C7 | N8 | C21 | 5.1(10) | I4 | Ag4 | I2 | Ag2 | -26.79(2) |
| Ag1 | Ag2 | C10 | N10 | 15.6(9) | I4 | Ag4 | I3 | Ag1 | 72.92(3) |
| Ag1 | Ag2 | C10 | N11 | -168.9(6) | I4 | Ag4 | I3 | Ag3 | -5.15(2) |

**Table S 25**

Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for Bis(μ-1,3-bis(4’-butyl-1’,2’,4’-triazol-2’-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**).

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H2 | 6212 | 7375 | 3822 | 75 |
| H3A | 7418 | 6331 | 3497 | 80 |
| H3B | 7442 | 6307 | 2845 | 80 |
| H4A | 8805 | 7334 | 3596 | 135 |
| H4B | 8910 | 7145 | 2970 | 135 |

| | | | | |
|---|---|---|---|---|
| H5A | 10268 | 6551 | 3777 | 257 |
| H5B | 9303 | 5937 | 3771 | 257 |
| H6A | 9394 | 5506 | 2951 | 512 |
| H6B | 10665 | 5680 | 3225 | 512 |
| H6C | 9964 | 6269 | 2786 | 512 |
| H7 | 6272 | 9118 | 1953 | 49 |
| H9 | 3537 | 8502 | 2557 | 73 |
| H10 | 2460 | 9356 | 1944 | 88 |
| H12 | 3229 | 10060 | 1289 | 75 |
| H14 | 5175 | 11480 | 401 | 77 |
| H15A | 6938 | 10033 | -51 | 63 |
| H15B | 6439 | 10866 | -222 | 63 |
| H16A | 8204 | 10639 | 717 | 241 |
| H16B | 7791 | 11441 | 432 | 241 |
| H17A | 9544 | 10858 | 197 | 388 |
| H17B | 8686 | 10345 | -245 | 388 |
| H18A | 7726 | 11513 | -520 | 317 |
| H18B | 8873 | 11402 | -713 | 317 |
| H18C | 8820 | 11934 | -186 | 317 |
| H20 | 4479 | 4873 | -1188 | 59 |
| H21A | 4248 | 6040 | 37 | 54 |
| H21B | 3525 | 5458 | -399 | 54 |
| H22A | 2869 | 6770 | -481 | 64 |
| H22B | 3954 | 6992 | -702 | 64 |
| H23A | 3362 | 6234 | -1506 | 86 |
| H23B | 2302 | 5963 | -1281 | 86 |
| H24A | 1549 | 7168 | -1404 | 179 |
| H24B | 1882 | 6918 | -1977 | 179 |
| H24C | 2650 | 7501 | -1560 | 179 |
| H25 | 8421 | 5963 | 124 | 44 |
| H27 | 7633 | 5685 | -1583 | 74 |
| H28 | 9507 | 5819 | -1604 | 101 |
| H29 | 10822 | 6139 | -794 | 92 |
| H32 | 12999 | 6328 | 859 | 67 |
| H33A | 11391 | 7587 | 1569 | 83 |
| H33B | 12647 | 7355 | 1581 | 83 |
| H34A | 11930 | 6955 | 2388 | 187 |
| H34B | 11166 | 6362 | 1986 | 187 |
| H35A | 12629 | 5709 | 2531 | 178 |
| H35B | 12744 | 5661 | 1892 | 178 |
| H36A | 14091 | 6632 | 2057 | 260 |
| H36B | 14466 | 5934 | 2480 | 260 |

| | | | | |
|---|---|---|---|---|
| H36C | 13966 | 6694 | 2695 | 260 |

Experimental

Single crystals of $C_{36}H_{48}Ag_4I_4N_{12}$ [bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**)] were [Crystallized Via Slow Vapor Diffussion of MeOH into a Saturated Solution of DMSO]. A suitable crystal was selected and [Mounted on a 1.0mm Cryoloop] on a Bruker Smart APEX II diffractometer. The crystal was kept at 100K K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using CGLS minimisation.

1. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.
2. SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122

Crystal structure determination of [bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3d**)]

**Crystal Data** for $C_{36}H_{48}Ag_4I_4N_{12}$ ($M$ =1587.94): monoclinic, space group $P2_1/c$ (no. 14), $a$ = 12.1183(2) Å, $b$ = 17.1196(3) Å, $c$ = 23.9166(4) Å, $\beta$ = 102.4310(10)°, $V$ = 4845.43(14) Å$^3$, $Z$ = 4, $T$ = 100K K, μ(CuKα) = 33.099 mm$^{-1}$, *Dcalc* = 2.177 g/mm$^3$, 37413 reflections measured ($6.4 \leq 2\Theta \leq 134.8$), 7895 unique ($R_{int}$ = 0.0723) which were used in all calculations. The final $R_1$ was 0.0480 (>2sigma(I)) and $wR_2$ was 0.1325 (all data).

This report has been created with Olex2, compiled on 2012.11.06 svn.r2526. Please let us know if there are any errors or if you would like to have additional featrues.

Crystallographic Report for bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e)

**Table S 26**

Crystal data and structure refinement for bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e)

| | |
|---|---|
| Identification code | bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e) |
| Empirical formula | $C_{36}H_{46}Ag_4Br_4N_{12}$ |
| Formula weight | 1397.97 |
| Temperature/K | 100K |
| Crystal system | orthorhombic |
| Space group | $P2_1cn$ |
| a/Å | 16.1580(4) |
| b/Å | 16.9023(4) |
| c/Å | 17.5083(4) |
| α/° | 90.00 |
| β/° | 90.00 |
| γ/° | 90.00 |
| Volume/$Å^3$ | 4781.6(2) |
| Z | 4 |
| $\rho_{calc}mg/mm^3$ | 1.942 |
| $m/mm^{-1}$ | 17.178 |
| F(000) | 2696.0 |
| Crystal size/$mm^3$ | 0.18 × 0.14 × 0.06 |
| 2Θ range for data collection | 7.26 to 138.98° |
| Index ranges | $-19 \leq h \leq 16$, $-20 \leq k \leq 20$, $-21 \leq l \leq 21$ |
| Reflections collected | 40231 |
| Independent reflections | 7437[R(int) = 0.0697] |
| Data/restraints/parameters | 7437/31/509 |
| Goodness-of-fit on $F^2$ | 1.035 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0453$, $wR_2 = 0.1162$ |
| Final R indexes [all data] | $R_1 = 0.0574$, $wR_2 = 0.1258$ |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.93/-0.64 |
| Flack parameter | 0.008(9) |

**Table S 27**

Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e). $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| C17 | 3395(8) | 8014(7) | 7274(6) | 87(3) |
| C18 | 3884(16) | 8703(14) | 7489(10) | 168(11) |
| C19 | 4430(30) | 8670(20) | 8112(19) | 300(30) |
| C20 | 4930(20) | 9323(19) | 8203(18) | 260(20) |
| C21' | 3365(8) | 11964(7) | 7672(7) | 89(4) |
| C22' | 3824(13) | 11271(11) | 7411(10) | 140(8) |
| C23' | 4368(19) | 11410(20) | 6779(17) | 250(20) |
| C24' | 5054(17) | 10959(19) | 6670(20) | 245(19) |
| C17' | -1484(9) | 9336(10) | 5507(10) | 118(5) |
| C18' | -2293(15) | 9467(15) | 5887(19) | 215(16) |
| C19' | -2682(19) | 8745(18) | 6130(30) | 340(30) |
| C20' | -3415(18) | 8870(30) | 6500(30) | 480(50) |
| C21 | -1621(8) | 10225(7) | 9657(7) | 92(4) |
| C22 | -2220(10) | 10173(9) | 9033(11) | 118(5) |
| C23 | -2567(16) | 10959(12) | 8852(18) | 195(14) |
| C24 | -3170(20) | 10950(20) | 8310(20) | 320(30) |
| Ag2 | 1571.5(6) | 8916.3(6) | 7770.8(5) | 93.2(3) |
| Ag1 | 209.3(7) | 9776.1(5) | 8741.7(7) | 103.1(4) |
| Ag3 | 73.0(6) | 10122.0(5) | 6619.7(5) | 86.2(3) |
| Ag4 | 1354.8(7) | 11211.0(5) | 7483.1(4) | 83.8(3) |
| Br1 | -122.6(8) | 8755.5(6) | 7411.4(6) | 71.0(3) |
| Br2 | 1766.0(7) | 10277.5(6) | 8733.8(5) | 70.5(3) |
| Br3 | -238.0(7) | 11105.8(6) | 7891.6(6) | 70.1(3) |
| Br4 | 1794.5(7) | 9834.2(6) | 6523.3(5) | 65.1(2) |
| N1 | 2140(6) | 7446(5) | 8840(5) | 69(2) |
| N2 | 2732(8) | 6867(7) | 8892(6) | 104(4) |
| C3 | 3227(10) | 7040(9) | 8336(9) | 114(6) |
| N4 | 2945(6) | 7652(5) | 7917(4) | 72(2) |
| C10 | 2233(6) | 7927(5) | 8247(5) | 65(2) |
| C6 | 1517(7) | 7462(6) | 9408(6) | 70(2) |
| C16 | 860(7) | 7960(6) | 9383(5) | 68(2) |
| C8 | 295(7) | 7980(6) | 9980(6) | 74(3) |
| C9 | 355(12) | 7462(9) | 10554(8) | 117(6) |
| C5 | 989(15) | 6957(14) | 10576(12) | 217(16) |
| C11 | 1579(12) | 6965(9) | 10008(8) | 141(9) |
| N12 | -398(6) | 8509(6) | 9975(5) | 79(2) |
| N13 | -1073(7) | 8283(9) | 10428(7) | 117(5) |
| C14 | -1511(11) | 8874(11) | 10358(9) | 145(9) |
| N15 | -1233(7) | 9433(7) | 9856(6) | 96(3) |
| C7 | -482(6) | 9200(6) | 9609(5) | 67(2) |
| N1' | -479(6) | 11155(6) | 5152(4) | 74(2) |

| | | | | |
|---|---|---|---|---|
| N2' | -1029(8) | 11136(8) | 4544(6) | 101(3) |
| C3' | -1392(10) | 10504(11) | 4607(9) | 114(5) |
| N4' | -1136(7) | 10078(7) | 5252(6) | 90(3) |
| C27 | -537(6) | 10512(7) | 5592(5) | 68(2) |
| C6' | 37(7) | 11818(6) | 5231(6) | 70(2) |
| C7' | 721(7) | 11819(6) | 5701(6) | 72(3) |
| C8' | 1209(8) | 12484(6) | 5756(6) | 77(3) |
| C9' | 1054(11) | 13143(8) | 5322(8) | 104(5) |
| C10' | 393(12) | 13130(9) | 4858(9) | 120(6) |
| C11' | -138(11) | 12497(8) | 4802(9) | 111(5) |
| N12' | 1923(7) | 12484(5) | 6227(5) | 85(3) |
| N13' | 2569(9) | 12977(8) | 6017(8) | 135(6) |
| C14' | 3108(11) | 12838(11) | 6569(10) | 133(7) |
| N15' | 2861(8) | 12273(6) | 7069(6) | 92(3) |
| C30 | 2086(7) | 12058(6) | 6868(5) | 69(2) |

**Table S 28**

Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| C17 | 88(8) | 92(8) | 82(6) | 19(5) | 30(6) | 32(7) |
| C18 | 180(20) | 210(20) | 112(12) | 52(14) | -10(13) | -90(20) |
| C19 | 350(60) | 310(50) | 230(30) | 100(30) | -130(40) | -210(40) |
| C20 | 270(50) | 300(50) | 200(30) | 70(30) | -30(30) | -90(40) |
| C21' | 80(8) | 89(8) | 99(7) | 18(6) | -31(6) | -25(7) |
| C22' | 144(18) | 140(15) | 137(14) | 8(12) | -66(14) | 4(14) |
| C23' | 170(30) | 340(50) | 230(40) | -50(40) | 40(30) | 80(30) |
| C24' | 160(30) | 270(40) | 310(50) | 110(30) | 20(30) | -40(30) |
| C17' | 96(11) | 128(12) | 131(12) | 1(10) | -32(9) | -40(10) |
| C18' | 140(20) | 220(30) | 280(40) | 110(30) | 10(20) | -40(20) |
| C19' | 150(30) | 360(60) | 520(90) | 210(60) | 60(40) | 0(40) |
| C20' | 100(20) | 910(150) | 420(80) | 90(90) | -10(40) | -30(50) |
| C21 | 80(8) | 99(8) | 98(7) | 18(6) | 26(7) | 30(7) |
| C22 | 70(8) | 125(12) | 160(16) | 12(10) | -7(9) | 4(8) |
| C23 | 160(20) | 126(16) | 300(40) | 50(20) | -50(20) | 54(16) |
| C24 | 140(30) | 260(40) | 550(80) | 120(50) | -100(40) | 30(30) |
| Ag2 | 94.5(7) | 89.7(5) | 95.5(5) | 36.7(4) | 33.3(5) | 39.0(5) |
| Ag1 | 105.8(8) | 68.0(4) | 135.7(8) | 22.0(4) | 65.1(7) | 14.3(5) |
| Ag3 | 91.0(6) | 86.1(5) | 81.4(4) | 16.1(4) | -28.7(4) | -20.8(5) |
| Ag4 | 94.2(6) | 89.0(5) | 68.2(3) | 15.8(3) | -10.0(4) | -30.5(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| Br1 | 71.8(7) | 66.7(5) | 74.7(5) | 0.7(4) | 7.2(5) | -18.5(5) |
| Br2 | 67.9(6) | 77.4(6) | 66.4(5) | 10.4(4) | -16.5(5) | -10.9(5) |
| Br3 | 67.3(6) | 71.8(6) | 71.1(5) | 2.4(4) | -1.8(4) | 19.2(5) |
| Br4 | 63.8(5) | 64.2(5) | 67.1(4) | 8.7(3) | 17.9(4) | 4.7(4) |
| N1 | 79(5) | 55(4) | 74(4) | 15(3) | 10(4) | 22(4) |
| N2 | 111(8) | 106(7) | 96(6) | 32(6) | 36(6) | 62(7) |
| C3 | 110(11) | 106(9) | 126(10) | 61(8) | 57(9) | 56(8) |
| N4 | 78(5) | 71(5) | 66(4) | 12(3) | 21(4) | 29(4) |
| C10 | 66(6) | 58(5) | 70(5) | 9(4) | 12(4) | 12(4) |
| C6 | 74(7) | 62(5) | 74(5) | 14(4) | 20(5) | 11(5) |
| C16 | 75(6) | 77(6) | 52(4) | 25(4) | 12(4) | 11(5) |
| C8 | 66(6) | 82(6) | 73(5) | 24(4) | 23(5) | 9(5) |
| C9 | 137(13) | 120(11) | 96(9) | 52(8) | 56(9) | 32(10) |
| C5 | 240(30) | 220(20) | 190(20) | 152(19) | 150(20) | 140(20) |
| C11 | 162(17) | 129(12) | 133(11) | 79(10) | 75(12) | 92(13) |
| N12 | 69(5) | 89(6) | 78(5) | 24(4) | 32(4) | 13(5) |
| N13 | 79(7) | 166(12) | 107(8) | 62(8) | 45(6) | 41(8) |
| C14 | 135(14) | 169(15) | 133(12) | 75(11) | 91(11) | 81(13) |
| N15 | 77(6) | 114(8) | 97(7) | 31(6) | 32(5) | 23(6) |
| C7 | 58(5) | 86(6) | 56(4) | 1(4) | 14(4) | 1(5) |
| N1' | 65(5) | 111(7) | 47(3) | 2(4) | -20(3) | 0(5) |
| N2' | 92(8) | 132(9) | 79(6) | 8(6) | -39(6) | -5(7) |
| C3' | 86(9) | 157(14) | 100(9) | 2(9) | -44(8) | -14(10) |
| N4' | 75(6) | 121(8) | 75(5) | -14(5) | -17(5) | -18(6) |
| C27 | 56(5) | 92(7) | 56(4) | -7(4) | -8(4) | -6(5) |
| C6' | 65(6) | 75(6) | 69(5) | 7(4) | -19(4) | 5(5) |
| C7' | 80(7) | 71(6) | 64(5) | 19(4) | -23(4) | -8(5) |
| C8' | 93(8) | 63(5) | 74(5) | 21(4) | -21(5) | -7(5) |
| C9' | 134(13) | 78(7) | 101(8) | 30(6) | -36(9) | -13(8) |
| C10' | 149(14) | 92(9) | 118(10) | 49(8) | -51(11) | -19(10) |
| C11' | 116(12) | 94(9) | 124(10) | 39(8) | -47(9) | 15(8) |
| N12' | 89(7) | 75(5) | 90(6) | 41(4) | -28(5) | -25(5) |
| N13' | 112(9) | 140(10) | 152(11) | 86(9) | -62(9) | -75(9) |
| C14' | 127(13) | 131(12) | 141(12) | 64(10) | -53(11) | -77(11) |
| N15' | 106(8) | 79(6) | 92(6) | 25(5) | -43(6) | -34(6) |
| C30 | 78(6) | 62(5) | 68(5) | 13(4) | -15(5) | -19(5) |

**Table S 29**

Bond Lengths for bis(μ-1,3-bis(4’-butyl-1’,2’,4’-triazol-2’-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e).

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C17 | C18 | 1.456(19) | N1 | C10 | 1.326(12) |
| C17 | N4 | 1.473(13) | N1 | C6 | 1.416(12) |
| C18 | C19 | 1.41(2) | N2 | C3 | 1.293(16) |
| C19 | C20 | 1.38(3) | C3 | N4 | 1.348(14) |
| C21' | C22' | 1.460(18) | N4 | C10 | 1.368(12) |
| C21' | N15' | 1.433(14) | C6 | C16 | 1.356(14) |
| C22' | C23' | 1.43(2) | C6 | C11 | 1.348(15) |
| C23' | C24' | 1.36(3) | C16 | C8 | 1.388(13) |
| C17' | C18' | 1.48(2) | C8 | C9 | 1.337(15) |
| C17' | N4' | 1.447(19) | C8 | N12 | 1.432(14) |
| C18' | C19' | 1.44(2) | C9 | C5 | 1.33(2) |
| C19' | C20' | 1.37(3) | C5 | C11 | 1.38(2) |
| C21 | C22 | 1.461(18) | N12 | N13 | 1.402(13) |
| C21 | N15 | 1.520(15) | N12 | C7 | 1.340(14) |
| C22 | C23 | 1.478(19) | N13 | C14 | 1.229(18) |
| C23 | C24 | 1.37(3) | C14 | N15 | 1.366(17) |
| Ag2 | Ag1 | 3.1379(12) | N15 | C7 | 1.347(15) |
| Ag2 | Br1 | 2.8218(17) | N1' | N2' | 1.388(12) |
| Ag2 | Br2 | 2.8697(16) | N1' | C27 | 1.334(14) |
| Ag2 | Br4 | 2.7032(11) | N1' | C6' | 1.403(14) |
| Ag2 | C10 | 2.153(9) | N2' | C3' | 1.223(19) |
| Ag1 | Br1 | 2.9475(16) | C3' | N4' | 1.402(18) |
| Ag1 | Br2 | 2.6543(15) | N4' | C27 | 1.352(13) |
| Ag1 | Br3 | 2.7908(14) | C6' | C7' | 1.379(13) |
| Ag1 | C7 | 2.122(9) | C6' | C11' | 1.401(15) |
| Ag3 | Ag4 | 3.1564(12) | C7' | C8' | 1.376(15) |
| Ag3 | Br1 | 2.7121(13) | C8' | C9' | 1.372(15) |
| Ag3 | Br3 | 2.8243(14) | C8' | N12' | 1.419(15) |
| Ag3 | Br4 | 2.8287(14) | C9' | C10' | 1.34(2) |
| Ag3 | C27 | 2.156(9) | C10' | C11' | 1.37(2) |
| Ag4 | Br2 | 2.7795(12) | N12' | N13' | 1.385(14) |
| Ag4 | Br3 | 2.6770(16) | N12' | C30 | 1.358(12) |
| Ag4 | Br4 | 2.9571(14) | N13' | C14' | 1.323(19) |
| Ag4 | C30 | 2.147(10) | C14' | N15' | 1.356(16) |
| N1 | N2 | 1.371(12) | N15' | C30 | 1.350(15) |

**Table S 30**

Bond Angles for bis(μ-1,3-bis(4’-butyl-1’,2’,4’-triazol-2’-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e).

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C18 | C17 | N4 | 113.8(12) | N2 | N1 | C6 | 117.5(8) |
| C19 | C18 | C17 | 120.6(19) | C10 | N1 | N2 | 114.3(9) |
| C20 | C19 | C18 | 115(2) | C10 | N1 | C6 | 128.2(8) |
| N15' | C21' | C22' | 110.5(12) | C3 | N2 | N1 | 102.7(9) |
| C23' | C22' | C21' | 114.8(18) | N2 | C3 | N4 | 111.9(11) |
| C24' | C23' | C22' | 121(3) | C3 | N4 | C17 | 124.6(10) |
| N4' | C17' | C18' | 110.6(15) | C3 | N4 | C10 | 108.4(9) |
| C19' | C18' | C17' | 113(2) | C10 | N4 | C17 | 126.6(8) |
| C20' | C19' | C18' | 113(3) | N1 | C10 | Ag2 | 136.3(7) |
| C22 | C21 | N15 | 113.1(12) | N1 | C10 | N4 | 102.6(8) |
| C21 | C22 | C23 | 111.0(15) | N4 | C10 | Ag2 | 121.1(6) |
| C24 | C23 | C22 | 115(2) | C16 | C6 | N1 | 123.1(8) |
| Br1 | Ag2 | Ag1 | 59.00(4) | C11 | C6 | N1 | 118.9(10) |
| Br1 | Ag2 | Br2 | 108.33(4) | C11 | C6 | C16 | 118.1(10) |
| Br2 | Ag2 | Ag1 | 52.21(4) | C6 | C16 | C8 | 120.4(8) |
| Br4 | Ag2 | Ag1 | 105.39(4) | C16 | C8 | N12 | 121.6(8) |
| Br4 | Ag2 | Br1 | 90.25(4) | C9 | C8 | C16 | 120.1(11) |
| Br4 | Ag2 | Br2 | 90.00(4) | C9 | C8 | N12 | 118.1(10) |
| C10 | Ag2 | Ag1 | 119.9(2) | C8 | C9 | C5 | 119.8(13) |
| C10 | Ag2 | Br1 | 119.5(3) | C9 | C5 | C11 | 120.3(12) |
| C10 | Ag2 | Br2 | 109.9(3) | C6 | C11 | C5 | 121.1(13) |
| C10 | Ag2 | Br4 | 133.9(2) | N13 | N12 | C8 | 115.8(9) |
| Br1 | Ag1 | Ag2 | 55.14(4) | C7 | N12 | C8 | 128.9(8) |
| Br2 | Ag1 | Ag2 | 58.69(4) | C7 | N12 | N13 | 115.3(9) |
| Br2 | Ag1 | Br1 | 110.80(4) | C14 | N13 | N12 | 99.9(11) |
| Br2 | Ag1 | Br3 | 89.17(4) | N13 | C14 | N15 | 115.9(12) |
| Br3 | Ag1 | Ag2 | 105.41(4) | C14 | N15 | C21 | 128.5(11) |
| Br3 | Ag1 | Br1 | 90.16(5) | C7 | N15 | C21 | 123.7(10) |
| C7 | Ag1 | Ag2 | 123.0(3) | C7 | N15 | C14 | 107.5(11) |
| C7 | Ag1 | Br1 | 101.6(3) | N12 | C7 | Ag1 | 133.5(7) |
| C7 | Ag1 | Br2 | 130.5(3) | N12 | C7 | N15 | 101.1(9) |
| C7 | Ag1 | Br3 | 127.9(3) | N15 | C7 | Ag1 | 124.8(8) |
| Br1 | Ag3 | Ag4 | 109.17(4) | N2' | N1' | C6' | 118.3(10) |
| Br1 | Ag3 | Br3 | 94.45(4) | C27 | N1' | N2' | 112.2(10) |
| Br1 | Ag3 | Br4 | 89.92(4) | C27 | N1' | C6' | 129.5(8) |
| Br3 | Ag3 | Ag4 | 52.83(4) | C3' | N2' | N1' | 105.0(11) |
| Br3 | Ag3 | Br4 | 108.86(4) | N2' | C3' | N4' | 112.3(12) |
| Br4 | Ag3 | Ag4 | 58.91(3) | C3' | N4' | C17' | 125.4(11) |
| C27 | Ag3 | Ag4 | 121.4(3) | C27 | N4' | C17' | 127.8(11) |
| C27 | Ag3 | Br1 | 129.3(3) | C27 | N4' | C3' | 106.7(11) |
| C27 | Ag3 | Br3 | 113.4(3) | N1' | C27 | Ag3 | 134.3(7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C27 | Ag3 | Br4 | 116.9(3) | N1' | C27 | N4' | 103.8(9) |
| Br2 | Ag4 | Ag3 | 101.72(3) | N4' | C27 | Ag3 | 121.9(8) |
| Br2 | Ag4 | Br4 | 86.76(4) | C7' | C6' | N1' | 122.4(9) |
| Br3 | Ag4 | Ag3 | 57.21(4) | C7' | C6' | C11' | 118.7(11) |
| Br3 | Ag4 | Br2 | 88.95(4) | C11' | C6' | N1' | 118.9(10) |
| Br3 | Ag4 | Br4 | 109.30(4) | C8' | C7' | C6' | 120.1(9) |
| Br4 | Ag4 | Ag3 | 55.01(3) | C7' | C8' | N12' | 120.4(8) |
| C30 | Ag4 | Ag3 | 120.7(3) | C9' | C8' | C7' | 121.3(11) |
| C30 | Ag4 | Br2 | 130.0(3) | C9' | C8' | N12' | 118.1(11) |
| C30 | Ag4 | Br3 | 135.0(3) | C10' | C9' | C8' | 117.9(13) |
| C30 | Ag4 | Br4 | 96.2(3) | C9' | C10' | C11' | 123.5(11) |
| Ag2 | Br1 | Ag1 | 65.86(4) | C10' | C11' | C6' | 118.3(12) |
| Ag3 | Br1 | Ag2 | 85.35(4) | N13' | N12' | C8' | 117.2(8) |
| Ag3 | Br1 | Ag1 | 83.35(4) | C30 | N12' | C8' | 129.6(9) |
| Ag1 | Br2 | Ag2 | 69.10(4) | C30 | N12' | N13' | 113.2(9) |
| Ag1 | Br2 | Ag4 | 87.64(4) | C14' | N13' | N12' | 101.2(10) |
| Ag4 | Br2 | Ag2 | 88.06(4) | N13' | C14' | N15' | 113.8(12) |
| Ag1 | Br3 | Ag3 | 84.28(4) | C14' | N15' | C21' | 124.4(12) |
| Ag4 | Br3 | Ag1 | 86.96(4) | C30 | N15' | C21' | 128.5(10) |
| Ag4 | Br3 | Ag3 | 69.97(4) | C30 | N15' | C14' | 107.1(10) |
| Ag2 | Br4 | Ag3 | 85.38(4) | N12' | C30 | Ag4 | 131.4(8) |
| Ag2 | Br4 | Ag4 | 87.74(4) | N15' | C30 | Ag4 | 124.0(7) |
| Ag3 | Br4 | Ag4 | 66.08(3) | N15' | C30 | N12' | 104.6(9) |

**Table S 31**

Torsion Angles for bis(μ-1,3-bis(4’-butyl-1’,2’,4’-triazol-2’-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e).

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C17 | C18 | C19 | C20 | 173(3) | Br4 | Ag3 | Br3 | Ag1 | -69.54(5) |
| C17 | N4 | C10 | Ag2 | 6.6(16) | Br4 | Ag3 | Br3 | Ag4 | 19.30(4) |
| C17 | N4 | C10 | N1 | -173.4(11) | Br4 | Ag3 | C27 | N1' | -64.0(11) |
| C18 | C17 | N4 | C3 | -95(2) | Br4 | Ag3 | C27 | N4' | 117.1(9) |
| C18 | C17 | N4 | C10 | 77.0(19) | Br4 | Ag4 | Br2 | Ag2 | -19.52(4) |
| C21' | C22' | C23' | C24' | 153(3) | Br4 | Ag4 | Br2 | Ag1 | -88.68(4) |
| C21' | N15' | C30 | Ag4 | 5(2) | Br4 | Ag4 | Br3 | Ag1 | 66.53(5) |
| C21' | N15' | C30 | N12' | -175.0(13) | Br4 | Ag4 | Br3 | Ag3 | -18.48(4) |
| C22' | C21' | N15' | C14' | -91(2) | Br4 | Ag4 | C30 | N12' | 84.1(12) |
| C22' | C21' | N15' | C30 | 86.5(19) | Br4 | Ag4 | C30 | N15' | -95.4(11) |
| C17' | C18' | C19' | C20' | 178(4) | N1 | N2 | C3 | N4 | -4(2) |
| C17' | N4' | C27 | Ag3 | 2.5(19) | N1 | C6 | C16 | C8 | -176.2(11) |

| | | | | |
|---|---|---|---|---|
| C17' | N4' | C27 | N1' | -176.7(13) |
| C18' | C17' | N4' | C3' | -76(2) |
| C18' | C17' | N4' | C27 | 101(2) |
| C21 | C22 | C23 | C24 | -176(3) |
| C21 | N15 | C7 | Ag1 | -11.9(18) |
| C21 | N15 | C7 | N12 | 175.7(12) |
| C22 | C21 | N15 | C14 | -88(2) |
| C22 | C21 | N15 | C7 | 99.1(17) |
| Ag2 | Ag1 | Br1 | Ag3 | -87.87(4) |
| Ag2 | Ag1 | Br2 | Ag4 | 88.82(4) |
| Ag2 | Ag1 | Br3 | Ag3 | 33.69(6) |
| Ag2 | Ag1 | Br3 | Ag4 | -36.47(5) |
| Ag2 | Ag1 | C7 | N12 | 13.4(13) |
| Ag2 | Ag1 | C7 | N15 | -156.3(9) |
| Ag1 | Ag2 | Br1 | Ag3 | 84.79(4) |
| Ag1 | Ag2 | Br2 | Ag4 | -88.22(4) |
| Ag1 | Ag2 | Br4 | Ag3 | -35.71(5) |
| Ag1 | Ag2 | Br4 | Ag4 | 30.47(6) |
| Ag1 | Ag2 | C10 | N1 | 14.7(13) |
| Ag1 | Ag2 | C10 | N4 | -165.3(7) |
| Ag3 | Ag4 | Br2 | Ag2 | 33.72(5) |
| Ag3 | Ag4 | Br2 | Ag1 | -35.43(5) |
| Ag3 | Ag4 | Br3 | Ag1 | 85.01(4) |
| Ag3 | Ag4 | Br4 | Ag2 | -85.95(4) |
| Ag3 | Ag4 | C30 | N12' | 31.4(13) |
| Ag3 | Ag4 | C30 | N15' | -148.0(9) |
| Ag4 | Ag3 | Br1 | Ag2 | -34.83(5) |
| Ag4 | Ag3 | Br1 | Ag1 | 31.36(6) |
| Ag4 | Ag3 | Br3 | Ag1 | -88.85(4) |
| Ag4 | Ag3 | Br4 | Ag2 | 89.57(4) |
| Ag4 | Ag3 | C27 | N1' | 4.4(12) |
| Ag4 | Ag3 | C27 | N4' | -174.5(8) |
| Br1 | Ag2 | Ag1 | Br2 | -158.46(4) |
| Br1 | Ag2 | Ag1 | Br3 | -79.14(5) |
| Br1 | Ag2 | Ag1 | C7 | 80.8(3) |
| Br1 | Ag2 | Br2 | Ag1 | 19.36(4) |
| Br1 | Ag2 | Br2 | Ag4 | -68.85(5) |
| Br1 | Ag2 | Br4 | Ag3 | 22.08(4) |
| Br1 | Ag2 | Br4 | Ag4 | 88.26(4) |
| Br1 | Ag2 | C10 | N1 | -54.4(12) |
| Br1 | Ag2 | C10 | N4 | 125.6(8) |
| Br1 | Ag1 | Br2 | Ag2 | -18.80(4) |
| N1 | C6 | C11 | C5 | 180(2) |
| N2 | N1 | C10 | Ag2 | 177.9(10) |
| N2 | N1 | C10 | N4 | -2.1(14) |
| N2 | N1 | C6 | C16 | -174.2(12) |
| N2 | N1 | C6 | C11 | 7(2) |
| N2 | C3 | N4 | C17 | 176.3(14) |
| N2 | C3 | N4 | C10 | 3(2) |
| C3 | N4 | C10 | Ag2 | 179.4(11) |
| C3 | N4 | C10 | N1 | -0.6(15) |
| N4 | C17 | C18 | C19 | 50(4) |
| C10 | Ag2 | Ag1 | Br1 | -108.5(3) |
| C10 | Ag2 | Ag1 | Br2 | 93.0(3) |
| C10 | Ag2 | Ag1 | Br3 | 172.3(3) |
| C10 | Ag2 | Ag1 | C7 | -27.8(5) |
| C10 | Ag2 | Br1 | Ag1 | 109.1(3) |
| C10 | Ag2 | Br1 | Ag3 | -166.1(3) |
| C10 | Ag2 | Br2 | Ag1 | -112.9(3) |
| C10 | Ag2 | Br2 | Ag4 | 158.9(3) |
| C10 | Ag2 | Br4 | Ag3 | 155.5(4) |
| C10 | Ag2 | Br4 | Ag4 | -138.3(4) |
| C10 | N1 | N2 | C3 | 4.1(18) |
| C10 | N1 | C6 | C16 | 5.7(19) |
| C10 | N1 | C6 | C11 | -173.6(15) |
| C6 | N1 | N2 | C3 | -176.0(13) |
| C6 | N1 | C10 | Ag2 | -2.0(19) |
| C6 | N1 | C10 | N4 | 178.0(11) |
| C6 | C16 | C8 | C9 | -6(2) |
| C6 | C16 | C8 | N12 | 179.0(11) |
| C16 | C6 | C11 | C5 | 1(3) |
| C16 | C8 | C9 | C5 | 4(3) |
| C16 | C8 | N12 | N13 | 156.5(13) |
| C16 | C8 | N12 | C7 | -25(2) |
| C8 | C9 | C5 | C11 | 0(4) |
| C8 | N12 | N13 | C14 | 174.1(15) |
| C8 | N12 | C7 | Ag1 | 12(2) |
| C8 | N12 | C7 | N15 | -176.7(12) |
| C9 | C8 | N12 | N13 | -19(2) |
| C9 | C8 | N12 | C7 | 159.4(14) |
| C9 | C5 | C11 | C6 | -2(5) |
| C11 | C6 | C16 | C8 | 3(2) |
| N12 | C8 | C9 | C5 | 180(2) |
| N12 | N13 | C14 | N15 | 6(2) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Br1 | Ag1 | Br2 | Ag4 | 70.02(5) | N13 | N12 | C7 | Ag1 | -169.8(10) |
| Br1 | Ag1 | Br3 | Ag3 | -20.01(4) | N13 | N12 | C7 | N15 | 1.7(15) |
| Br1 | Ag1 | Br3 | Ag4 | -90.16(4) | N13 | C14 | N15 | C21 | -178.8(17) |
| Br1 | Ag1 | C7 | N12 | 69.2(11) | N13 | C14 | N15 | C7 | -5(3) |
| Br1 | Ag1 | C7 | N15 | -100.5(10) | C14 | N15 | C7 | Ag1 | 174.1(12) |
| Br1 | Ag3 | Ag4 | Br2 | 0.26(7) | C14 | N15 | C7 | N12 | 1.6(16) |
| Br1 | Ag3 | Ag4 | Br3 | -80.77(5) | N15 | C21 | C22 | C23 | -179.0(17) |
| Br1 | Ag3 | Ag4 | Br4 | 77.81(5) | C7 | Ag1 | Br1 | Ag2 | -122.3(3) |
| Br1 | Ag3 | Ag4 | C30 | 152.6(4) | C7 | Ag1 | Br1 | Ag3 | 149.8(3) |
| Br1 | Ag3 | Br3 | Ag1 | 21.90(5) | C7 | Ag1 | Br2 | Ag2 | 108.6(4) |
| Br1 | Ag3 | Br3 | Ag4 | 110.74(5) | C7 | Ag1 | Br2 | Ag4 | -162.6(4) |
| Br1 | Ag3 | Br4 | Ag2 | -23.02(4) | C7 | Ag1 | Br3 | Ag3 | -124.9(4) |
| Br1 | Ag3 | Br4 | Ag4 | -112.59(4) | C7 | Ag1 | Br3 | Ag4 | 165.0(4) |
| Br1 | Ag3 | C27 | N1' | -178.5(9) | C7 | N12 | N13 | C14 | -4(2) |
| Br1 | Ag3 | C27 | N4' | 2.6(11) | N1' | N2' | C3' | N4' | 2(2) |
| Br2 | Ag2 | Ag1 | Br1 | 158.46(4) | N1' | C6' | C7' | C8' | 179.7(11) |
| Br2 | Ag2 | Ag1 | Br3 | 79.32(5) | N1' | C6' | C11' | C10' | -177.1(15) |
| Br2 | Ag2 | Ag1 | C7 | -120.8(3) | N2' | N1' | C27 | Ag3 | -178.9(9) |
| Br2 | Ag2 | Br1 | Ag1 | -17.80(4) | N2' | N1' | C27 | N4' | 0.2(13) |
| Br2 | Ag2 | Br1 | Ag3 | 67.00(4) | N2' | N1' | C6' | C7' | -165.0(11) |
| Br2 | Ag2 | Br4 | Ag3 | -86.25(4) | N2' | N1' | C6' | C11' | 13.3(18) |
| Br2 | Ag2 | Br4 | Ag4 | -20.07(5) | N2' | C3' | N4' | C17' | 175.9(15) |
| Br2 | Ag2 | C10 | N1 | 71.8(12) | N2' | C3' | N4' | C27 | -2(2) |
| Br2 | Ag2 | C10 | N4 | -108.2(8) | C3' | N4' | C27 | Ag3 | 179.9(10) |
| Br2 | Ag1 | Br1 | Ag2 | 19.61(4) | C3' | N4' | C27 | N1' | 0.7(14) |
| Br2 | Ag1 | Br1 | Ag3 | -68.26(5) | N4' | C17' | C18' | C19' | 178(3) |
| Br2 | Ag1 | Br3 | Ag3 | 90.79(4) | C27 | Ag3 | Ag4 | Br2 | 177.9(3) |
| Br2 | Ag1 | Br3 | Ag4 | 20.64(4) | C27 | Ag3 | Ag4 | Br3 | 96.9(3) |
| Br2 | Ag1 | C7 | N12 | -61.5(12) | C27 | Ag3 | Ag4 | Br4 | -104.5(3) |
| Br2 | Ag1 | C7 | N15 | 128.8(10) | C27 | Ag3 | Ag4 | C30 | -29.7(5) |
| Br2 | Ag4 | Br3 | Ag1 | -19.67(4) | C27 | Ag3 | Br1 | Ag2 | 147.7(4) |
| Br2 | Ag4 | Br3 | Ag3 | -104.68(4) | C27 | Ag3 | Br1 | Ag1 | -146.1(4) |
| Br2 | Ag4 | Br4 | Ag2 | 20.79(5) | C27 | Ag3 | Br3 | Ag1 | 158.5(3) |
| Br2 | Ag4 | Br4 | Ag3 | 106.74(4) | C27 | Ag3 | Br3 | Ag4 | -112.7(3) |
| Br2 | Ag4 | C30 | N12' | 175.0(10) | C27 | Ag3 | Br4 | Ag2 | -158.3(3) |
| Br2 | Ag4 | C30 | N15' | -4.4(13) | C27 | Ag3 | Br4 | Ag4 | 112.1(3) |
| Br3 | Ag1 | Br1 | Ag2 | 108.78(4) | C27 | N1' | N2' | C3' | -1.1(17) |
| Br3 | Ag1 | Br1 | Ag3 | 20.91(5) | C27 | N1' | C6' | C7' | 15.9(18) |
| Br3 | Ag1 | Br2 | Ag2 | -108.65(4) | C27 | N1' | C6' | C11' | -165.8(13) |
| Br3 | Ag1 | Br2 | Ag4 | -19.83(4) | C6' | N1' | N2' | C3' | 179.7(13) |
| Br3 | Ag1 | C7 | N12 | 168.6(10) | C6' | N1' | C27 | Ag3 | 0.2(18) |
| Br3 | Ag1 | C7 | N15 | -1.1(12) | C6' | N1' | C27 | N4' | 179.3(11) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Br3 | Ag3 | Ag4 | Br2 | 81.03(5) | C6' | C7' | C8' | C9' | -3(2) |
| Br3 | Ag3 | Ag4 | Br4 | 158.58(4) | C6' | C7' | C8' | N12' | -178.8(11) |
| Br3 | Ag3 | Ag4 | C30 | -126.6(4) | C7' | C6' | C11' | C10' | 1(2) |
| Br3 | Ag3 | Br1 | Ag2 | -86.91(4) | C7' | C8' | C9' | C10' | 2(3) |
| Br3 | Ag3 | Br1 | Ag1 | -20.72(5) | C7' | C8' | N12' | N13' | 151.3(14) |
| Br3 | Ag3 | Br4 | Ag2 | 71.66(4) | C7' | C8' | N12' | C30 | -28(2) |
| Br3 | Ag3 | Br4 | Ag4 | -17.91(4) | C8' | C9' | C10' | C11' | 1(3) |
| Br3 | Ag3 | C27 | N1' | 63.9(11) | C8' | N12' | N13' | C14' | 179.2(15) |
| Br3 | Ag3 | C27 | N4' | -115.0(9) | C8' | N12' | C30 | Ag4 | -1(2) |
| Br3 | Ag4 | Br2 | Ag2 | 89.87(4) | C8' | N12' | C30 | N15' | 178.3(13) |
| Br3 | Ag4 | Br2 | Ag1 | 20.72(4) | C9' | C8' | N12' | N13' | -24(2) |
| Br3 | Ag4 | Br4 | Ag2 | -66.96(5) | C9' | C8' | N12' | C30 | 156.4(14) |
| Br3 | Ag4 | Br4 | Ag3 | 18.99(4) | C9' | C10' | C11' | C6' | -2(3) |
| Br3 | Ag4 | C30 | N12' | -41.3(13) | C11' | C6' | C7' | C8' | 1.4(19) |
| Br3 | Ag4 | C30 | N15' | 139.3(9) | N12' | C8' | C9' | C10' | 177.8(16) |
| Br4 | Ag2 | Ag1 | Br1 | 80.79(5) | N12' | N13' | C14' | N15' | 3(3) |
| Br4 | Ag2 | Ag1 | Br2 | -77.67(5) | N13' | N12' | C30 | Ag4 | 179.5(11) |
| Br4 | Ag2 | Ag1 | Br3 | 1.65(7) | N13' | N12' | C30 | N15' | -1.0(17) |
| Br4 | Ag2 | Ag1 | C7 | 161.6(3) | N13' | C14' | N15' | C21' | 173.9(16) |
| Br4 | Ag2 | Br1 | Ag1 | -107.88(4) | N13' | C14' | N15' | C30 | -4(3) |
| Br4 | Ag2 | Br1 | Ag3 | -23.08(4) | C14' | N15' | C30 | Ag4 | -177.5(12) |
| Br4 | Ag2 | Br2 | Ag1 | 109.62(5) | C14' | N15' | C30 | N12' | 2.9(17) |
| Br4 | Ag2 | Br2 | Ag4 | 21.41(5) | N15' | C21' | C22' | C23' | 60(2) |
| Br4 | Ag2 | C10 | N1 | -177.8(9) | C30 | Ag4 | Br2 | Ag2 | -114.9(4) |
| Br4 | Ag2 | C10 | N4 | 2.2(11) | C30 | Ag4 | Br2 | Ag1 | 176.0(4) |
| Br4 | Ag3 | Ag4 | Br2 | -77.55(5) | C30 | Ag4 | Br3 | Ag1 | -172.7(4) |
| Br4 | Ag3 | Ag4 | Br3 | -158.58(4) | C30 | Ag4 | Br3 | Ag3 | 102.3(4) |
| Br4 | Ag3 | Ag4 | C30 | 74.8(4) | C30 | Ag4 | Br4 | Ag2 | 150.7(3) |
| Br4 | Ag3 | Br1 | Ag2 | 22.00(4) | C30 | Ag4 | Br4 | Ag3 | -123.4(3) |
| Br4 | Ag3 | Br1 | Ag1 | 88.20(4) | C30 | N12' | N13' | C14' | -1(2) |

**Table S 32**

Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for bis(μ-1,3-bis(4’-butyl-1’,2’,4’-triazol-2’-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e).

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H17A | 3766 | 7613 | 7047 | 105 |
| H17B | 2990 | 8173 | 6878 | 105 |
| H18 | 3831 | 9180 | 7206 | 201 |
| H19 | 4460 | 8226 | 8446 | 359 |
| H20A | 5498 | 9195 | 8041 | 385 |

| | | | | |
|---|---|---|---|---|
| H20B | 4937 | 9481 | 8741 | 385 |
| H20C | 4720 | 9759 | 7891 | 385 |
| H21A | 3011 | 11817 | 8111 | 107 |
| H21B | 3758 | 12376 | 7846 | 107 |
| H22A | 4154 | 11064 | 7843 | 168 |
| H22B | 3423 | 10856 | 7264 | 168 |
| H23A | 4031 | 11372 | 6308 | 295 |
| H23B | 4555 | 11969 | 6817 | 295 |
| H24A | 5474 | 11102 | 7052 | 367 |
| H24B | 5274 | 11050 | 6158 | 367 |
| H24C | 4908 | 10400 | 6730 | 367 |
| H17C | -1098 | 9078 | 5869 | 142 |
| H17D | -1560 | 8979 | 5064 | 142 |
| H18A | -2210 | 9811 | 6339 | 258 |
| H18B | -2667 | 9749 | 5531 | 258 |
| H19A | -2785 | 8409 | 5673 | 411 |
| H19B | -2301 | 8454 | 6470 | 411 |
| H20D | -3415 | 9401 | 6724 | 716 |
| H20E | -3482 | 8475 | 6904 | 716 |
| H20F | -3874 | 8825 | 6136 | 716 |
| H21C | -1901 | 10440 | 10115 | 111 |
| H21D | -1177 | 10600 | 9510 | 111 |
| H22C | -2673 | 9809 | 9180 | 142 |
| H22D | -1946 | 9953 | 8574 | 142 |
| H23C | -2797 | 11192 | 9326 | 234 |
| H23D | -2113 | 11308 | 8677 | 234 |
| H24D | -3157 | 10450 | 8028 | 476 |
| H24E | -3083 | 11391 | 7948 | 476 |
| H24F | -3715 | 11015 | 8551 | 476 |
| H3 | 3730 | 6769 | 8236 | 137 |
| H7 | 786 | 8298 | 8955 | 81 |
| H9 | -52 | 7453 | 10945 | 141 |
| H10 | 1033 | 6590 | 10985 | 260 |
| H11 | 2038 | 6614 | 10039 | 170 |
| H14 | -2012 | 8937 | 10635 | 174 |
| H3' | -1801 | 10323 | 4259 | 137 |
| H7' | 856 | 11359 | 5988 | 86 |
| H9' | 1403 | 13594 | 5349 | 125 |
| H10' | 287 | 13583 | 4551 | 144 |
| H11' | -611 | 12520 | 4480 | 134 |
| H14' | 3621 | 13109 | 6611 | 159 |

Experimental

Single crystals of $C_{36}H_{46}Ag_4Br_4N_{12}$ [bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e)] were [Crystallized Via Slow Vapor Diffusion of MeOH into a Saturated Solution of DMSO]. A suitable crystal was selected and [Mounted on a 1.0mm Cryoloop] on a Bruker Smart APEX II diffractometer. The crystal was kept at 100K K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using CGLS minimisation.

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2. SHELXS, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122
3. SHELXL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122

Crystal structure determination of [bis(μ-1,3-bis(4'-butyl-1',2',4'-triazol-2'-ylidene)benzene-κ-C)tetra-μ3-bromotetrasilver(I) (3e)]

**Crystal Data** for $C_{36}H_{46}Ag_4Br_4N_{12}$ ($M$ =1397.97): orthorhombic, space group $P2_1cn$ (no. 33), $a$ = 16.1580(4) Å, $b$ = 16.9023(4) Å, $c$ = 17.5083(4) Å, $V$ = 4781.6(2) Å$^3$, $Z$ = 4, $T$ = 100K K, μ(CuKα) = 17.178 mm$^{-1}$, *Dcalc* = 1.942 g/mm$^3$, 40231 reflections measured ($7.26 \leq 2\Theta \leq 138.98$), 7437 unique ($R_{int}$ = 0.0697) which were used in all calculations. The final $R_1$ was 0.0453 (>2sigma(I)) and $wR_2$ was 0.1258 (all data).

This report has been created with Olex2, compiled on 2012.11.06 svn.r2526. Please let us know if there are any errors or if you would like to have additional featrues.

NMR Spectra

**Figure S 3**. **$^{1}$H NMR spectrum of Complex 3a in $CD_2Cl_2$. 300MHz.**

**Figure S 4**. **$^{13}C\{^{1}H\}$ NMR spectrum of Complex 3a in $CD_2Cl_2$. 75.5 MHz.**

**Figure S 5. HMQC of Complex 3a in $CD_2Cl_2$.**

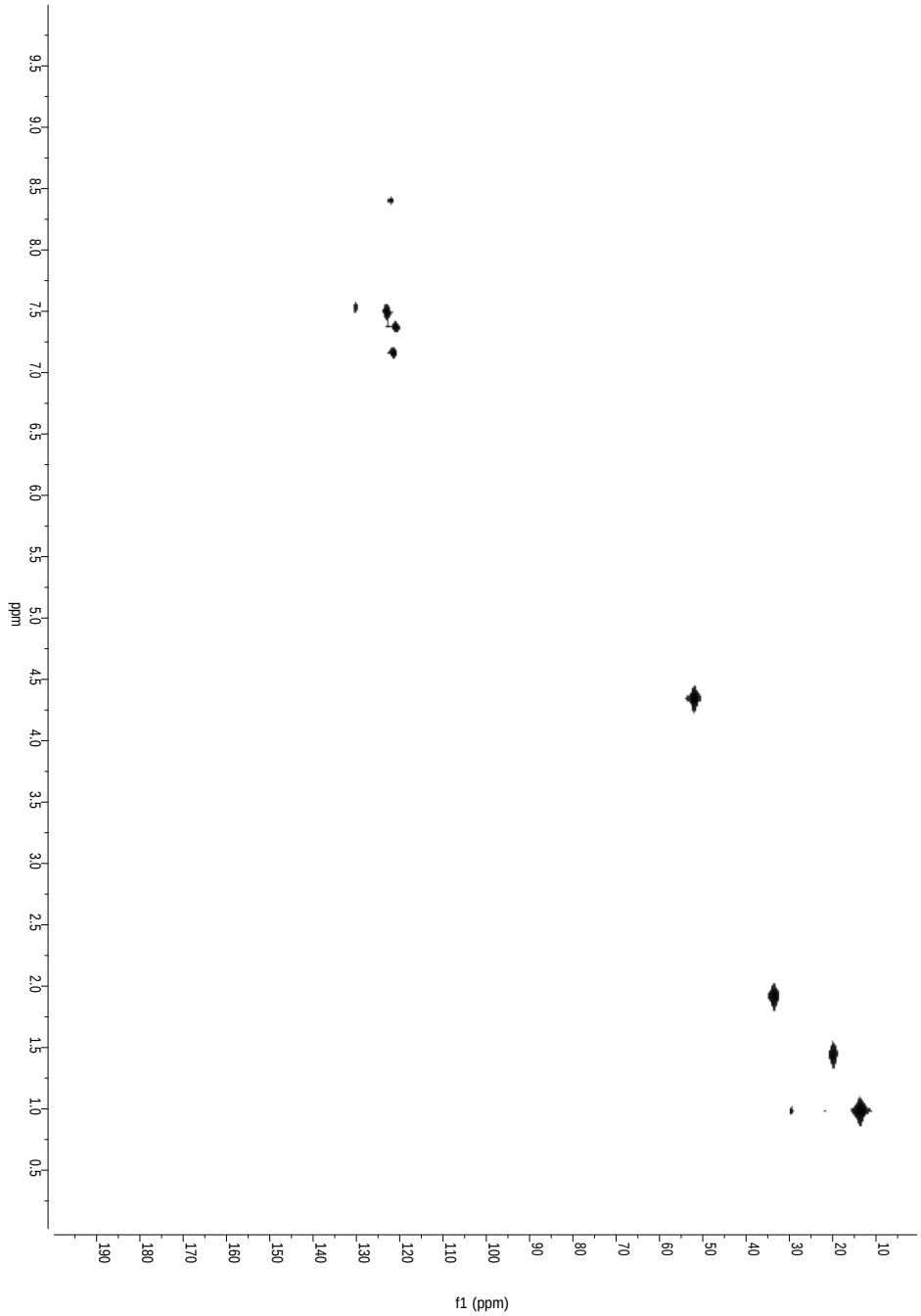


**Figure S 6**. Excerpt from HMQC of Complex 3a in $CD_2Cl_2$.

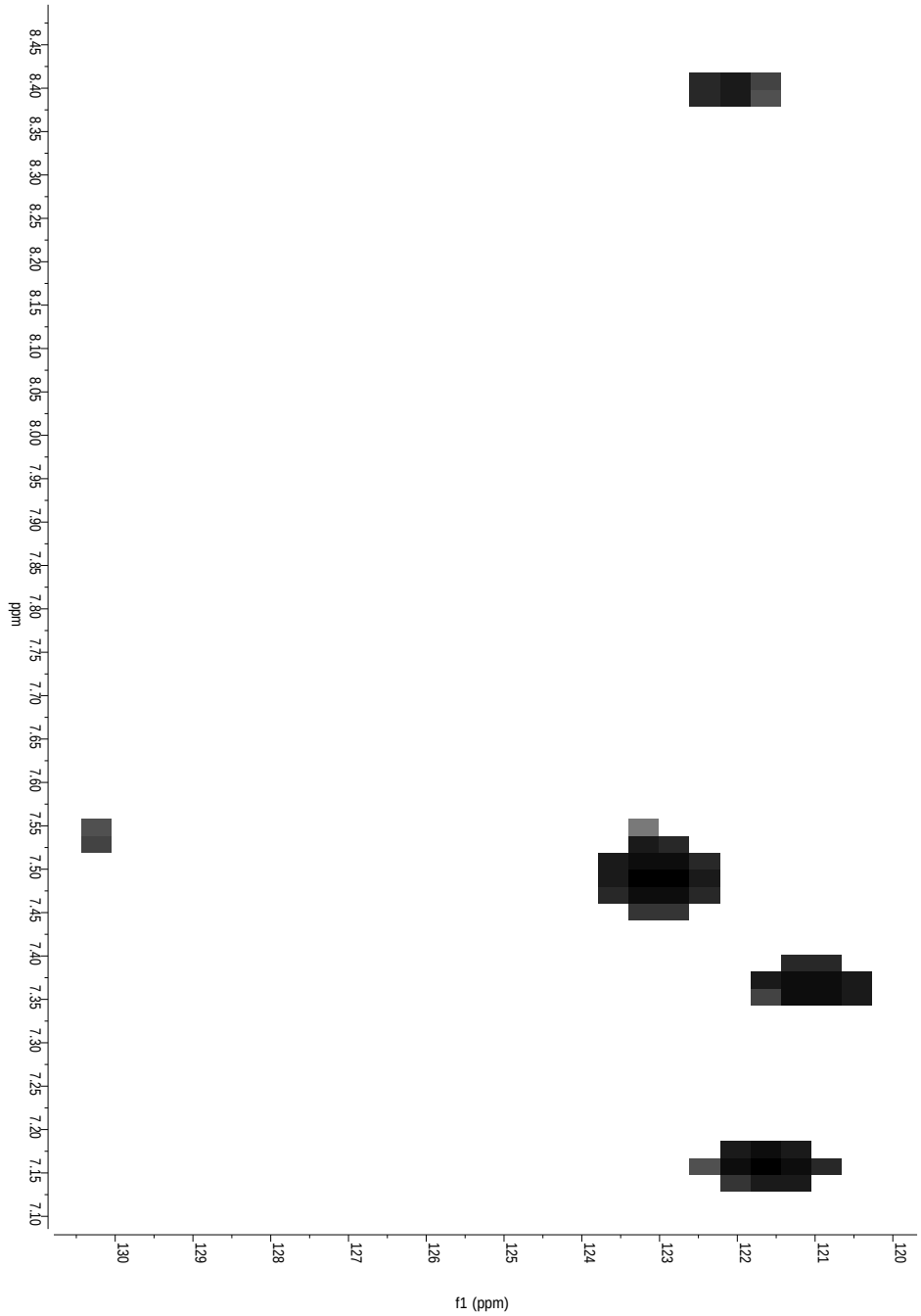


**Figure S 7. VT $^{13}C$ NMR of Imidazole-AgI complex 3a in 2:1 DMF: $CD_2Cl_2$. 125.8 MHz.**

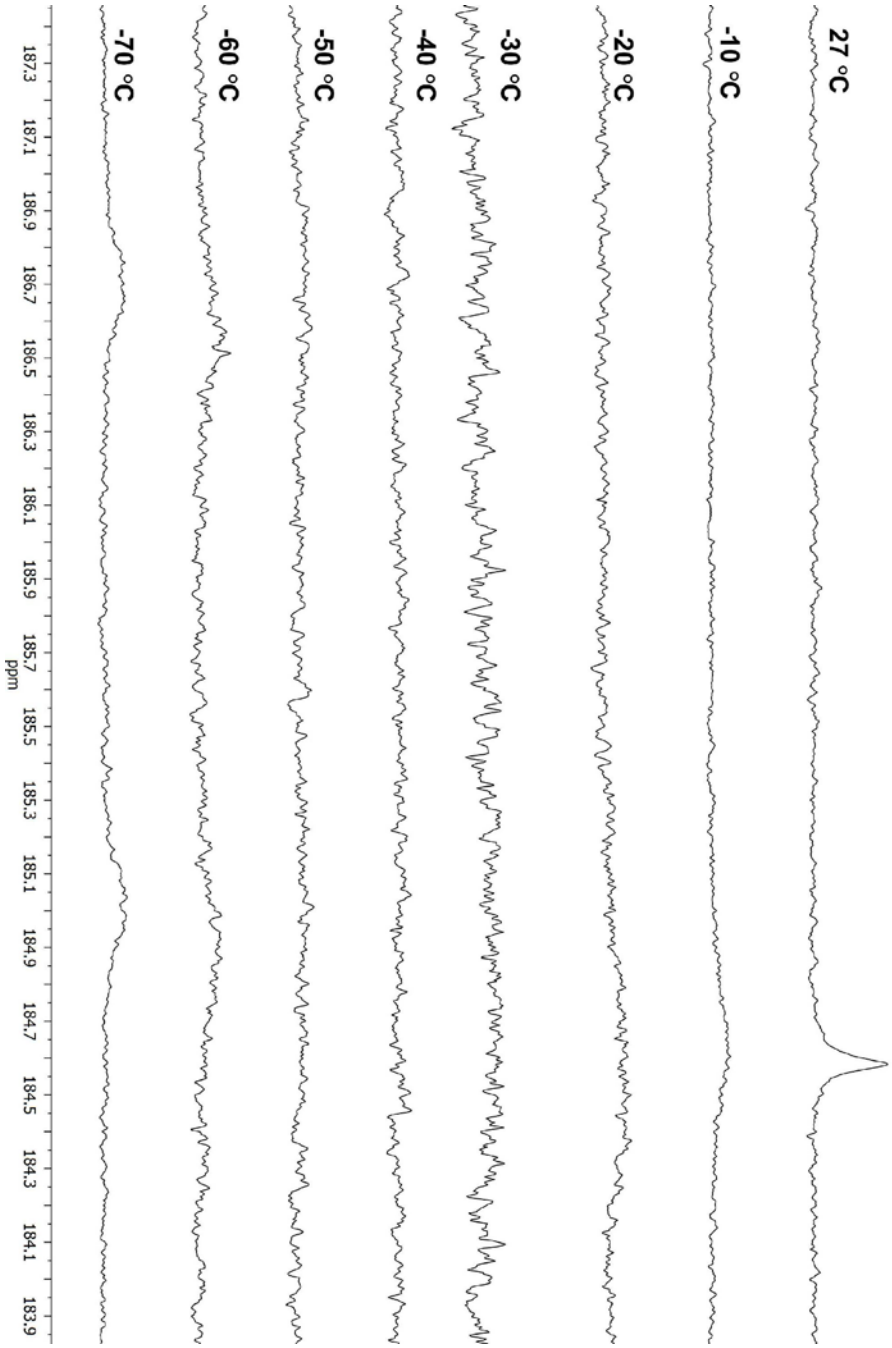


**Figure S 8 $^{1}$H NMR of Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^{3}$-iodotetrasilver(I) (3b) in $CD_2Cl_2$. 75.5 MHz.**

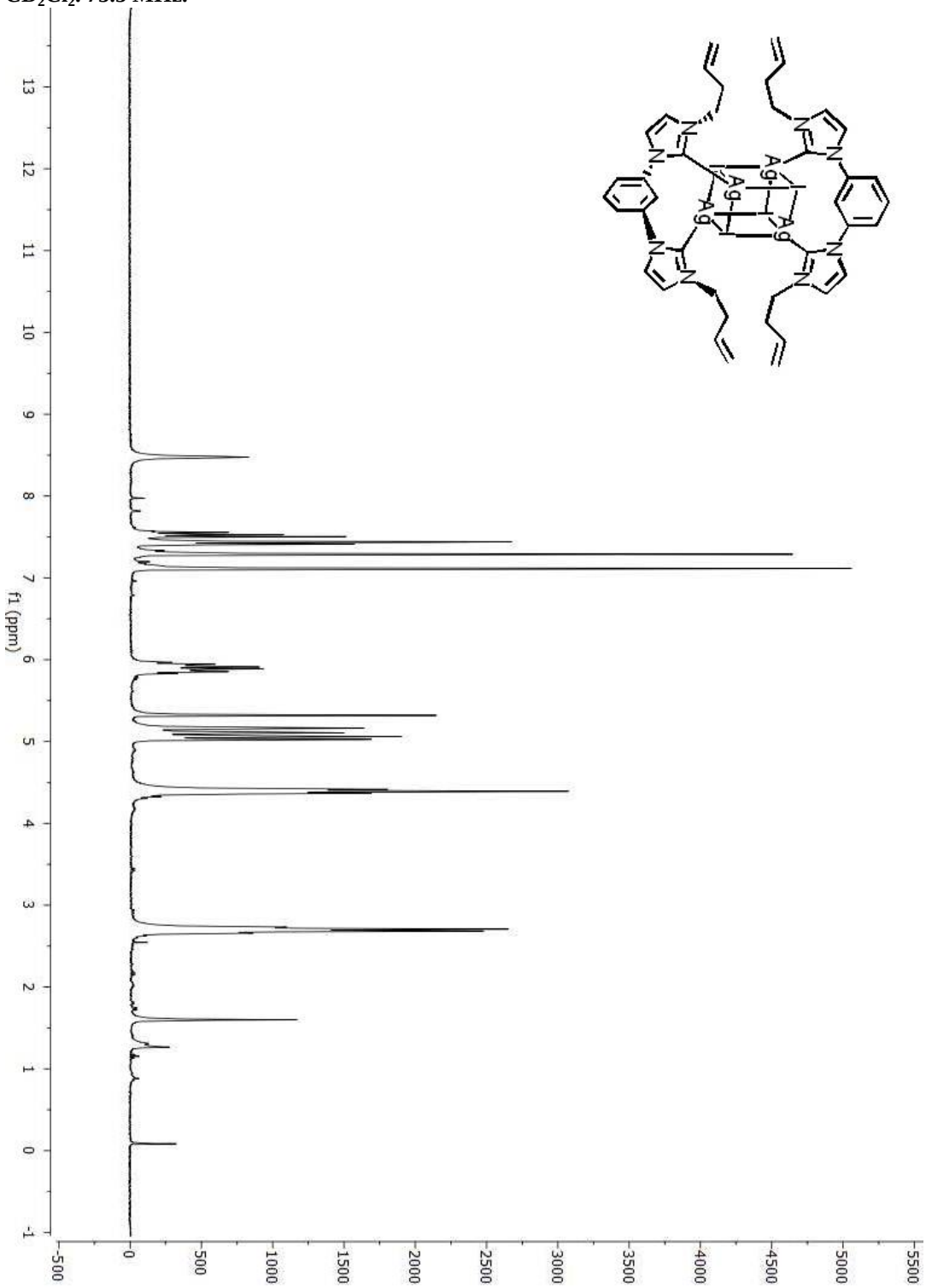


**Figure S 9 $^{13}$C NMR of Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (3b) in $CD_2Cl_2$. 75.5 MHz.**

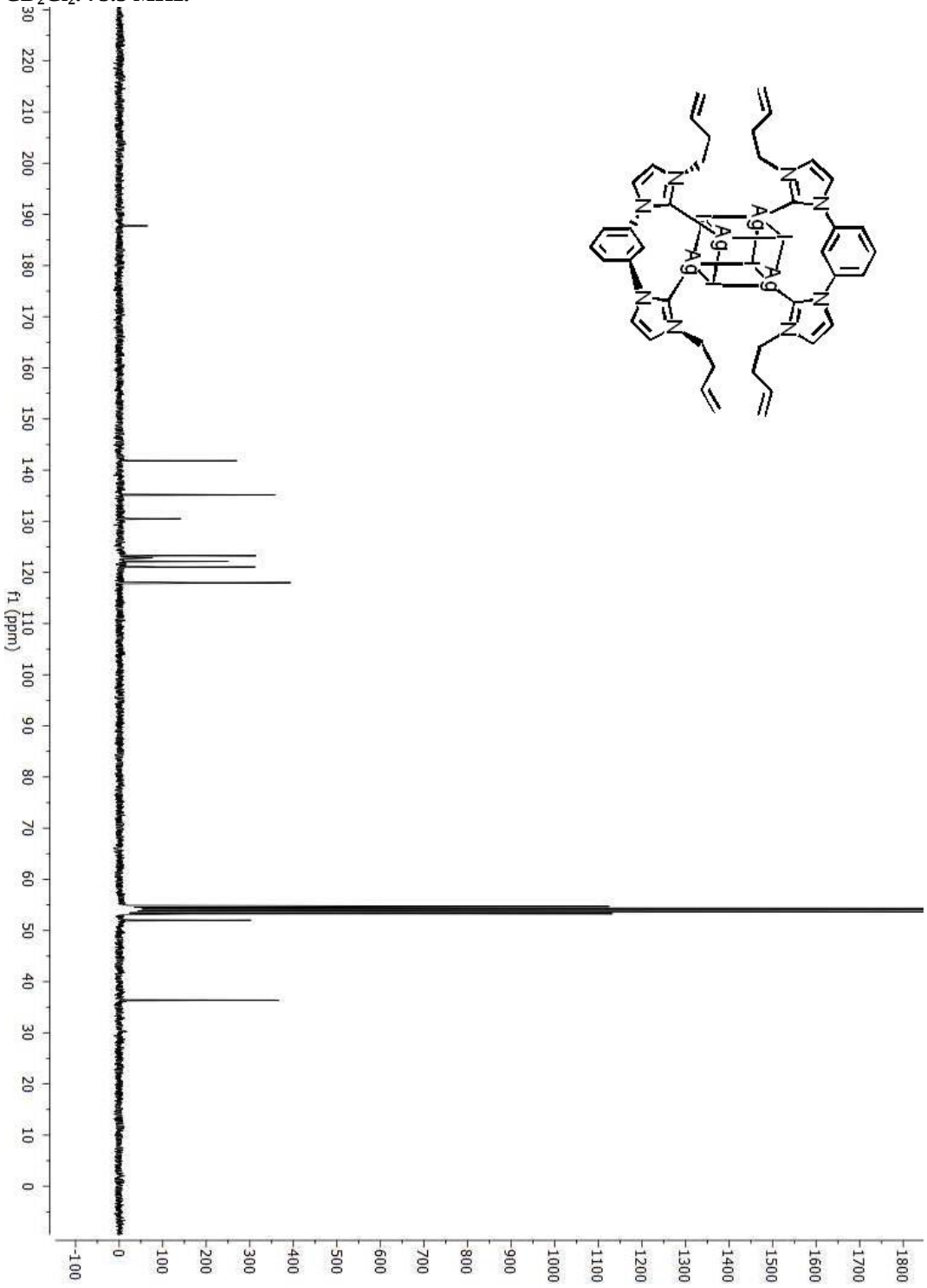


**Figure S 10 VT $^{13}$C NMR of Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-μ$^3$-iodotetrasilver(I) (3b) (0.5 N) in 2:1 DMF: $CD_2Cl_2$. 125.8 MHz.**

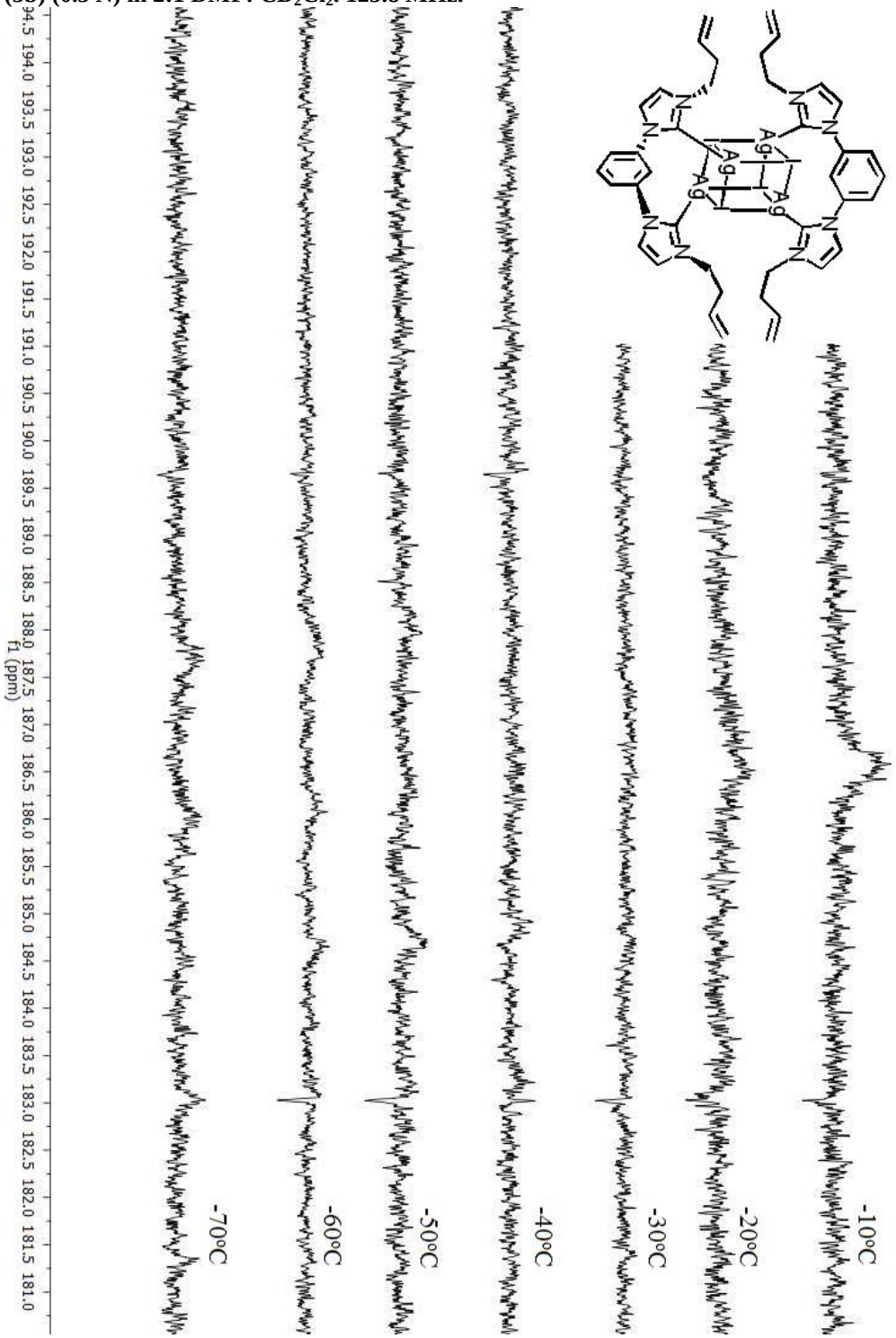


**Figure S 11**. **$^{1}$H NMR of Pentenyl-AgI complex** 3c **in $CD_2Cl_2$, 500 MHz.**

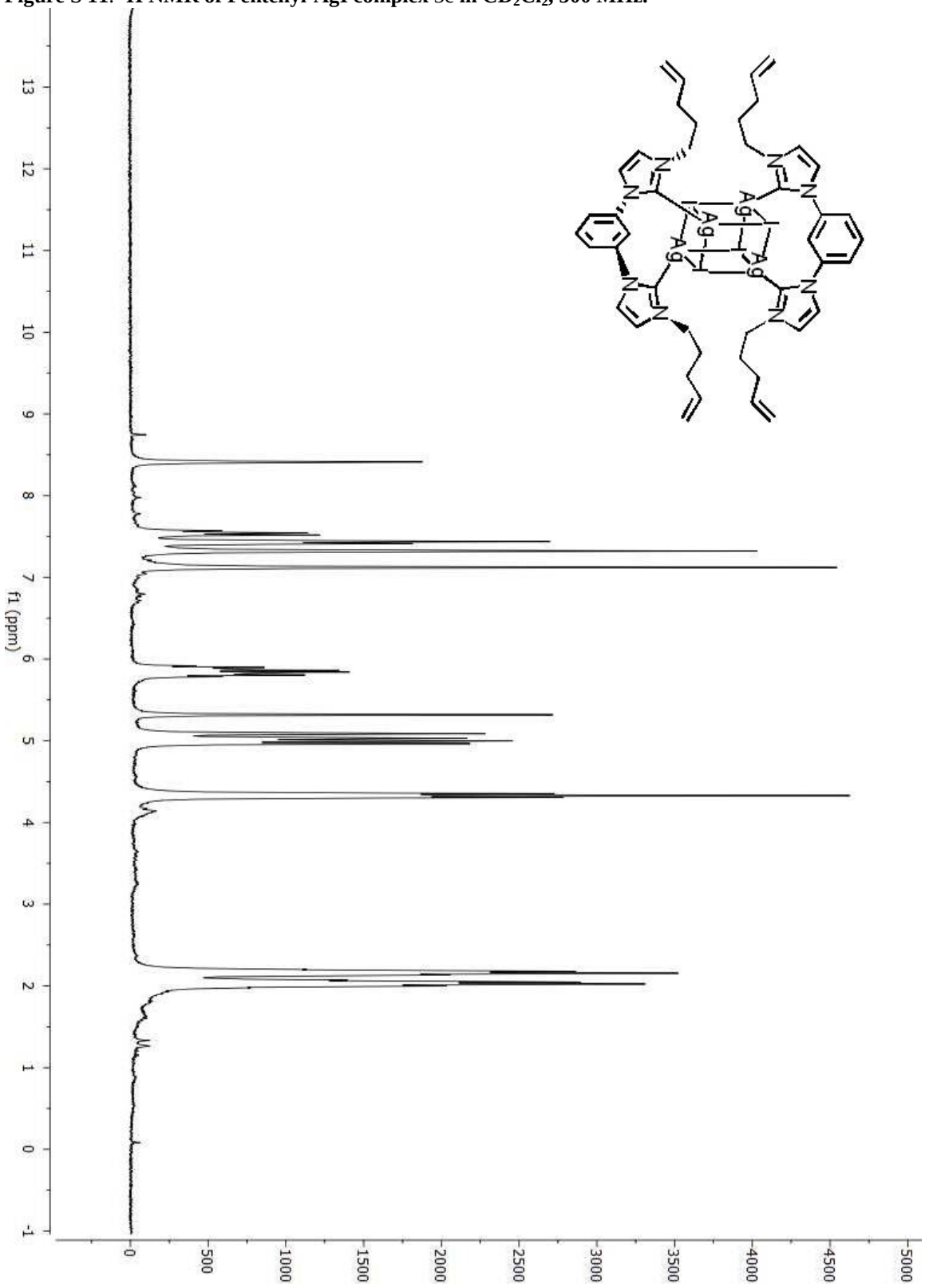


**Figure S 12. $^{13}C$ NMR of Pentenyl-AgI complex** 3c **in $CD_2Cl_2$, 125.8 MHz.**

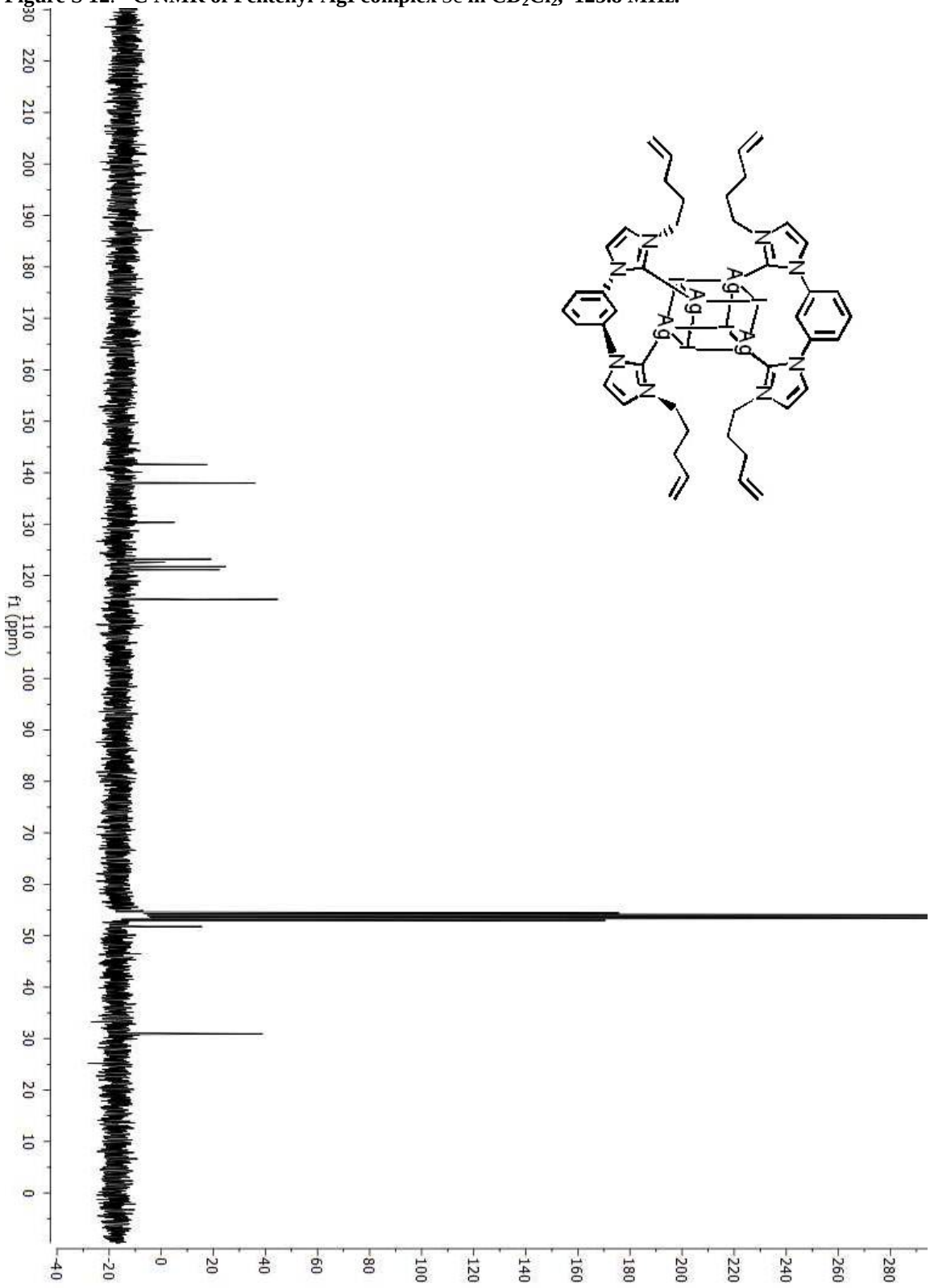


**Figure S 13. VT $^{13}C$ NMR of Penteyl-AgI complex 3c (0.5 N) in 2:1 DMF: $CD_2Cl_2$. 125.8 MHz.**

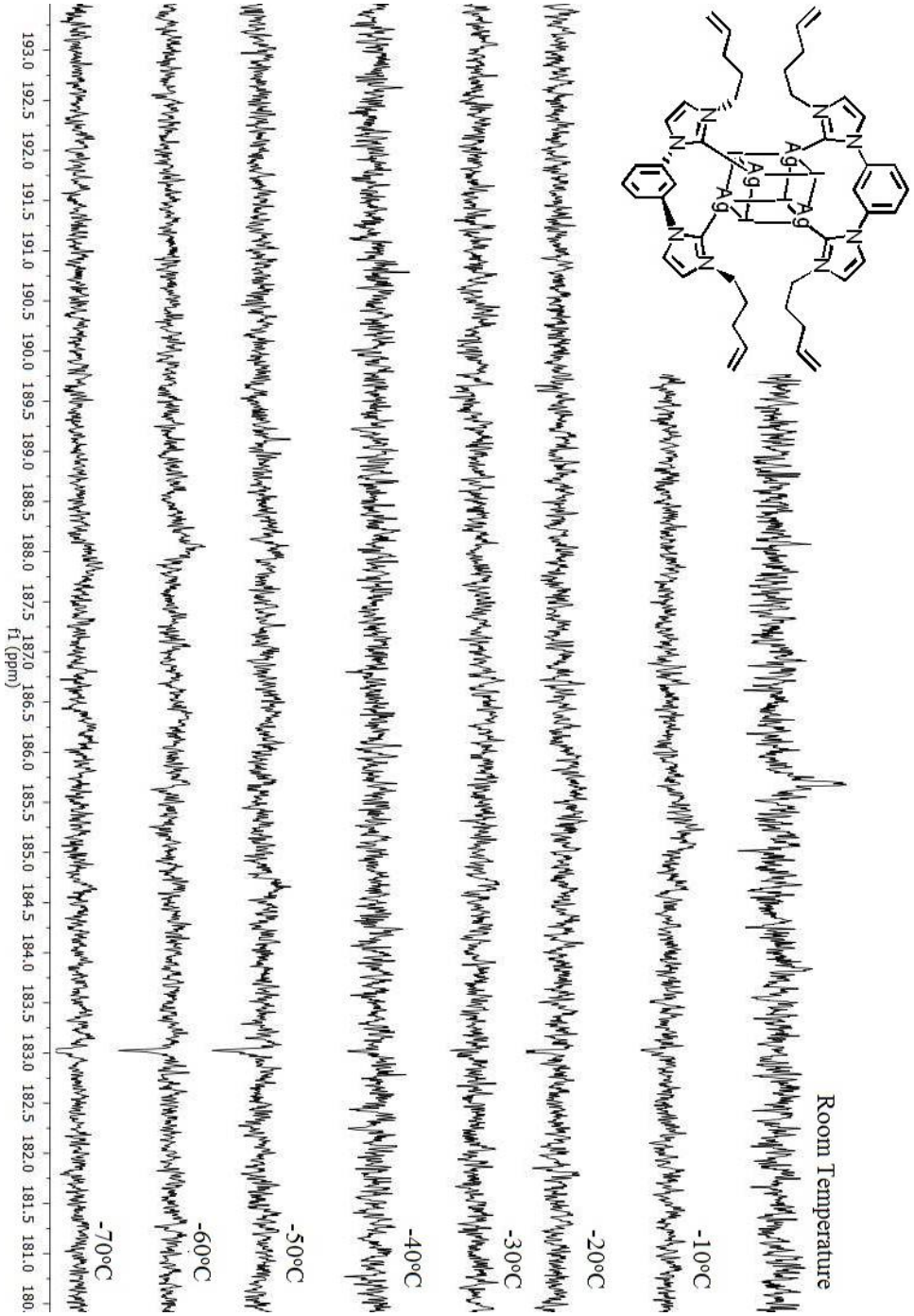


**Figure S 14**. **$^{1}$H NMR of Triazole-AgI complex** 3d **in DMF. 125.8 MHz.**

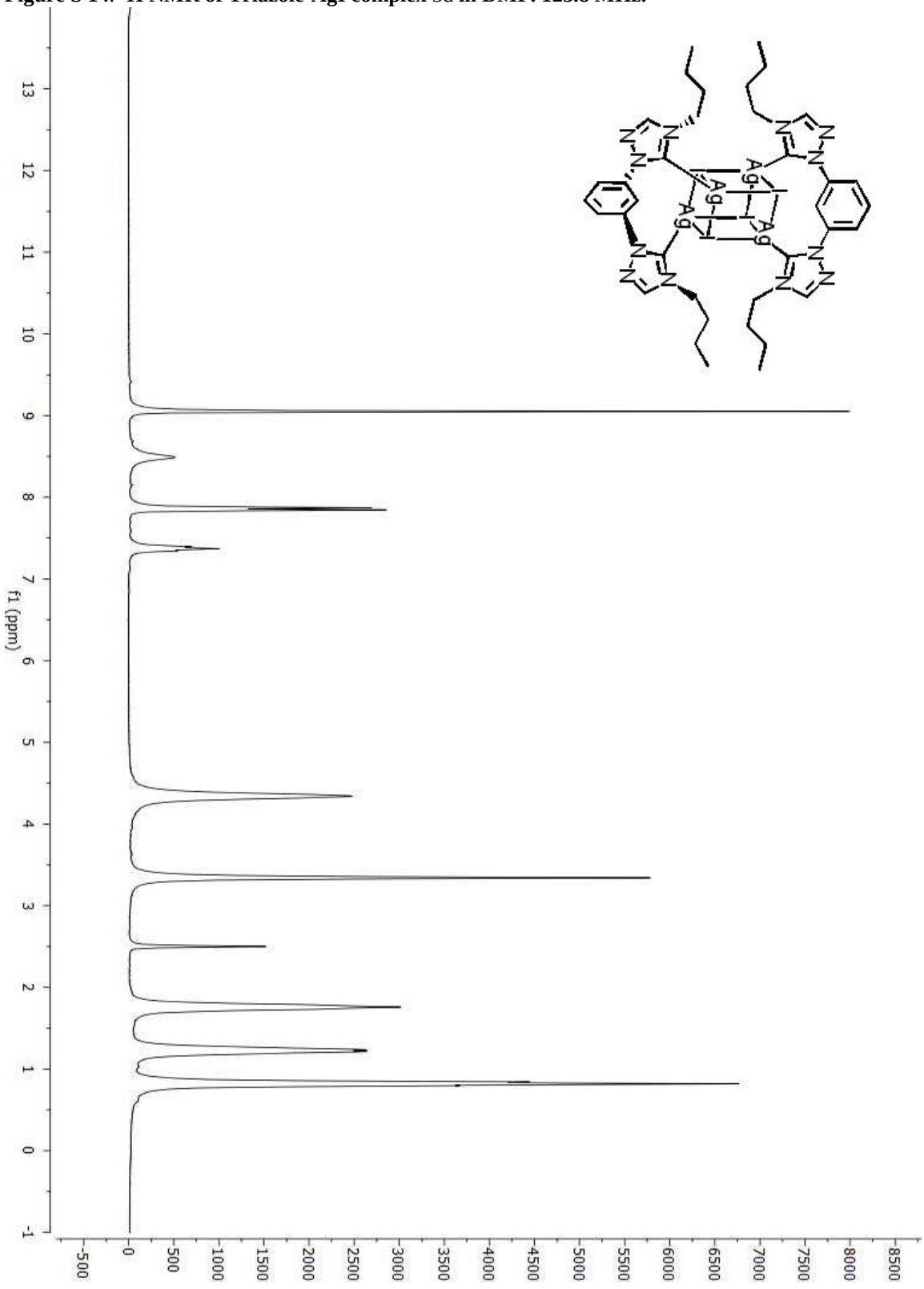


**Figure S 15. $^{13}$C NMR of Triazole-AgI complex** 3d **in DMF. 125.8 MHz.**

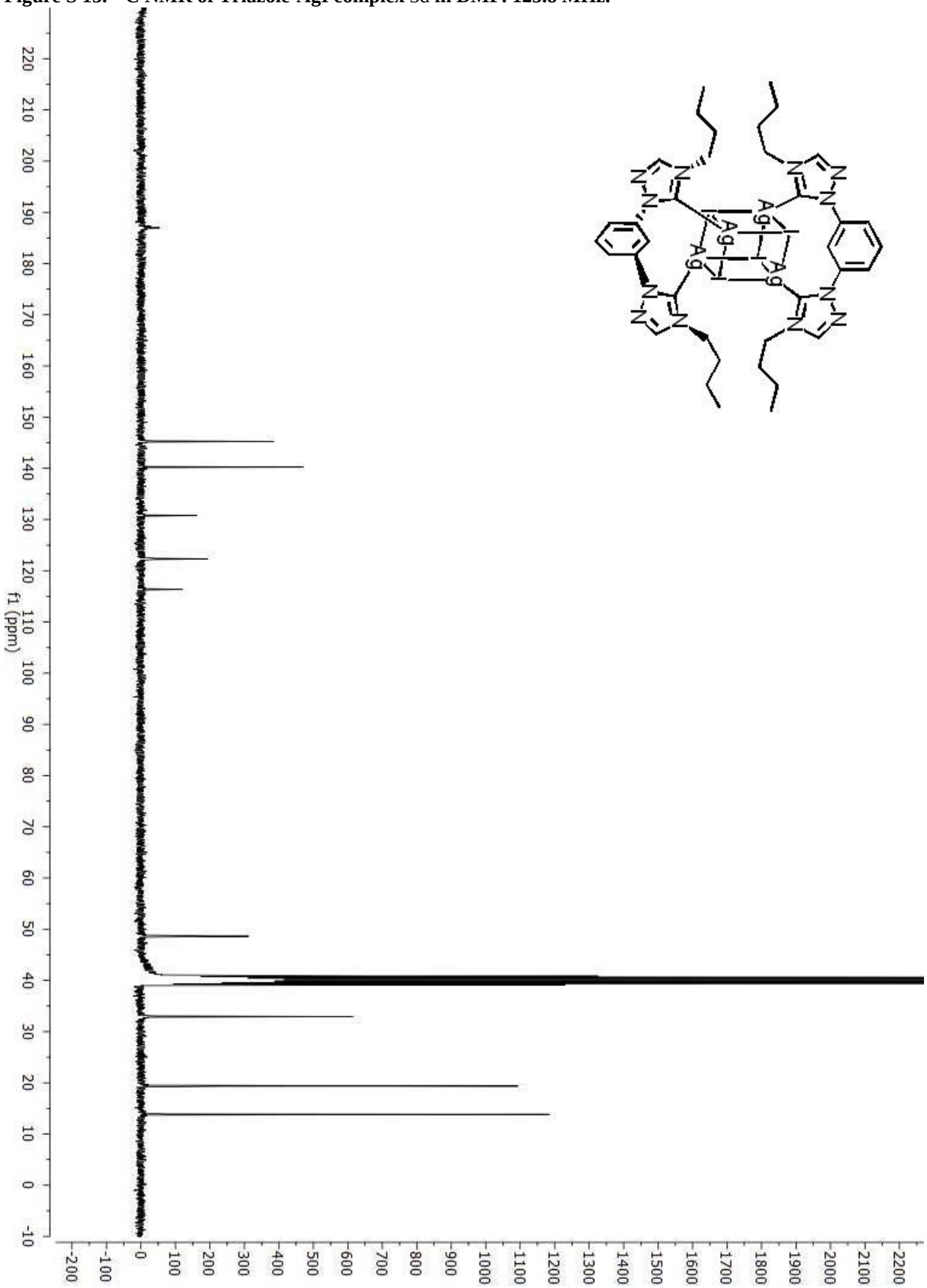


**Figure S 16. VT $^{13}$C NMR of Triazole-AgI complex** 3d **(0.02 N ) in DMF. 125.8 MHz.**

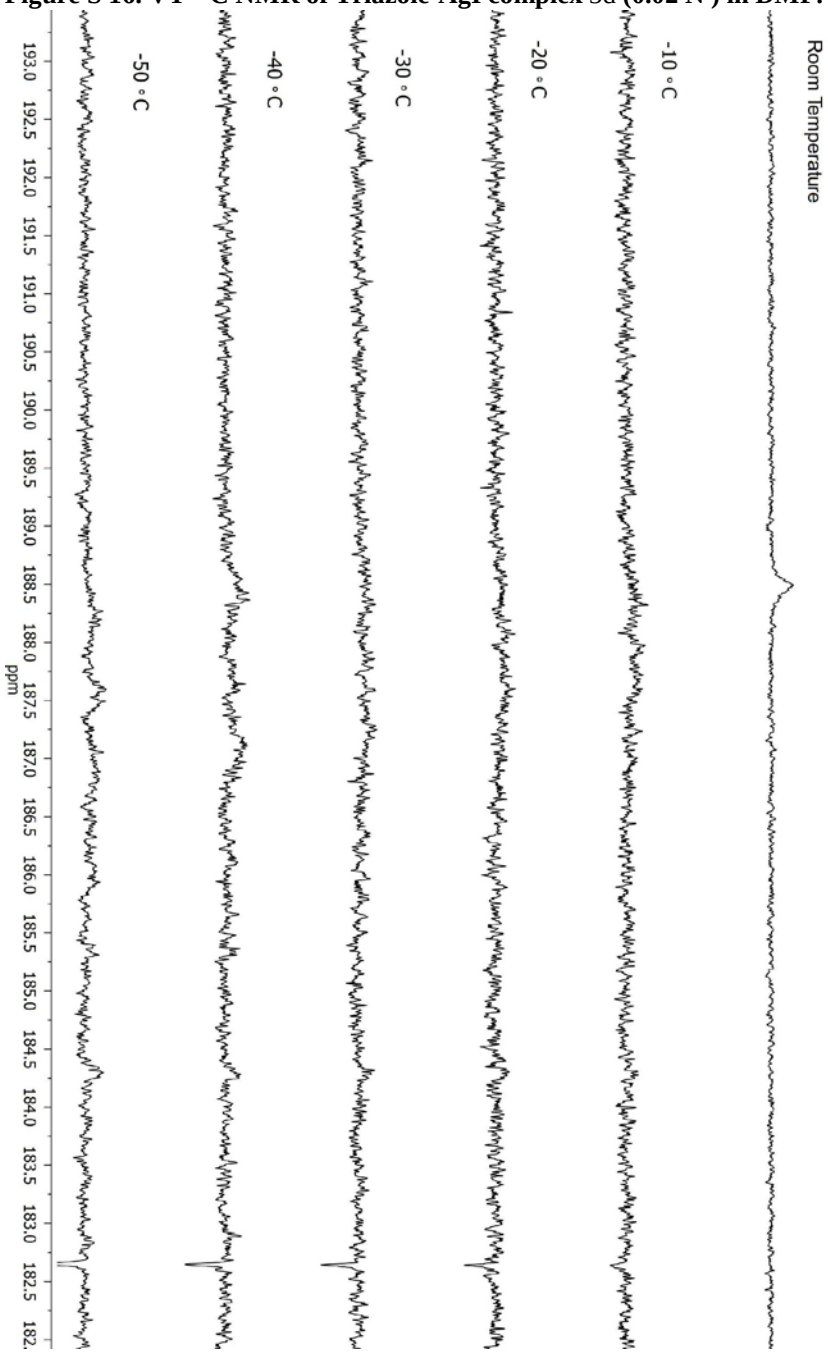


**Figure S 17. $^{1}$H NMR of Triazole-AgBr complex 3e in DMF. 125.8 MHz.**

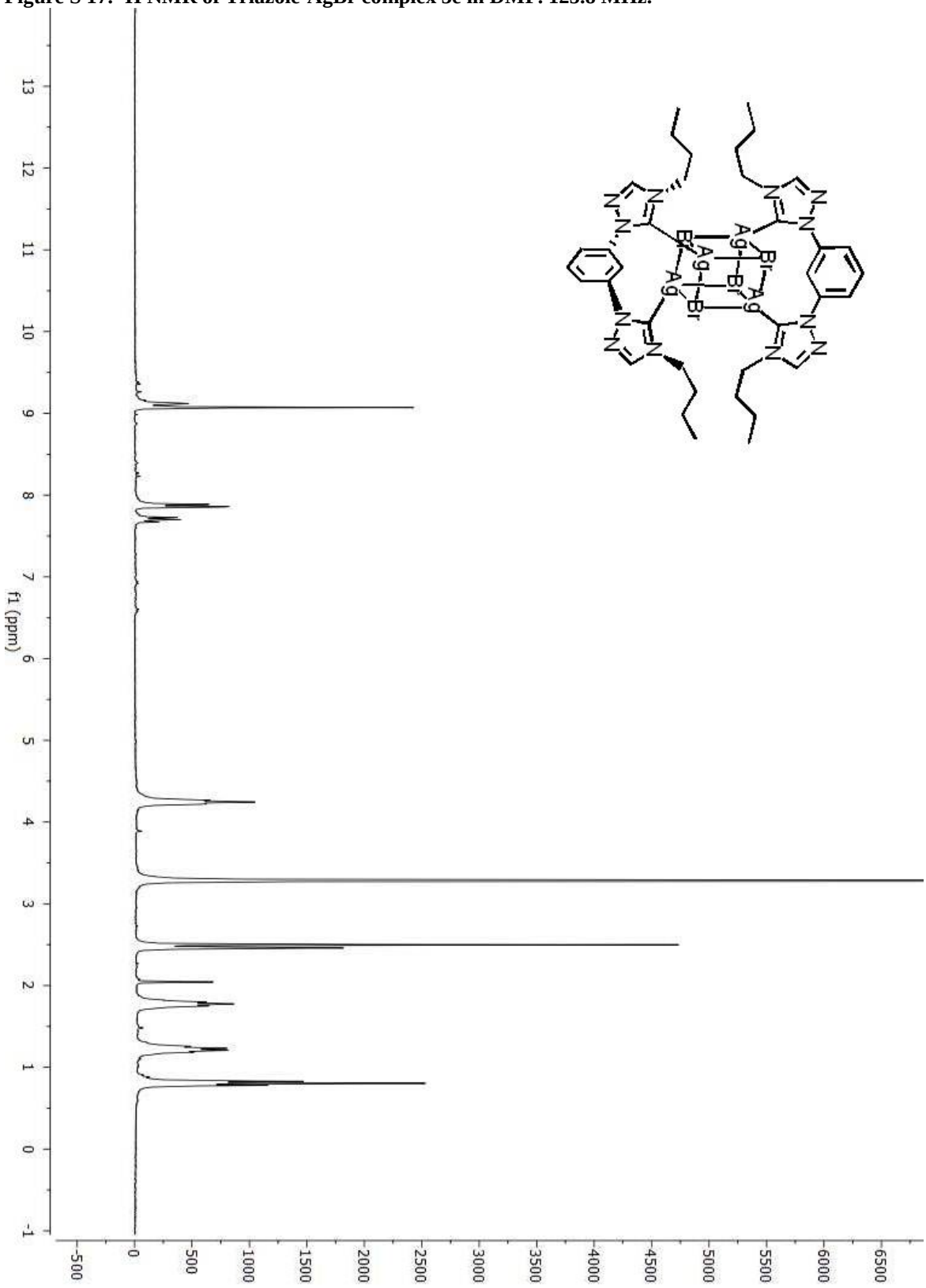


**Figure S 18. $^{13}$C NMR of Triazole-AgBr complex 3e in DMF. 125.8 MHz.**

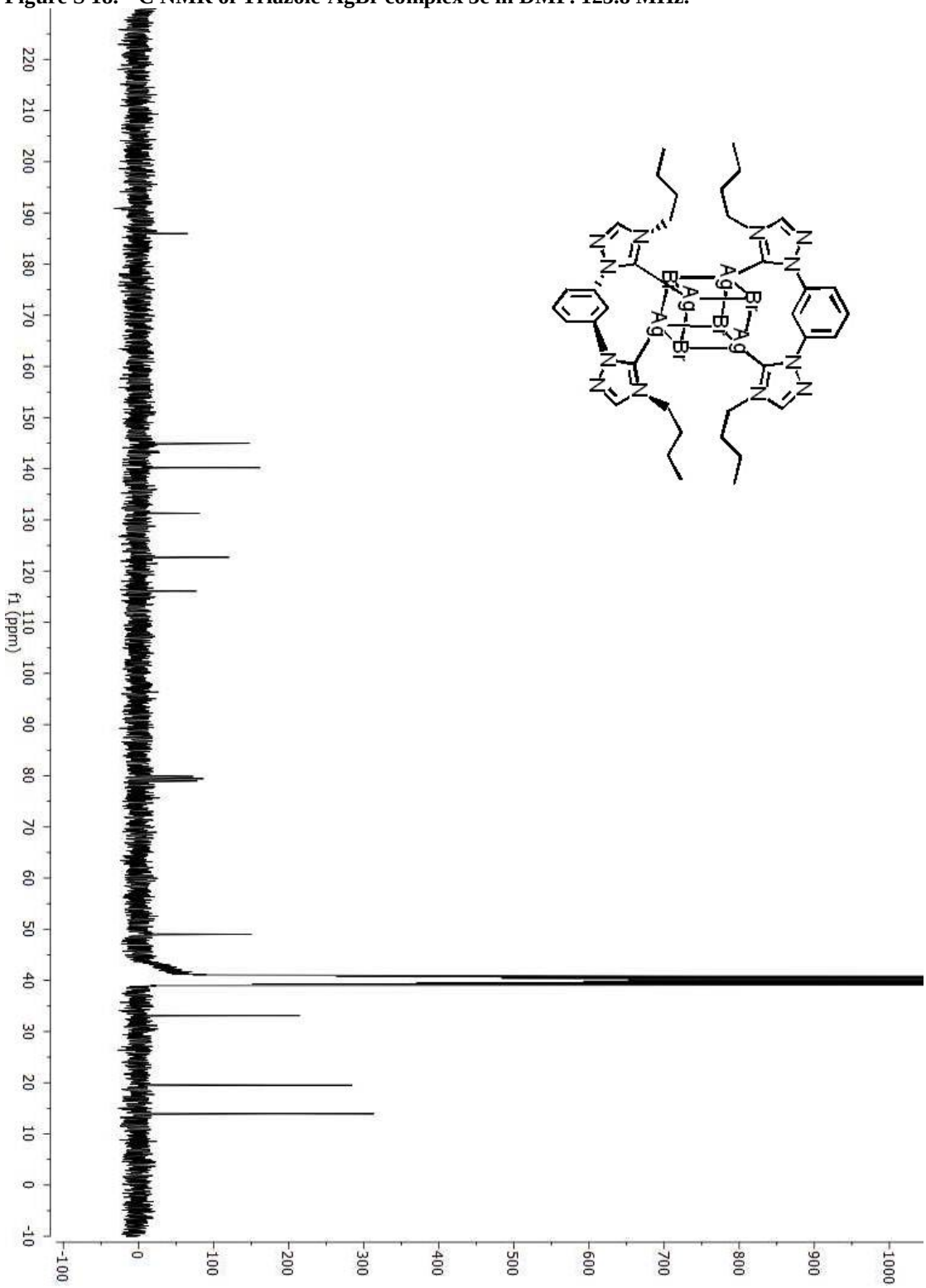


**Figure S 19. VT $^{13}$C NMR of Triazole-AgBr complex 3e (0.002 N) in DMF. 125.8 MHz.**

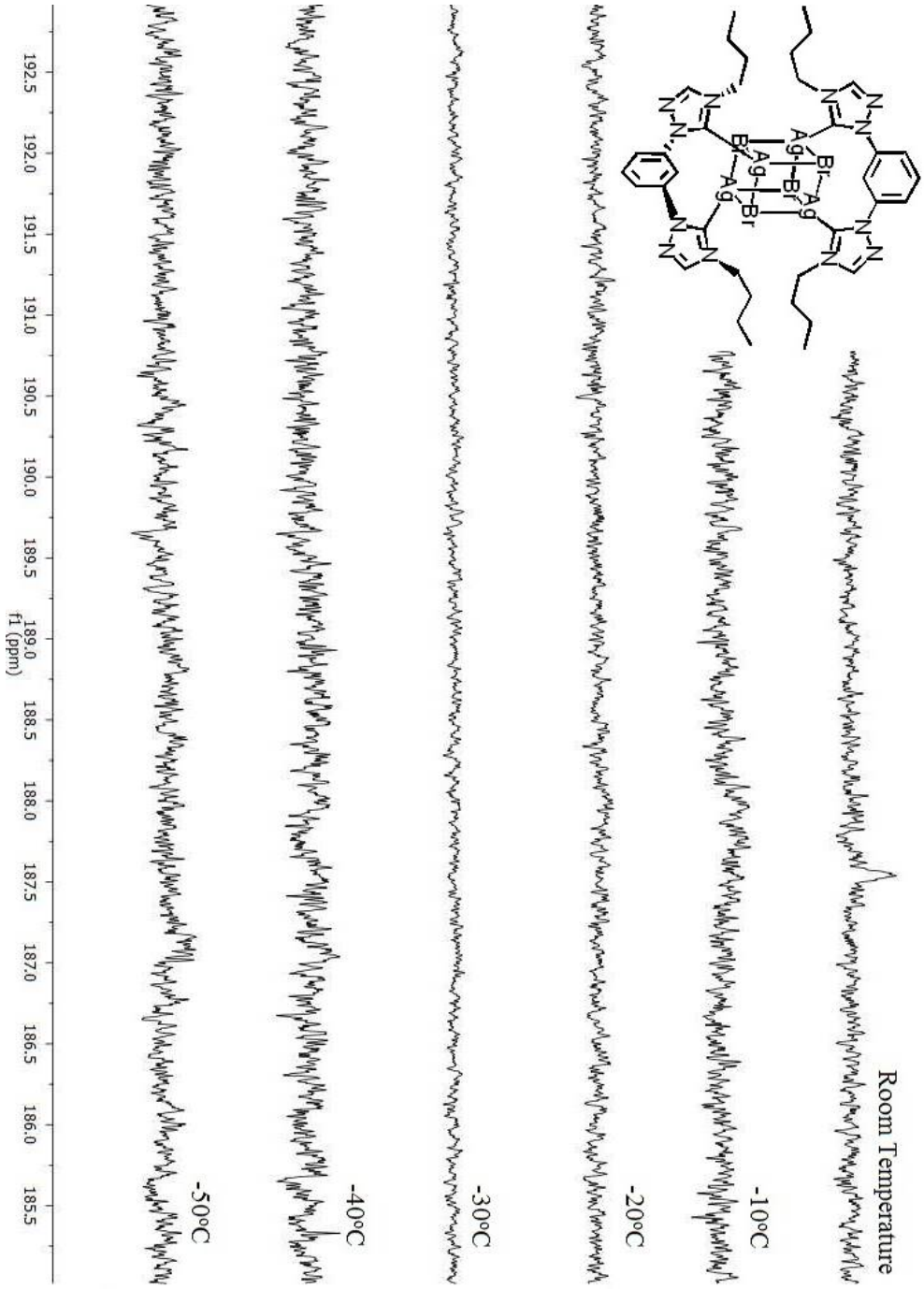


**Figure S 20**. $^{1}$H NMR of Cross-Over Experiments

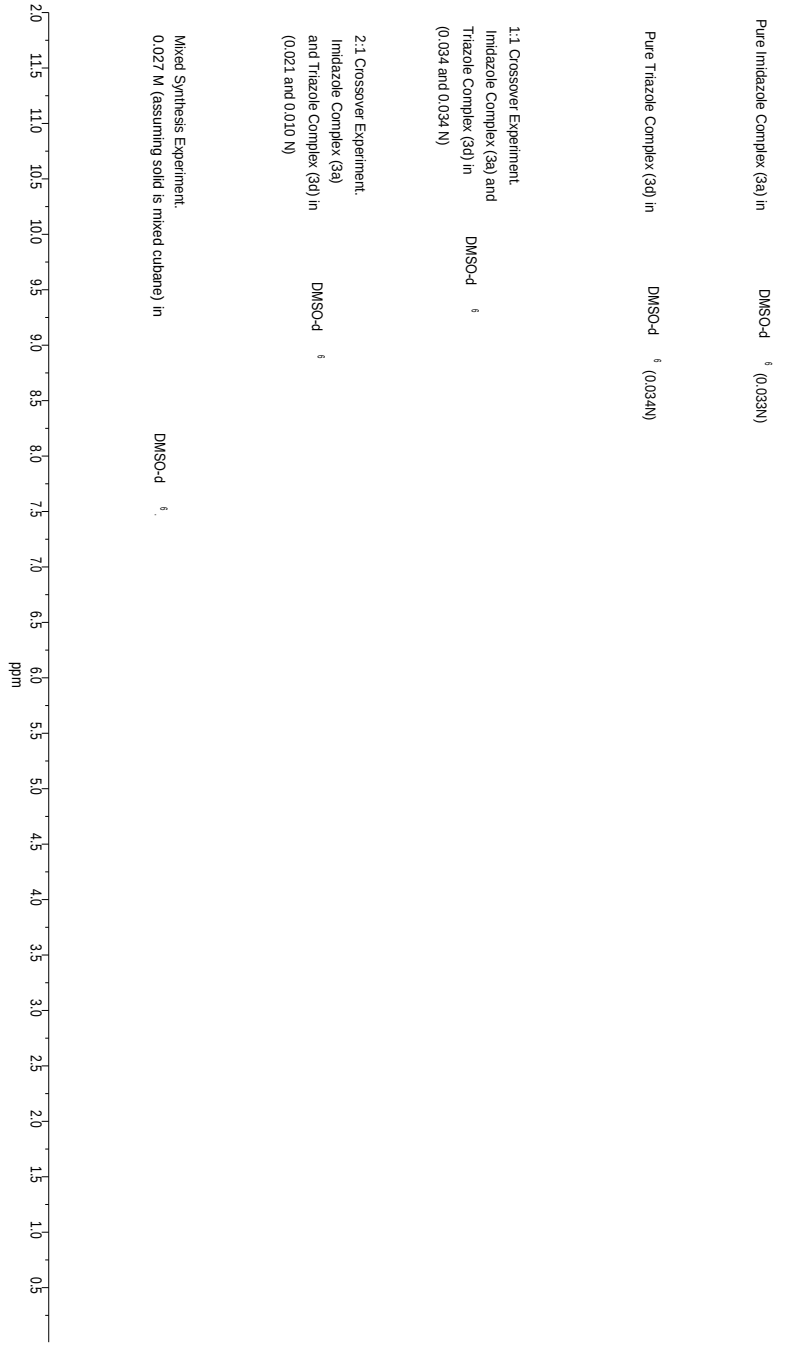


**Figure S 21**. $^{13}C$ NMR of Cross-Over Experiments.

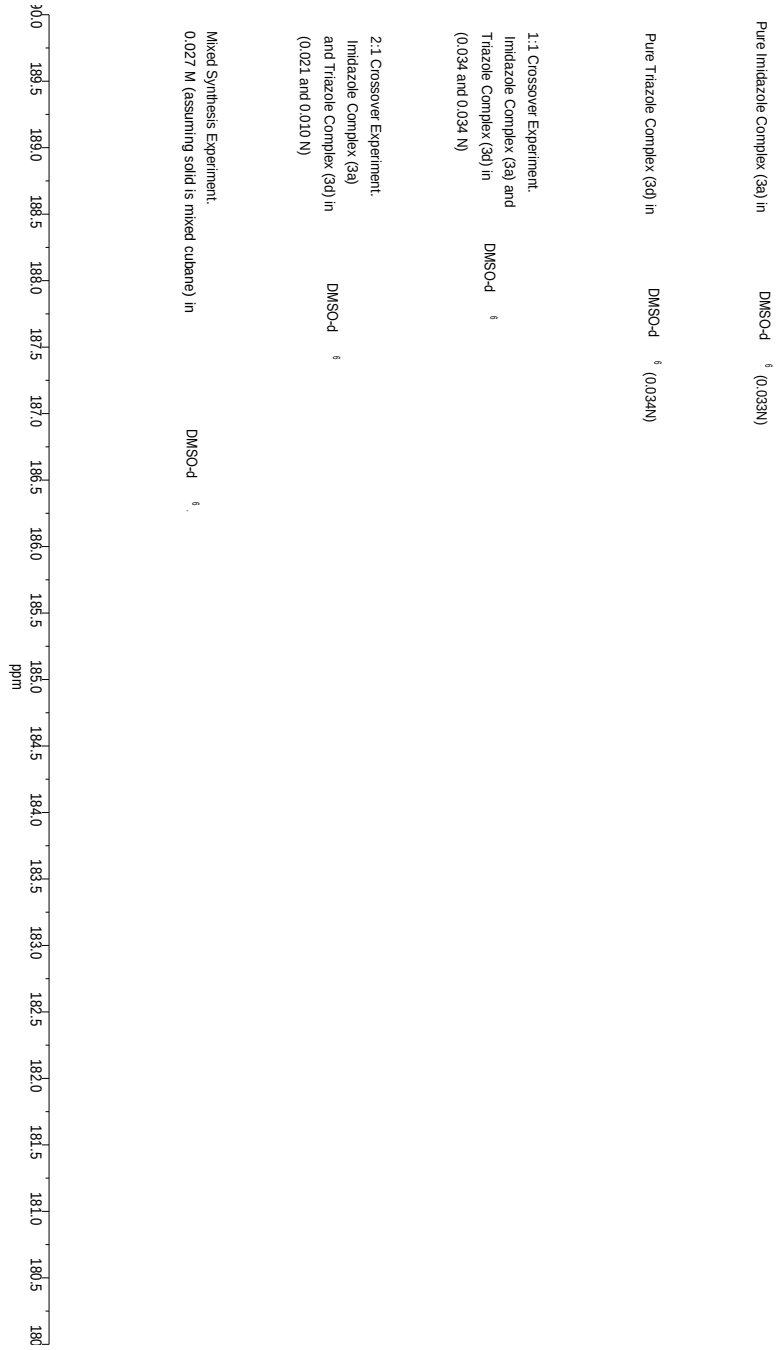


**Table S 33** Crossover Experiment Triazolyl $^{13}C_{carbene}$ Data

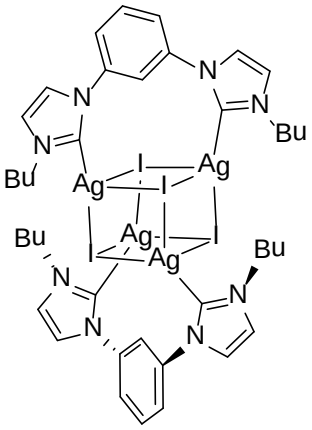
| | Triazolyl $^{13}C_{carbene}$ | $\Delta^a$ | [**3d**] |
|---|---|---|---|
| Pure **3d** | 186.15 | 0 | 0.034 |
| 1:1 (3a:3d) | 186.28 | 0.13 | 0.034 |
| 2:1 (3a:3d) | 186.29 | 0.14 | 0.010 |
| Mixed Synthesis | 186.29 | 0.14 | 0.027 |

[a] Difference between $^{13}C_{carbene}$ signal observed and for pure Triazole complex **3d** in DMSO-$d^6$.

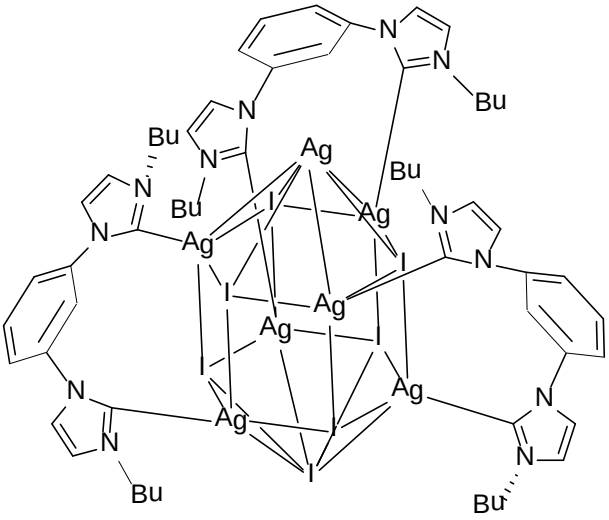
**Table S 34** Crossover Experiment Imidazolyl $^{13}C_{carbene}$ Data

| | Imidazolyl $^{13}C_{carbene}$ | $\Delta^a$ | [**3a**] |
|---|---|---|---|
| Pure **3a** | 181.91 | 0 | 0.033 |
| 1:1 (3a:3d) | 182.36 | 0.45 | 0.034 |
| 2:1 (3a:3d) | 182.20 | 0.29 | 0.021 |
| Mixed Synthesis | 182.28 | 0.37 | 0.027 |

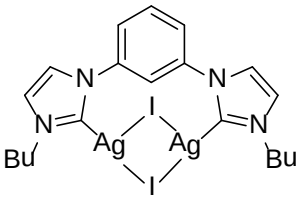
[a] Difference between $^{13}C_{carbene}$ signal observed and for pure imidazol complex **3a** in DMSO-$d^6$.



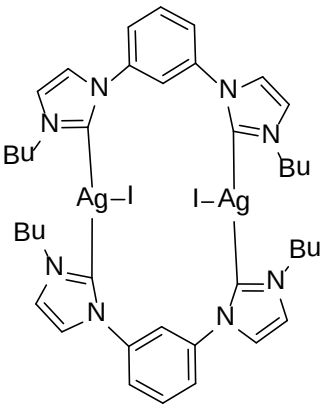
**3**



**6**



**4**



**5**

**Figure S 22**

**Figure S 23. ESI-TOF MS spectrum of a solution of Complex 3.**

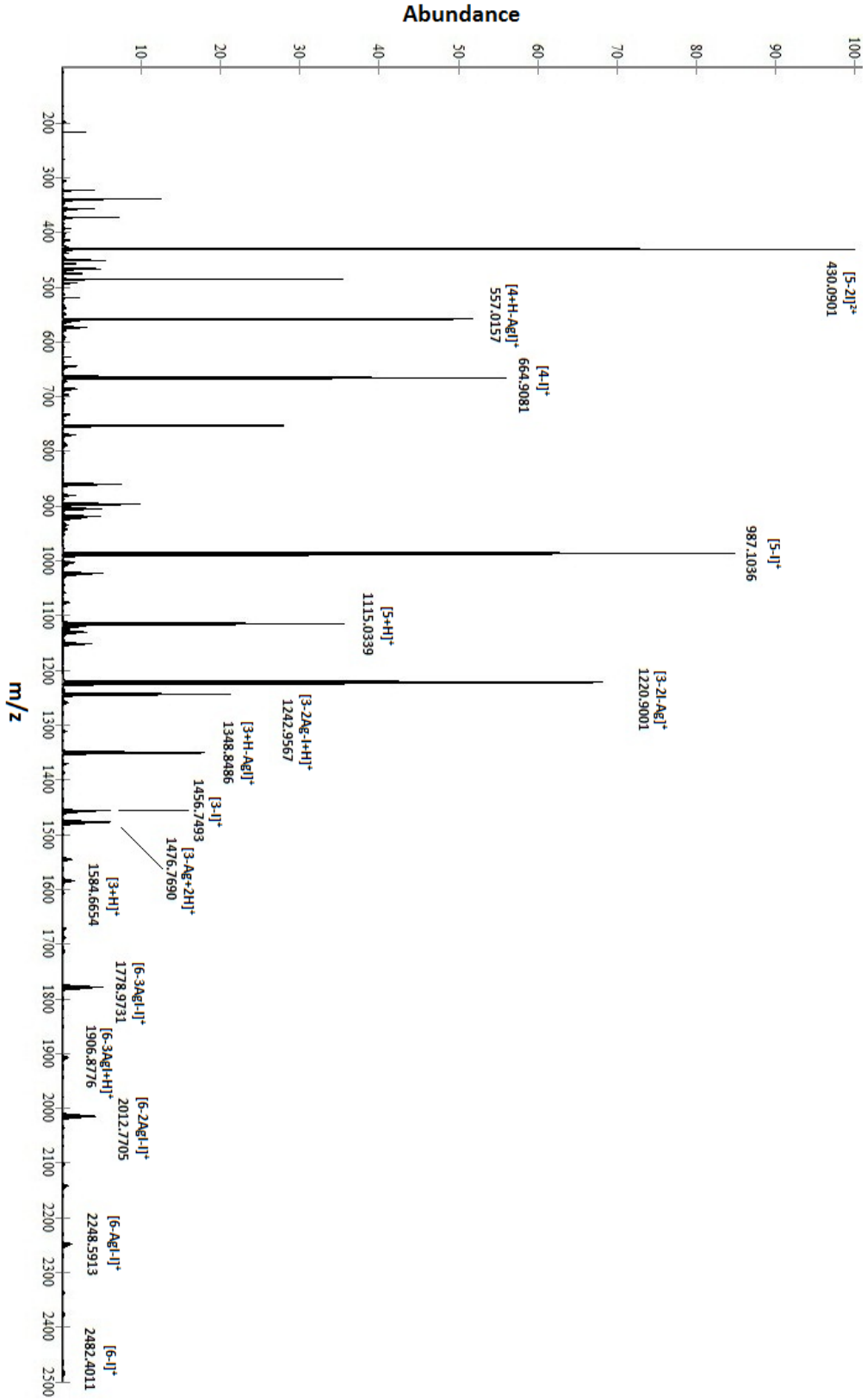


**Figure S 24**

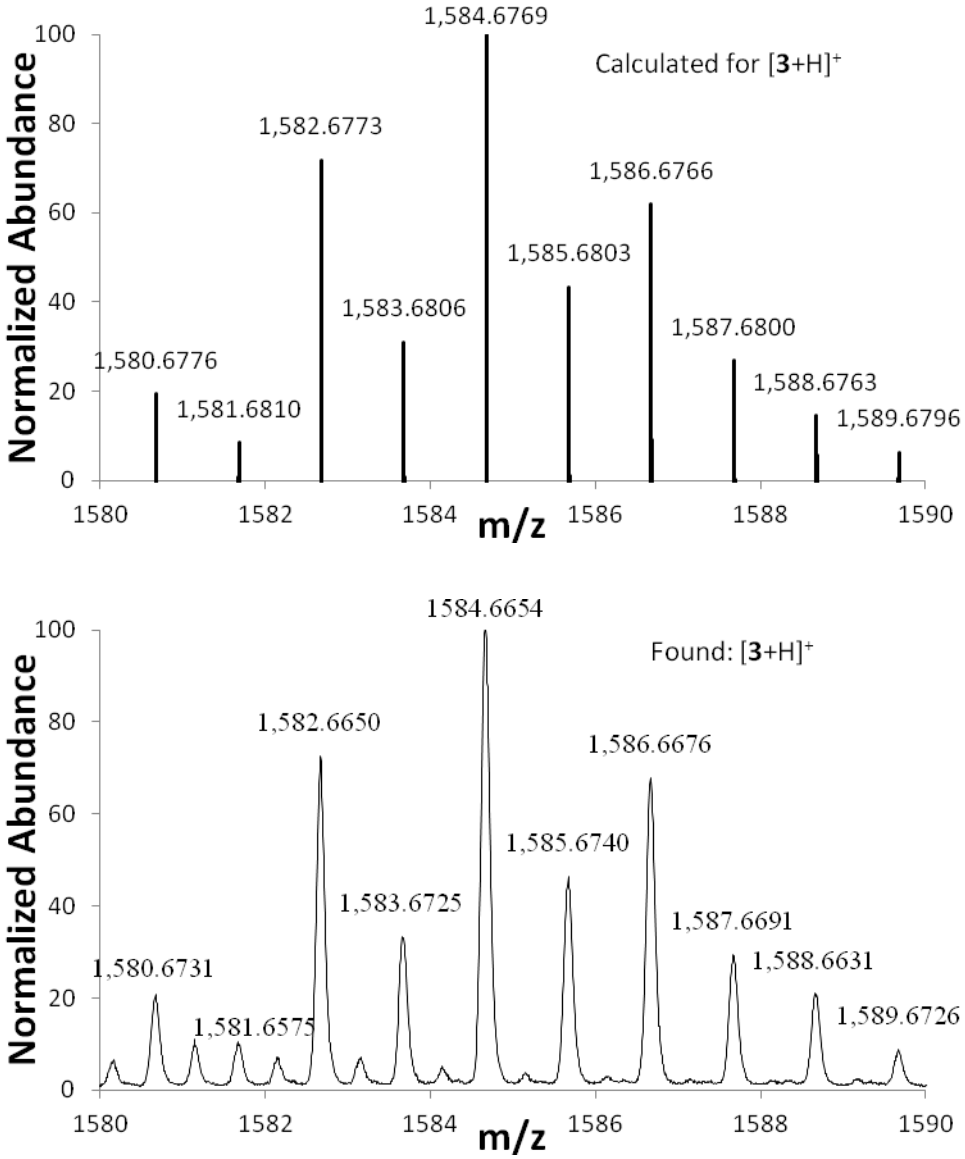
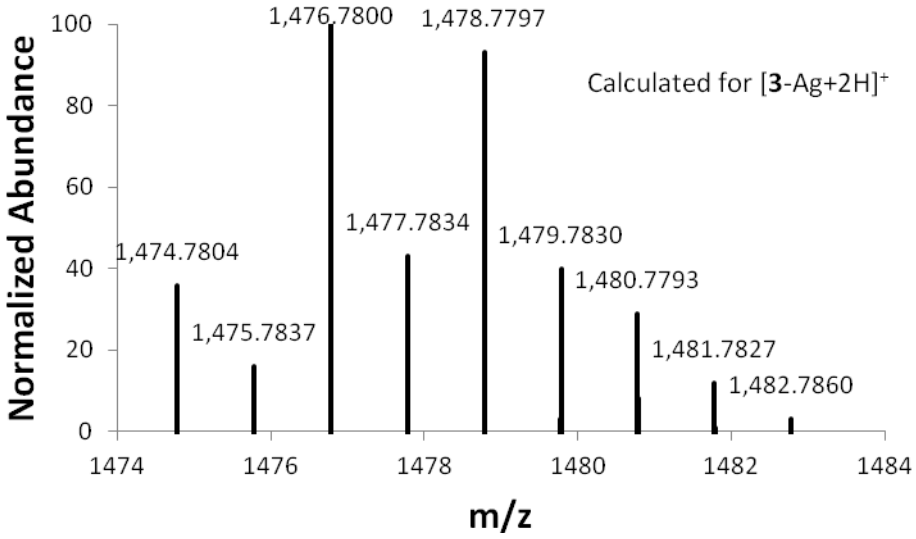

Calculated for [3+H]+
1,584.6769
1,582.6773
1,586.6766
1,585.6803
1,583.6806
1,587.6800
1,580.6776
1,588.6763
1,581.6810
1,589.6796
Normalized Abundance
m/z
Found: [3+H]+
1584.6654
1,582.6650
1,586.6676
1,585.6740
1,583.6725
1,587.6691
1,588.6631
1,580.6731
1,589.6726
1,581.6575
Normalized Abundance
m/z

**Figure S 25**


Normalized Abundance
100
80
60
40
20
0
1,476.7800
1,478.7797
Calculated for [3-Ag+2H]+
1,477.7834
1,479.7830
1,474.7804
1,480.7793
1,475.7837
1,481.7827
1,482.7860
1474
1476
1478
1480
1482
1484
m/z

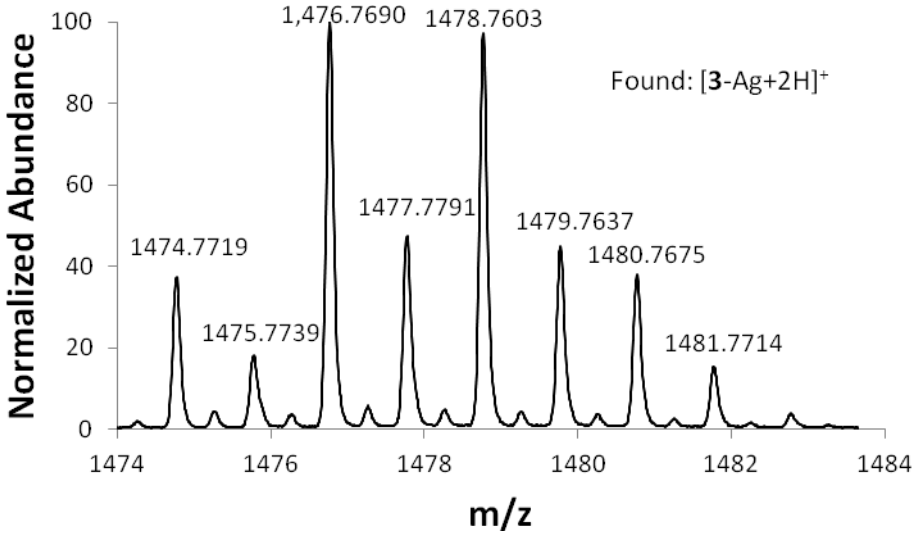
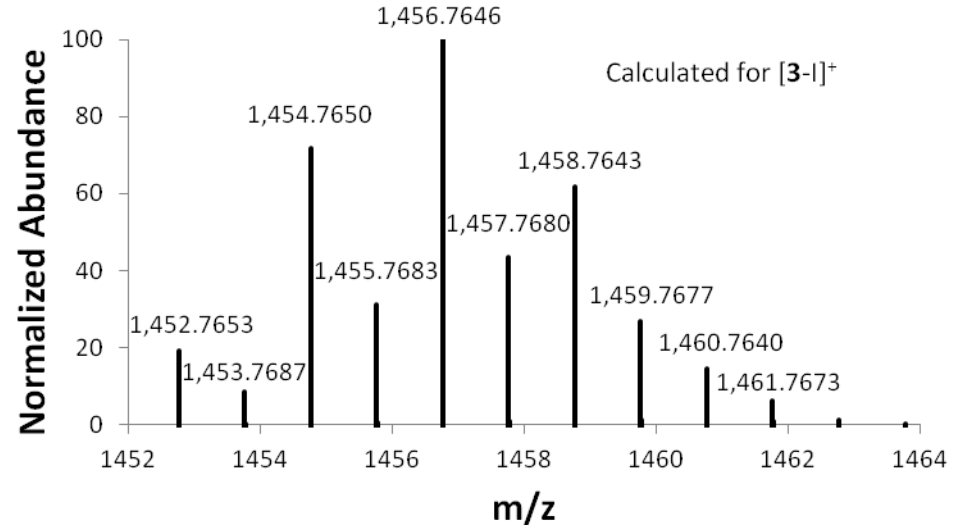

Normalized Abundance
100
80
60
40
20
0
1,476.7690
1478.7603
Found: [3-Ag+2H]+
1477.7791
1479.7637
1474.7719
1480.7675
1475.7739
1481.7714
1474
1476
1478
1480
1482
1484
m/z

**Figure S 26**


Calculated for [3-I]+
Normalized Abundance
m/z
1,456.7646
1,454.7650
1,458.7643
1,457.7680
1,455.7683
1,459.7677
1,452.7653
1,460.7640
1,453.7687
1,461.7673
100
80
60
40
20
0
1452
1454
1456
1458
1460
1462
1464

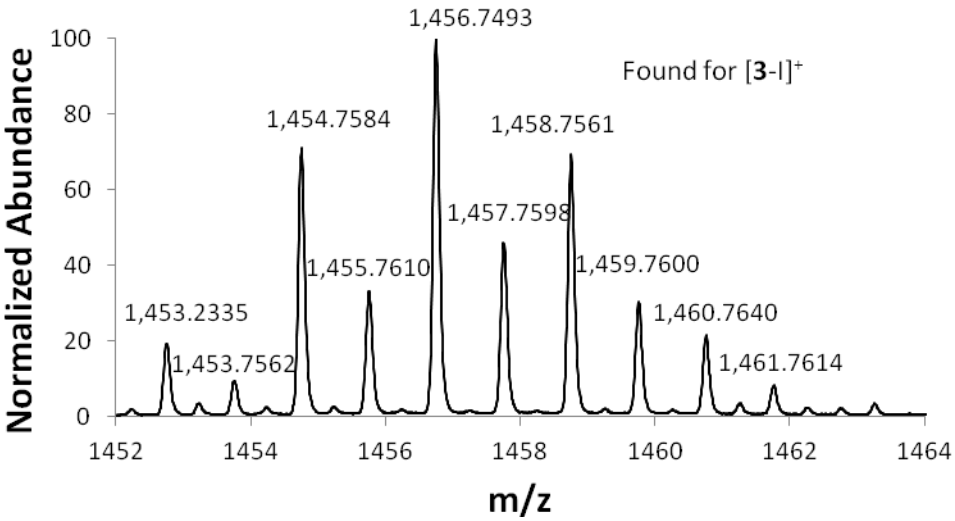
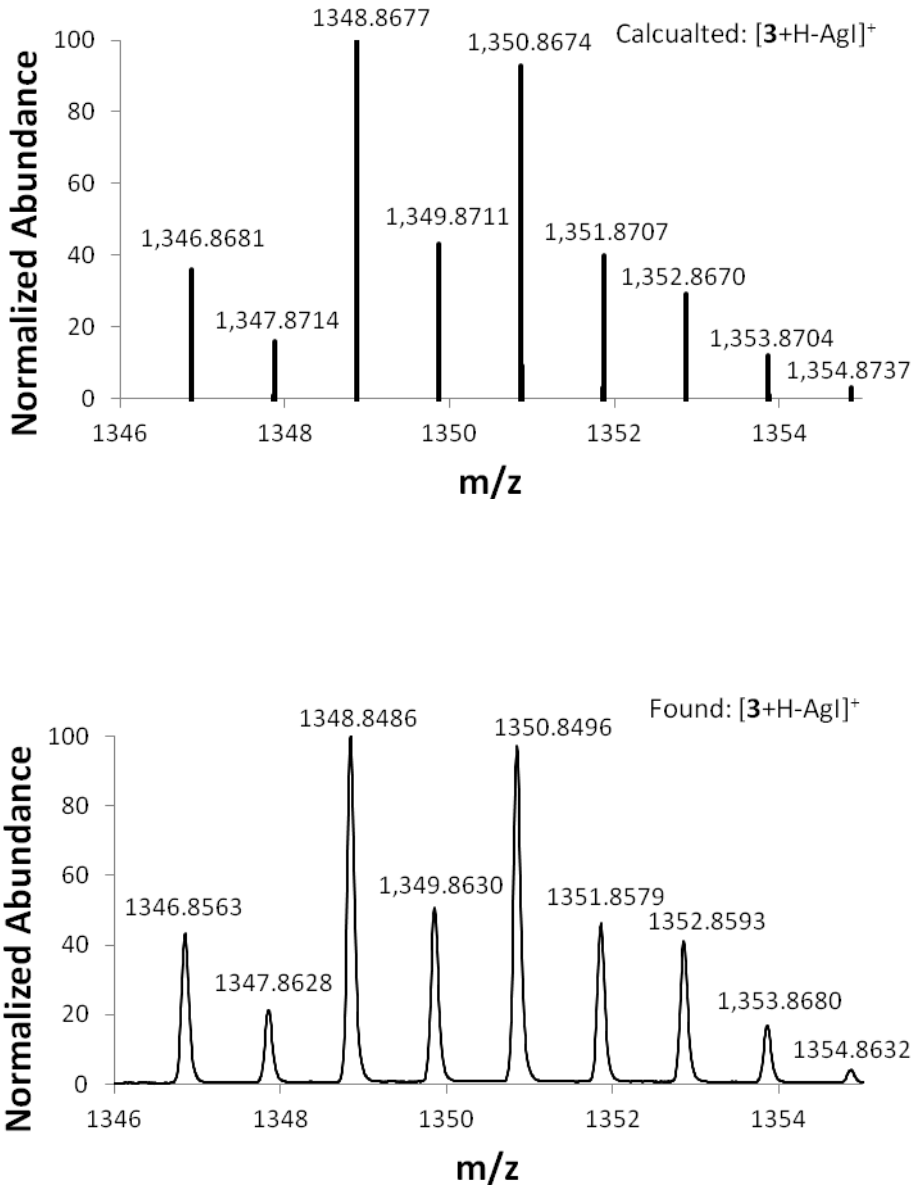
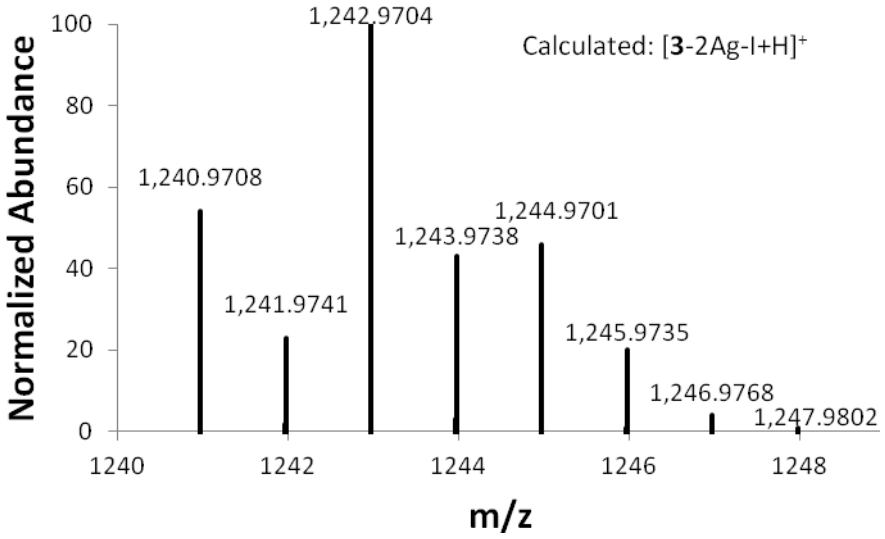

Found for [3-I]+
Normalized Abundance
m/z
1,456.7493
1,454.7584
1,458.7561
1,457.7598
1,455.7610
1,459.7600
1,453.2335
1,460.7640
1,453.7562
1,461.7614
100
80
60
40
20
0
1452
1454
1456
1458
1460
1462
1464

**Figure S 27**


Calcualted: [3+H-AgI]+
1348.8677
1,350.8674
1,349.8711
1,351.8707
1,352.8670
1,353.8704
1,354.8737
1,346.8681
1,347.8714
Normalized Abundance
m/z
Found: [3+H-AgI]+
1348.8486
1350.8496
1,349.8630
1351.8579
1352.8593
1,353.8680
1354.8632
1346.8563
1347.8628
Normalized Abundance
m/z


Calculated: [3-2Ag-I+H]+
1,242.9704
1,240.9708
1,241.9741
1,243.9738
1,244.9701
1,245.9735
1,246.9768
1,247.9802
Normalized Abundance
m/z

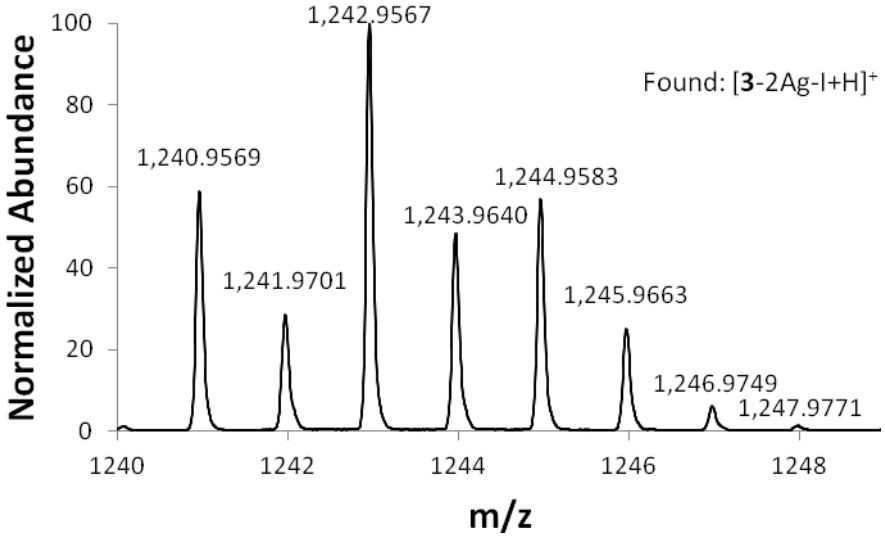

Found: [3-2Ag-I+H]+
1,242.9567
1,240.9569
1,241.9701
1,243.9640
1,244.9583
1,245.9663
1,246.9749
1,247.9771
Normalized Abundance
m/z

**Figure S 28**

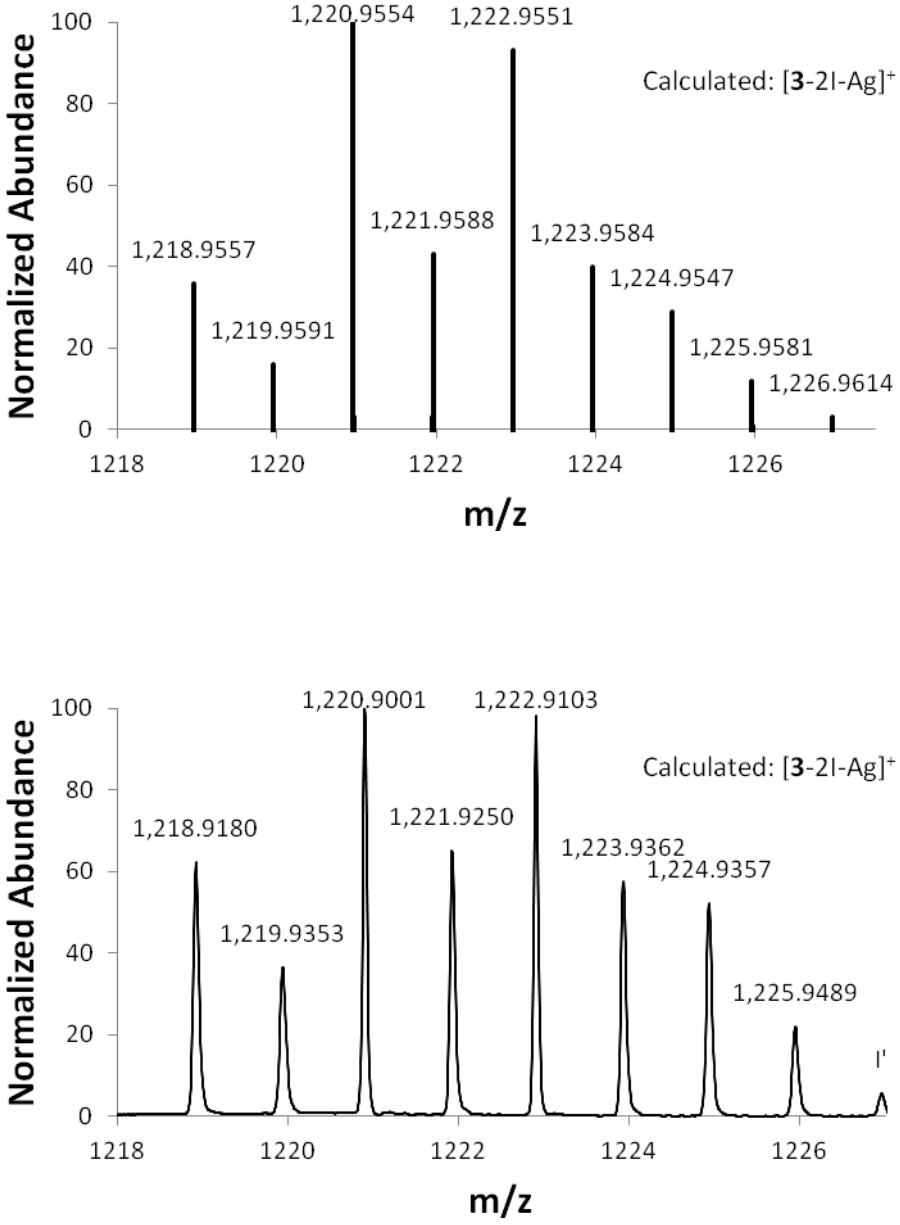

Normalized Abundance
m/z
Calculated: [3-2I-Ag]+
1,218.9557
1,219.9591
1,220.9554
1,221.9588
1,222.9551
1,223.9584
1,224.9547
1,225.9581
1,226.9614
1,218.9180
1,219.9353
1,220.9001
1,221.9250
1,222.9103
1,223.9362
1,224.9357
1,225.9489

**Figure S 29**

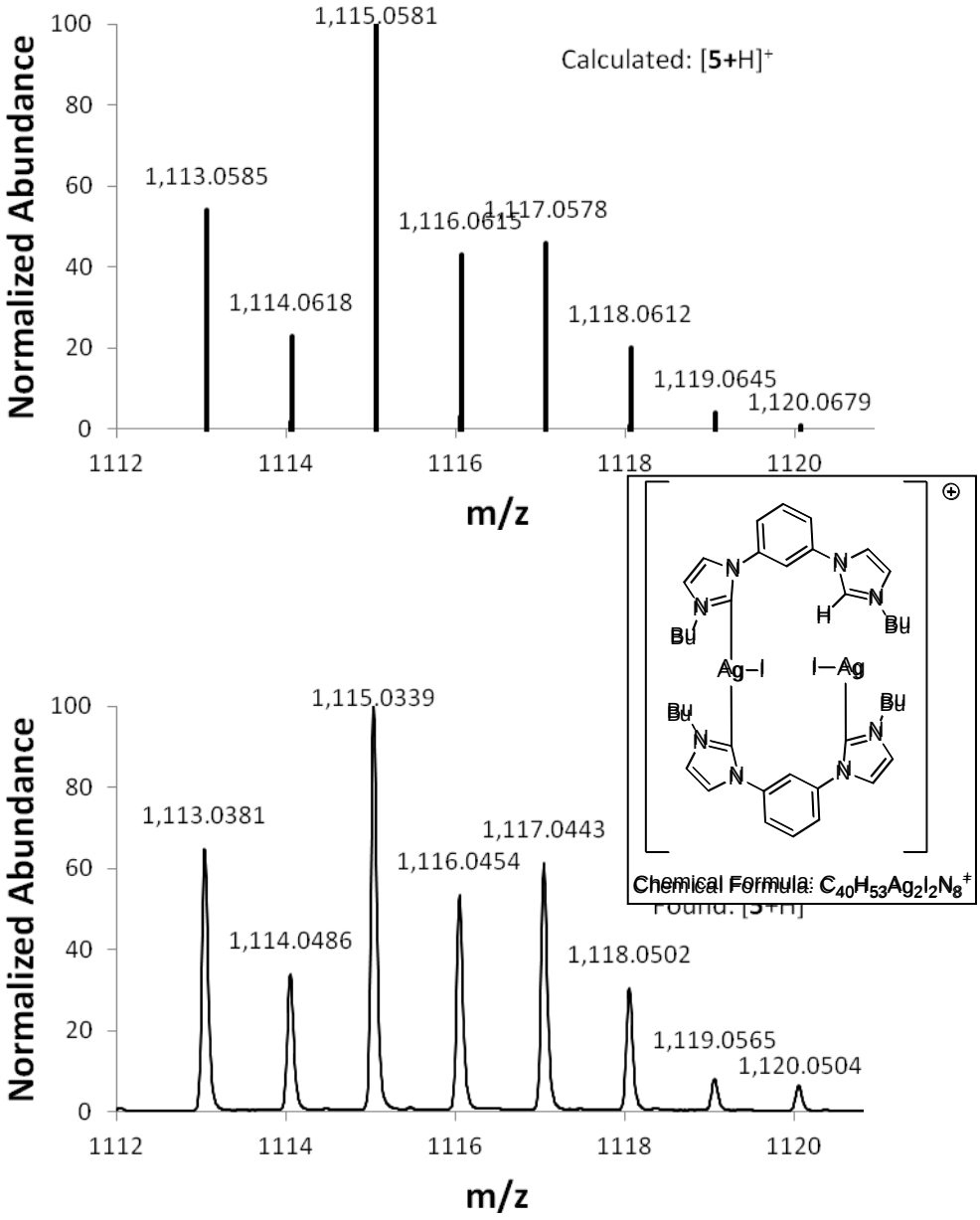

Calculated: [5+H]+
1,115.0581
1,113.0585
1,114.0618
1,116.0615
1,117.0578
1,118.0612
1,119.0645
1,120.0679
Normalized Abundance
m/z
Found: [5+H]+
1,115.0339
1,113.0381
1,114.0486
1,116.0454
1,117.0443
1,118.0502
1,119.0565
1,120.0504
Chemical Formula: C40H53Ag2I2N8+

**Figure S 30**

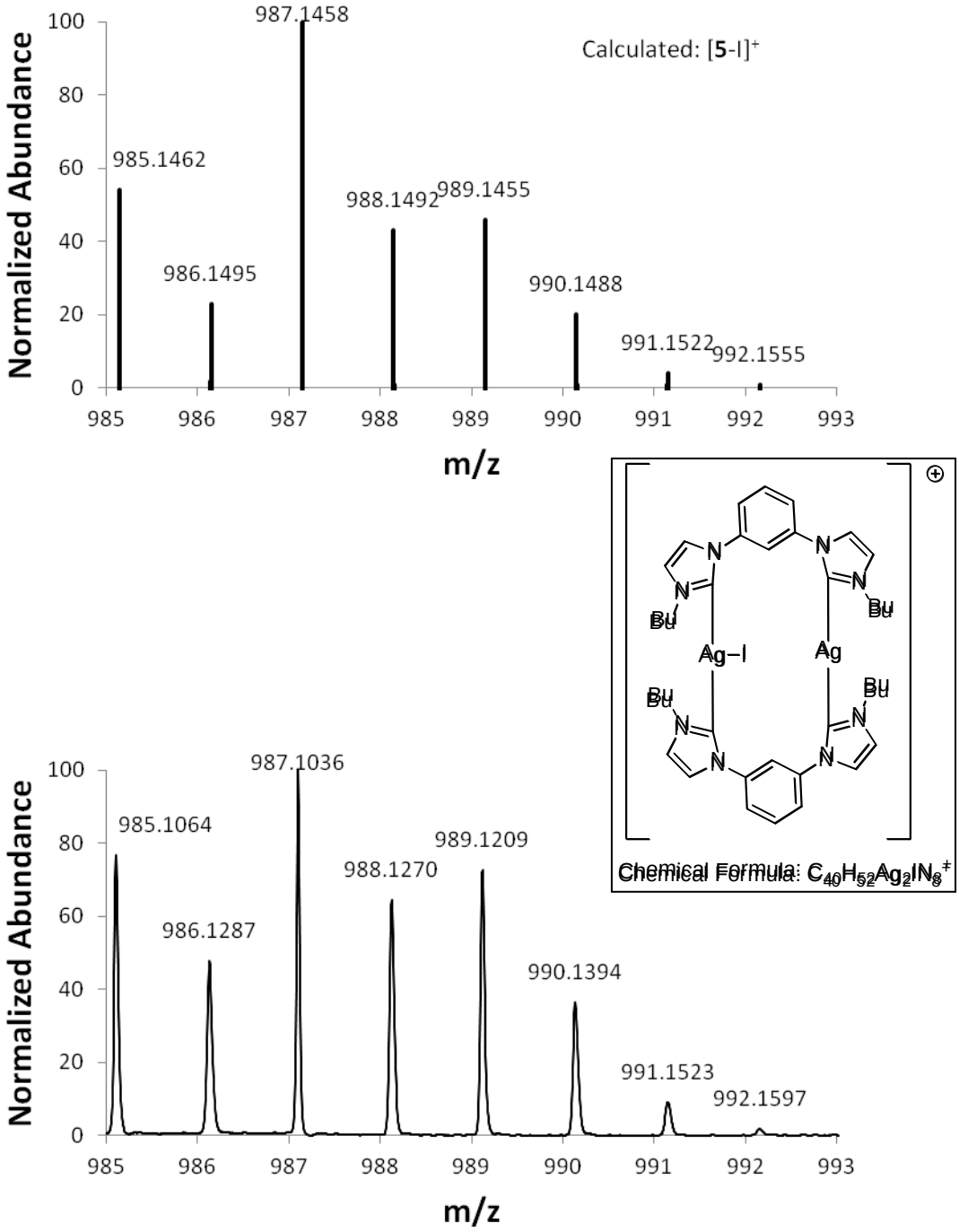

Calculated: [5-I]+
987.1458
985.1462
986.1495
988.1492
989.1455
990.1488
991.1522
992.1555
Normalized Abundance
m/z
Ag–I
Ag
Chemical Formula: C40H52Ag2IN8+
987.1036
985.1064
986.1287
988.1270
989.1209
990.1394
991.1523
992.1597
Normalized Abundance
m/z

**Figure S 31**

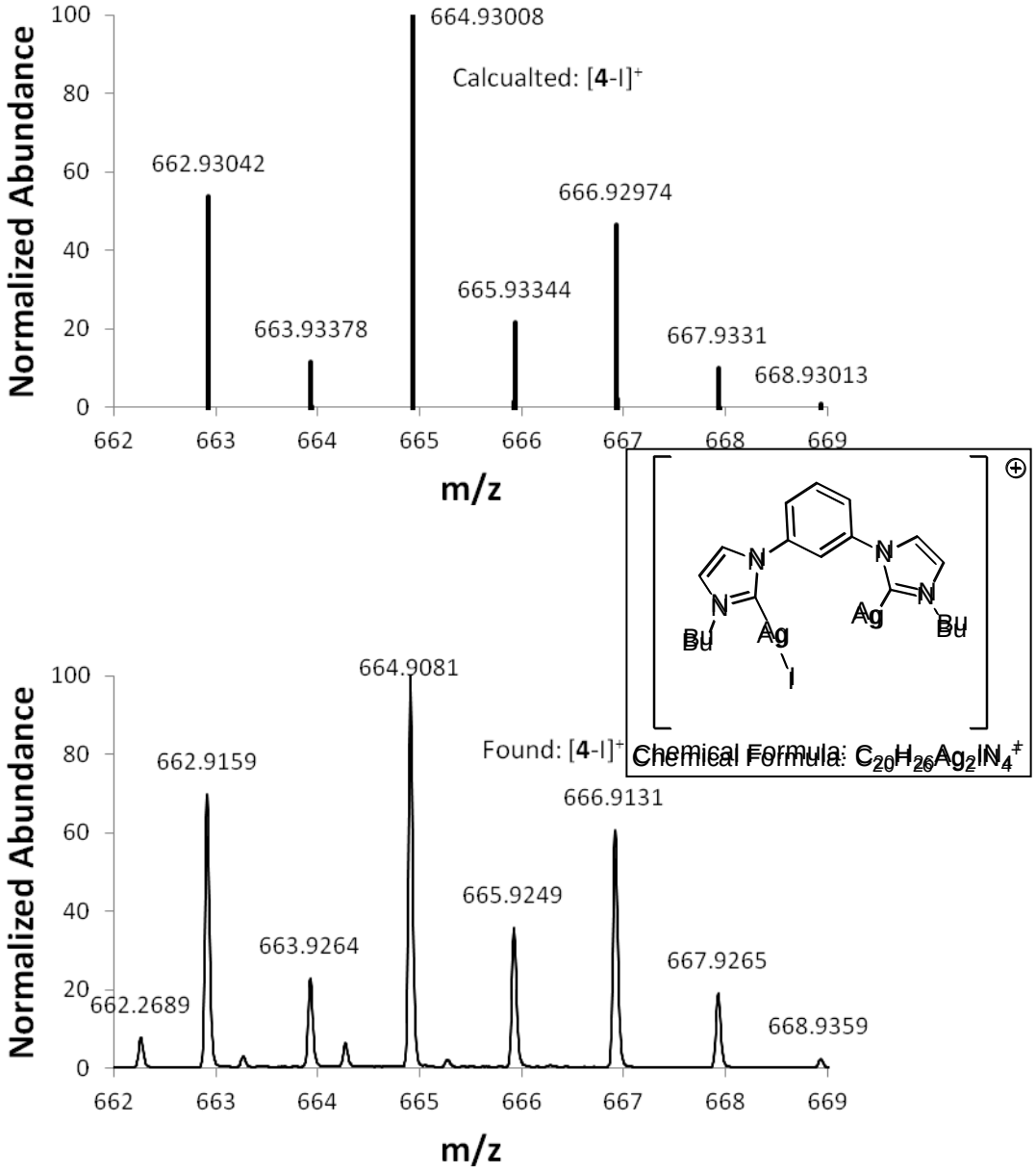

Normalized Abundance
m/z
664.93008
Calcualted: [4-I]+
662.93042
666.92974
665.93344
663.93378
667.9331
668.93013
Found: [4-I]+
664.9081
662.9159
666.9131
665.9249
663.9264
667.9265
662.2689
668.9359
Chemical Formula: C20H26Ag2IN4+

**Figure S 32**

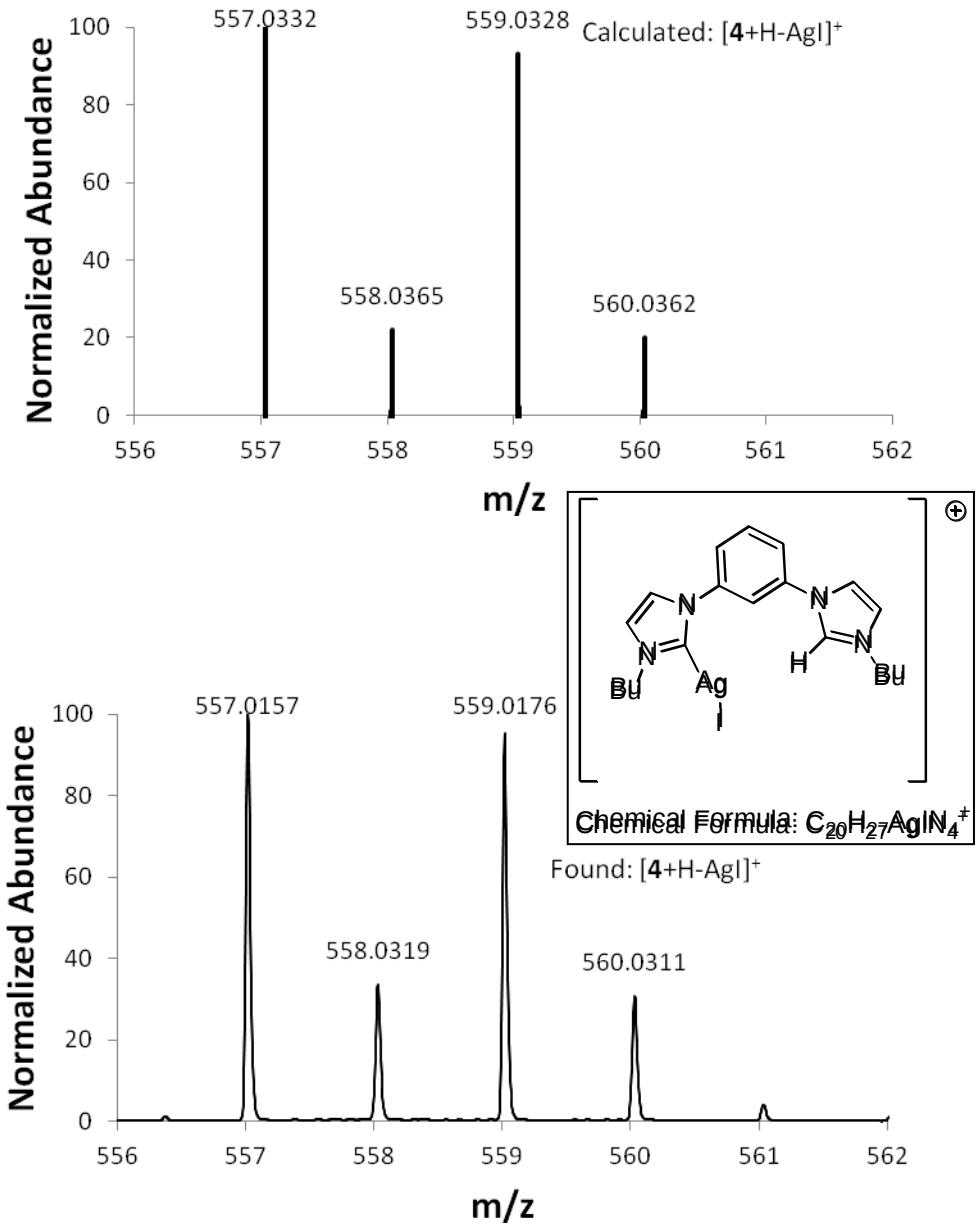

557.0332
559.0328
Calculated: [4+H-AgI]+
558.0365
560.0362
Normalized Abundance
m/z
557.0157
559.0176
Found: [4+H-AgI]+
558.0319
560.0311
Chemical Formula: C20H27AgIN4+

**Figure S 33**

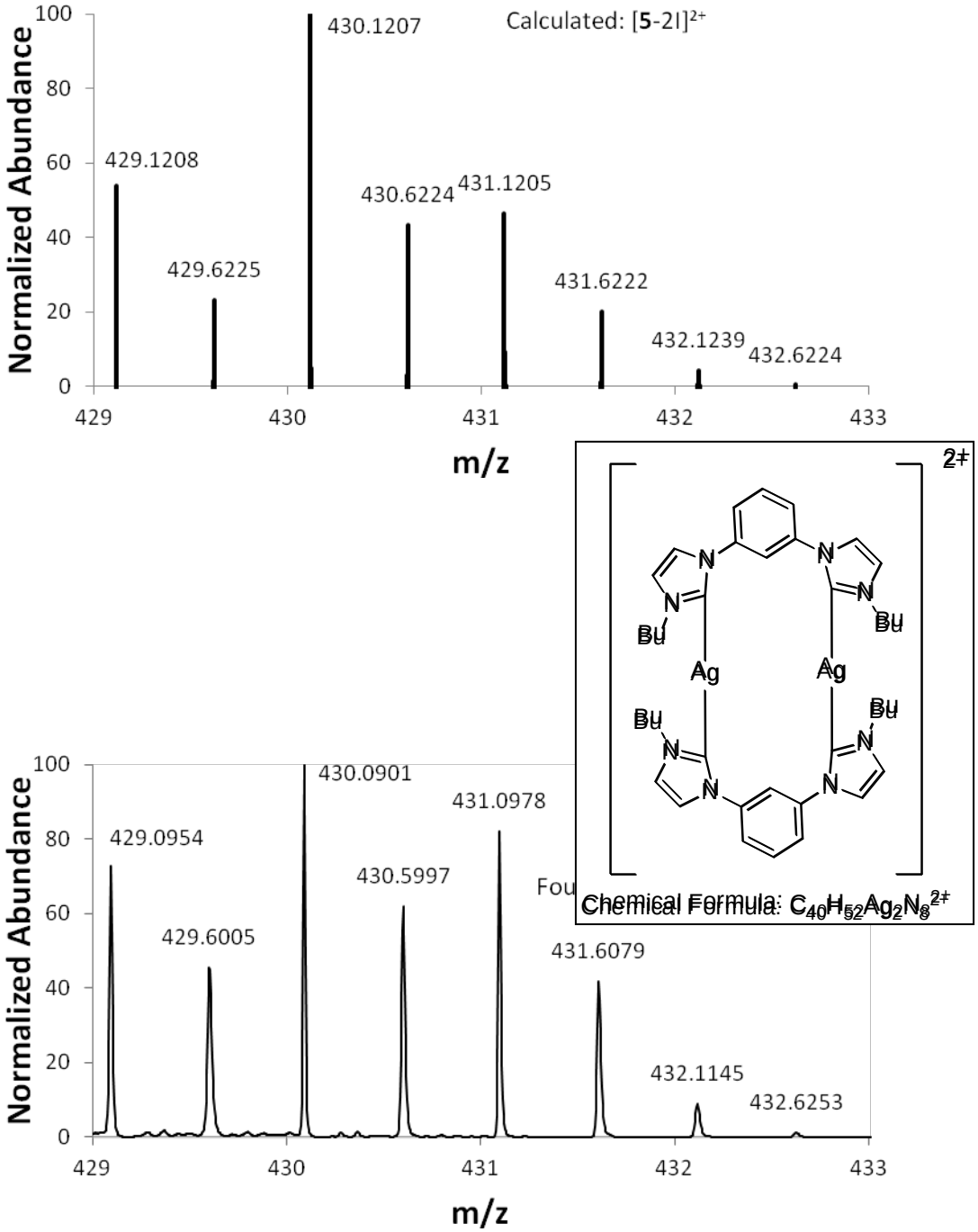

Calculated: [5-2I]2+
430.1207
429.1208
429.6225
430.6224
431.1205
431.6222
432.1239
432.6224
Normalized Abundance
m/z
2+
Chemical Formula: C40H52Ag2N8
430.0901
431.0978
429.0954
430.5997
429.6005
431.6079
432.1145
432.6253
Normalized Abundance
m/z

**Figure S 34**

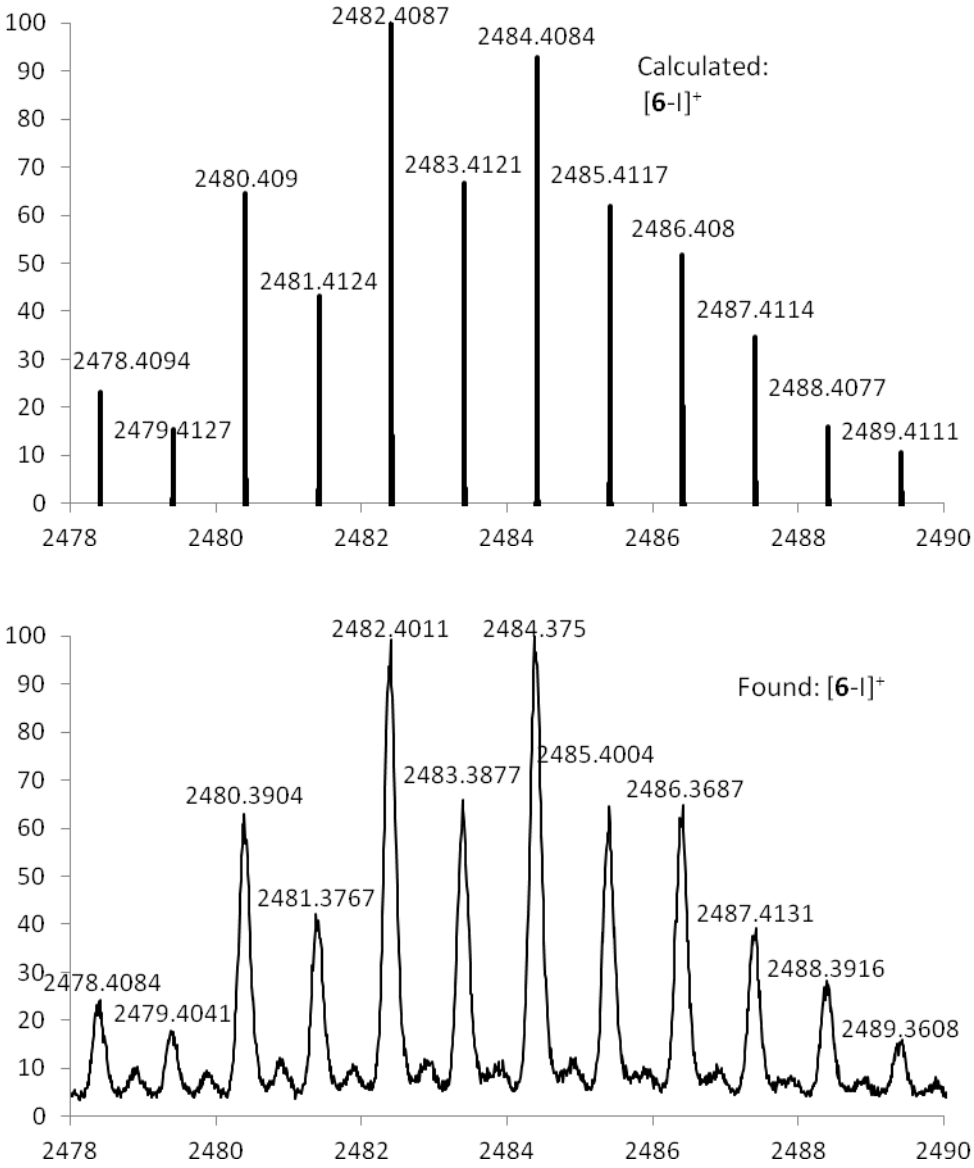

Calculated:
[6-I]+
2482.4087
2484.4084
2480.409
2483.4121
2485.4117
2486.408
2481.4124
2487.4114
2478.4094
2488.4077
2479.4127
2489.4111
Found: [6-I]+
2482.4011
2484.375
2485.4004
2480.3904
2483.3877
2486.3687
2481.3767
2487.4131
2478.4084
2488.3916
2479.4041
2489.3608
100
90
80
70
60
50
40
30
20
10
0
2478
2480
2482
2484
2486
2488
2490

**Figure S 35**

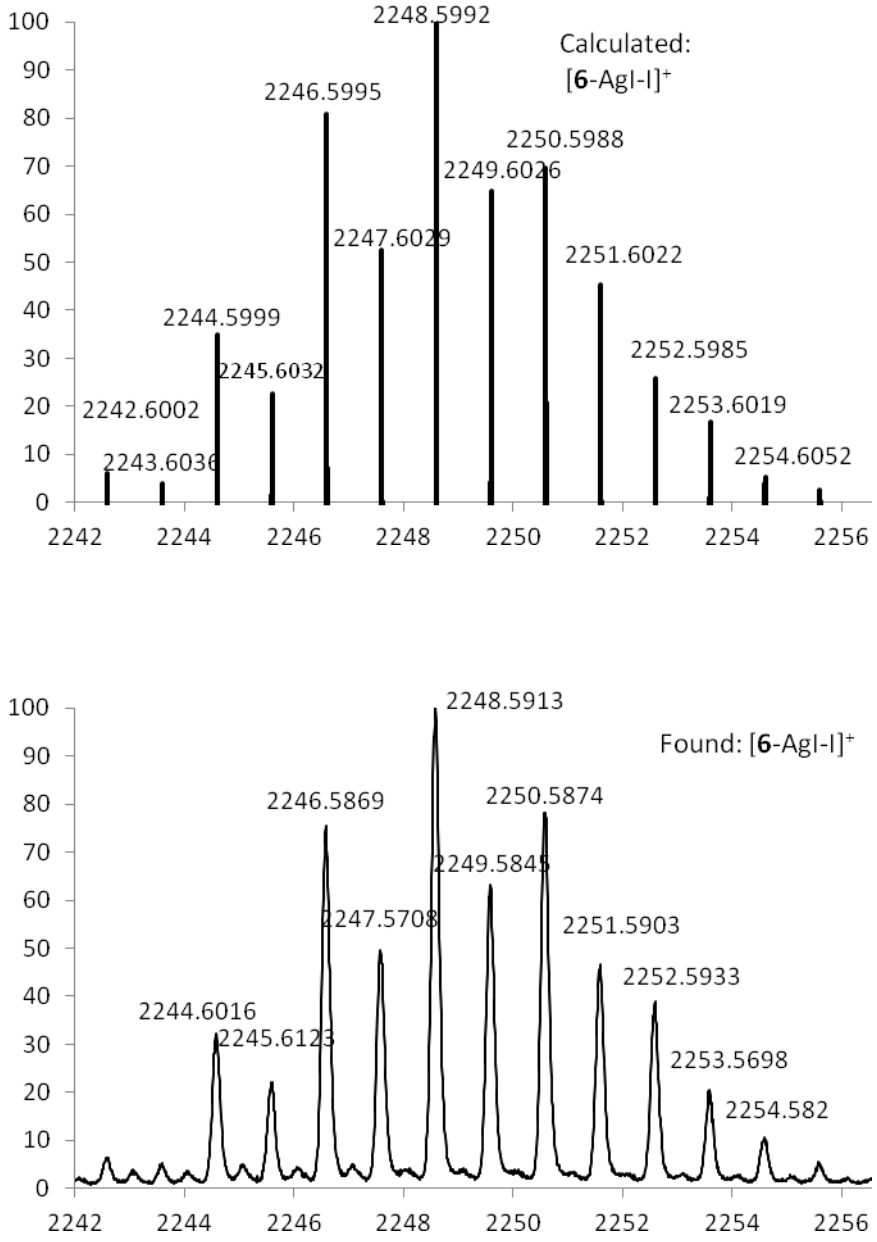

Calculated:
[6-AgI-I]+
2248.5992
2246.5995
2250.5988
2249.6026
2247.6029
2251.6022
2244.5999
2252.5985
2245.6032
2253.6019
2242.6002
2254.6052
2243.6036
Found: [6-AgI-I]+
2248.5913
2246.5869
2250.5874
2249.5845
2247.5708
2251.5903
2252.5933
2244.6016
2245.6123
2253.5698
2254.582
100
90
80
70
60
50
40
30
20
10
0
2242
2244
2246
2248
2250
2252
2254
2256

**Figure S 36**

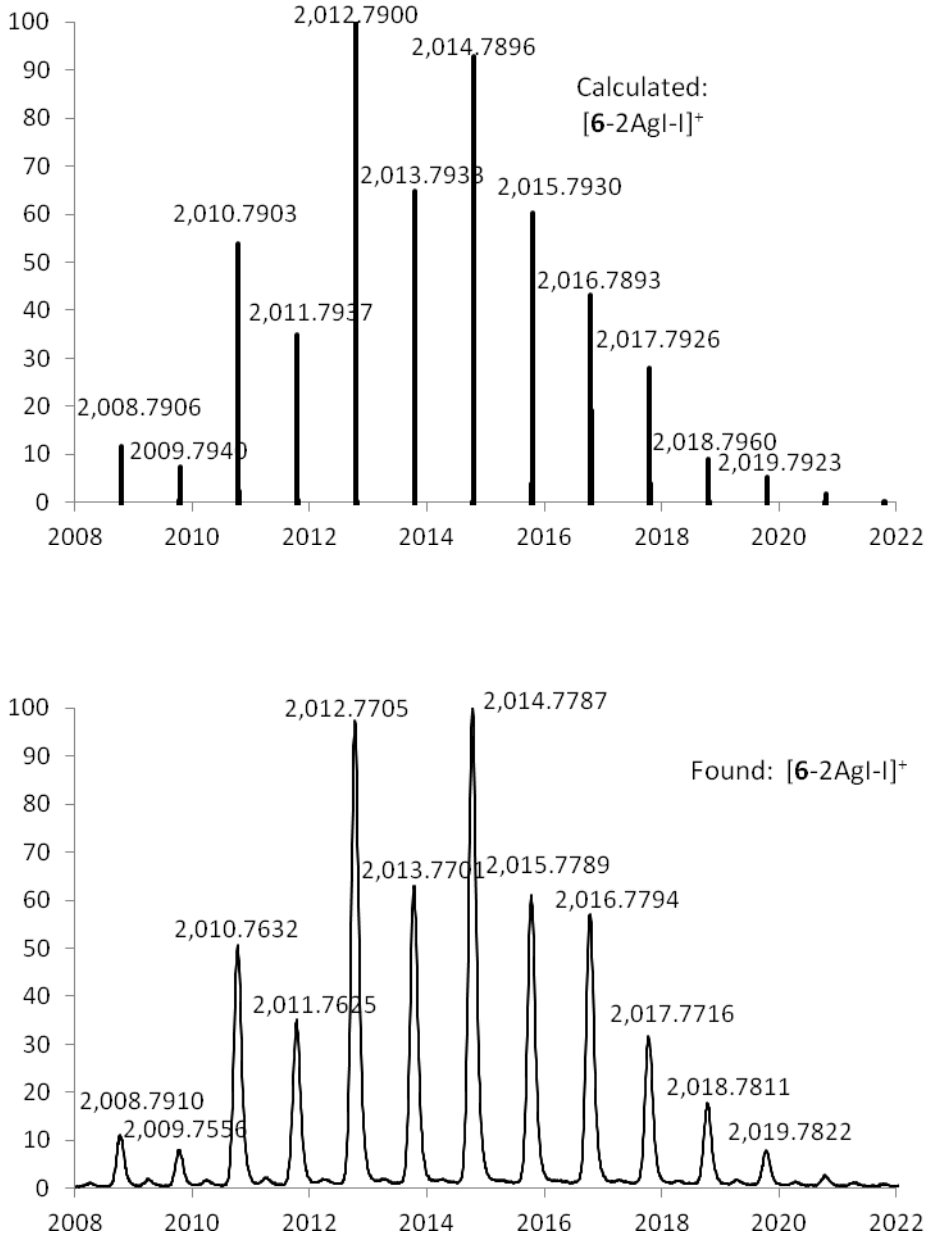

2,012.7900
2,014.7896
Calculated:
[6-2AgI-I]+
2,013.7933
2,015.7930
2,010.7903
2,016.7893
2,011.7937
2,017.7926
2,008.7906
2,018.7960
2009.7940
2,019.7923
2,012.7705
2,014.7787
Found: [6-2AgI-I]+
2,013.7701
2,015.7789
2,016.7794
2,010.7632
2,011.7625
2,017.7716
2,018.7811
2,008.7910
2,009.7556
2,019.7822
100
90
80
70
60
50
40
30
20
10
0
2008
2010
2012
2014
2016
2018
2020
2022

**Figure S 37**

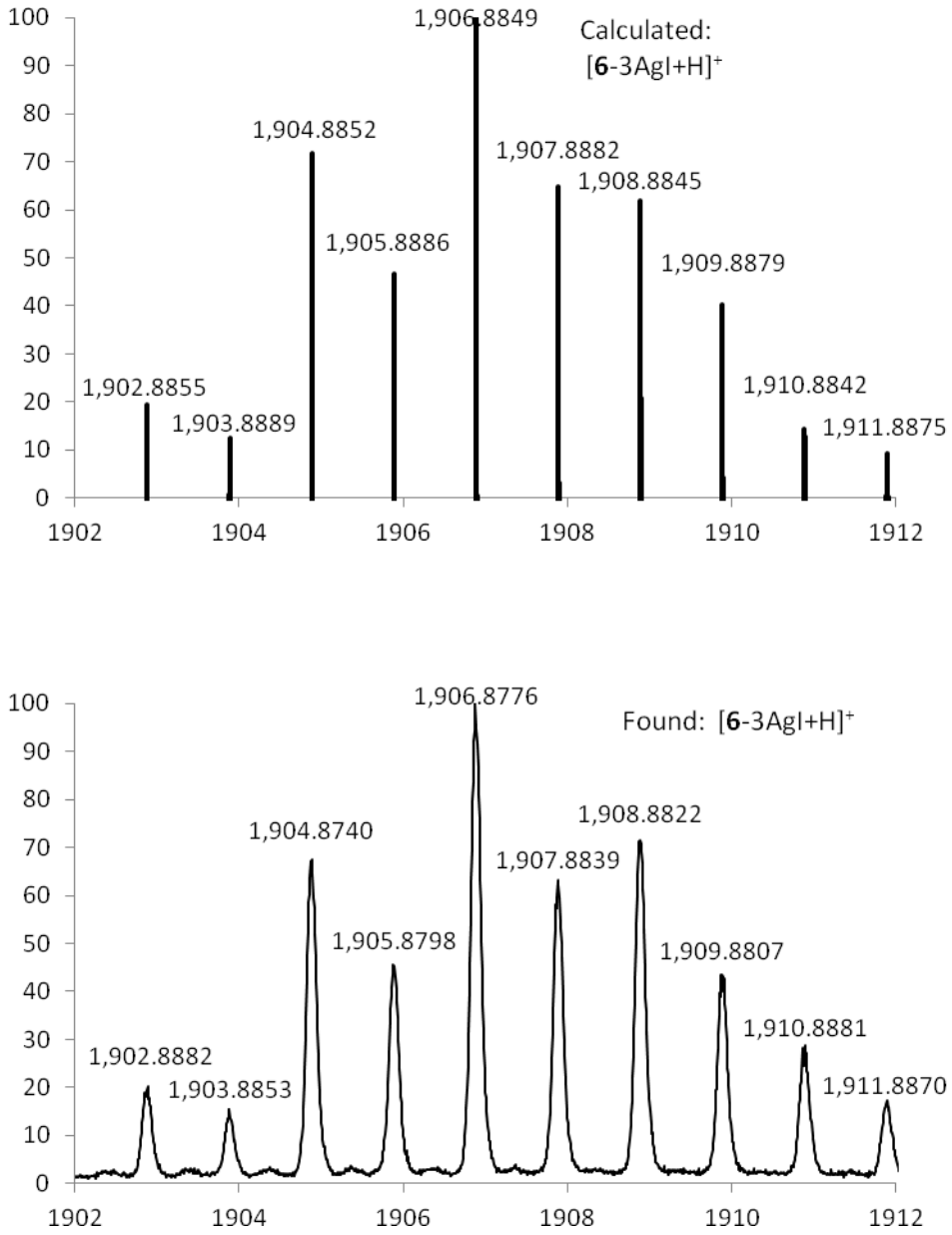

Calculated:
[6-3AgI+H]+
1,902.8855
1,903.8889
1,904.8852
1,905.8886
1,906.8849
1,907.8882
1,908.8845
1,909.8879
1,910.8842
1,911.8875
Found: [6-3AgI+H]+
1,902.8882
1,903.8853
1,904.8740
1,905.8798
1,906.8776
1,907.8839
1,908.8822
1,909.8807
1,910.8881
1,911.8870
100
90
80
70
60
50
40
30
20
10
0
1902
1904
1906
1908
1910
1912

**Figure S 38**

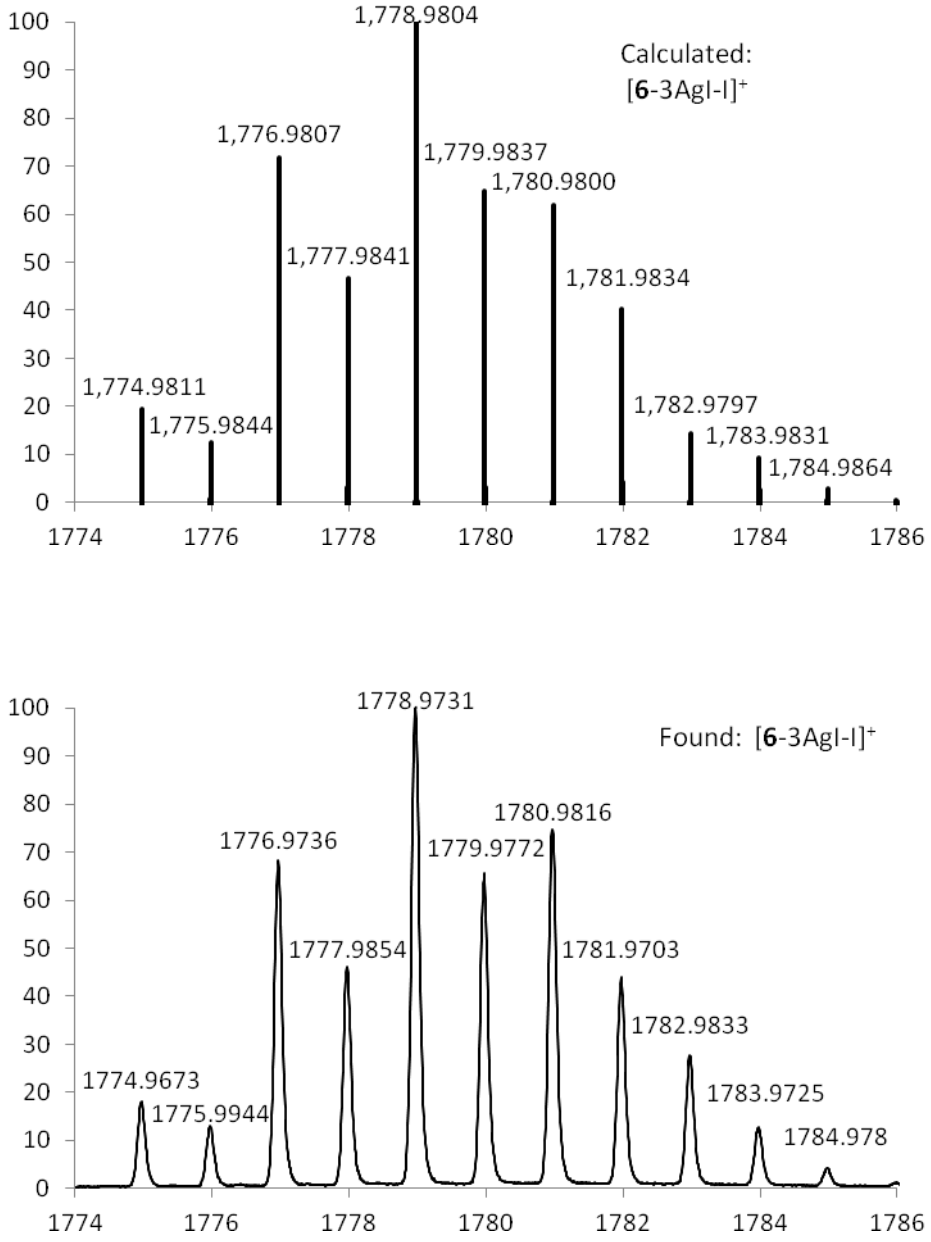

Calculated:
[6-3AgI-I]+
1,778.9804
1,776.9807
1,779.9837
1,780.9800
1,777.9841
1,781.9834
1,774.9811
1,775.9844
1,782.9797
1,783.9831
1,784.9864
Found: [6-3AgI-I]+
1778.9731
1780.9816
1776.9736
1779.9772
1777.9854
1781.9703
1782.9833
1774.9673
1775.9944
1783.9725
1784.978
100
90
80
70
60
50
40
30
20
10
0
1774
1776
1778
1780
1782
1784
1786

**Figure S 39.** Mass Spectrum of Bis(μ-1,3-bis(3'-but-3"-enyl-imidazol-2'-ylidene)benzene-κ-C)tetra-$\mu^3$-iodotetrasilver(I) (**3b**).

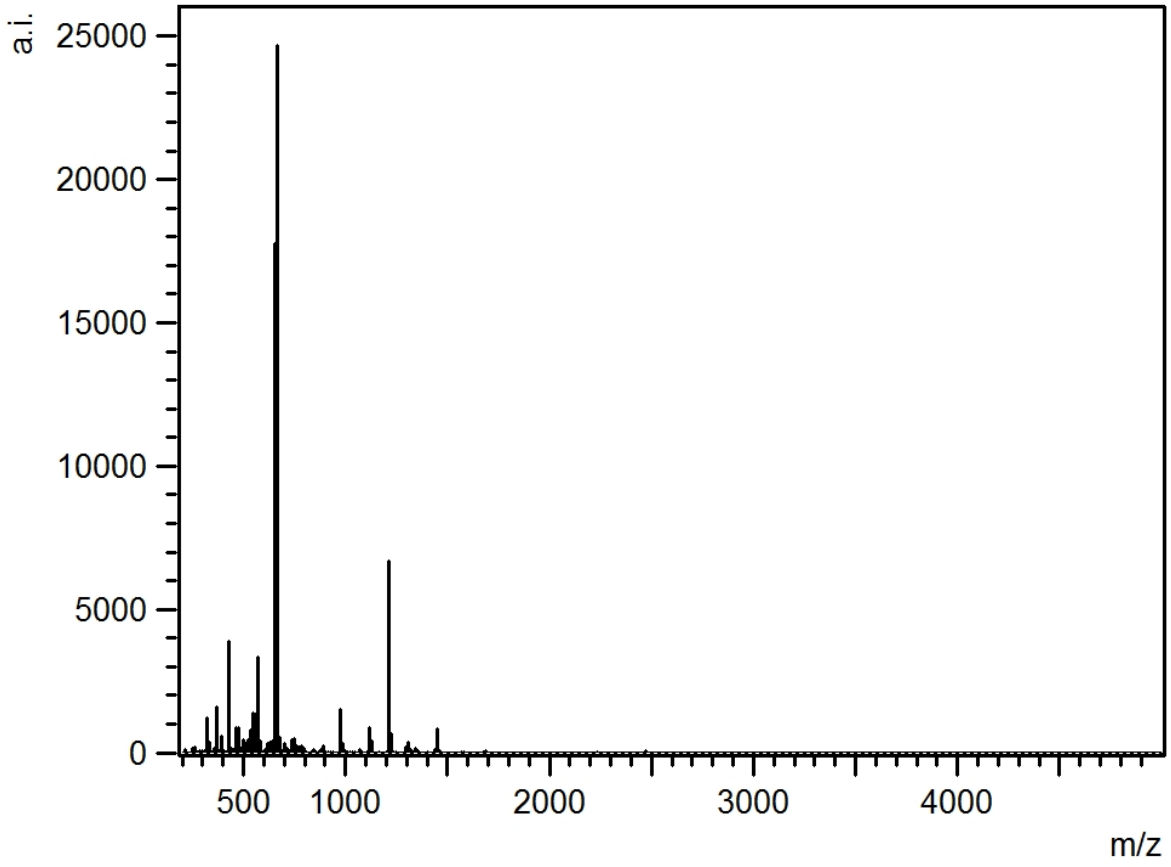
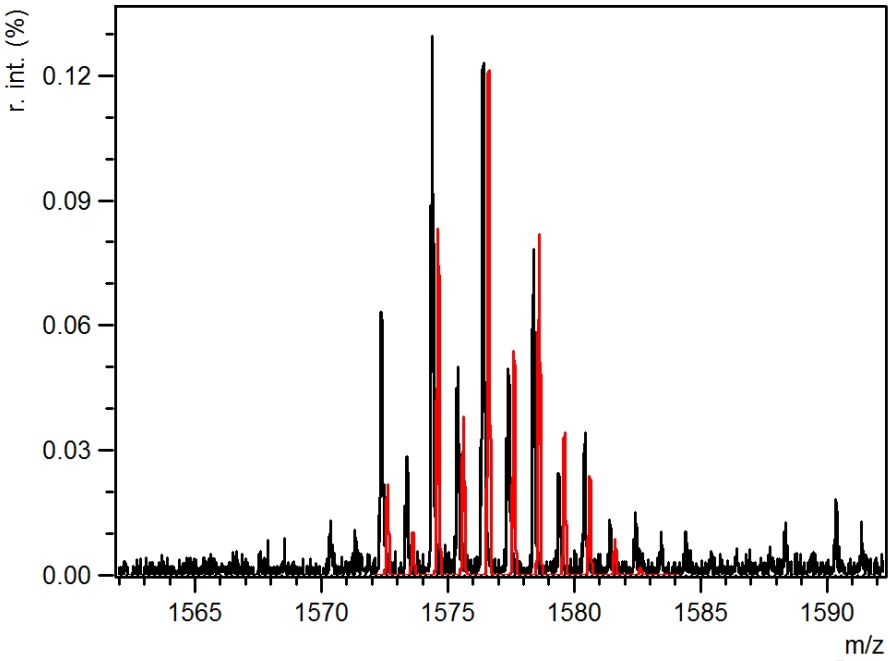



**Figure S 40.** Calculated for $C_{40}H_{45}Ag_4I_4N_8$ [**3b**+H] (red) and Observed (black).




Figures S37-S56 were made using the computer program mmass.[7]

**Figure S 41.** Calculated for $C_{40}H_{44}Ag_4I_3N_8$ [**3b**-I] (red) and Observed (black).

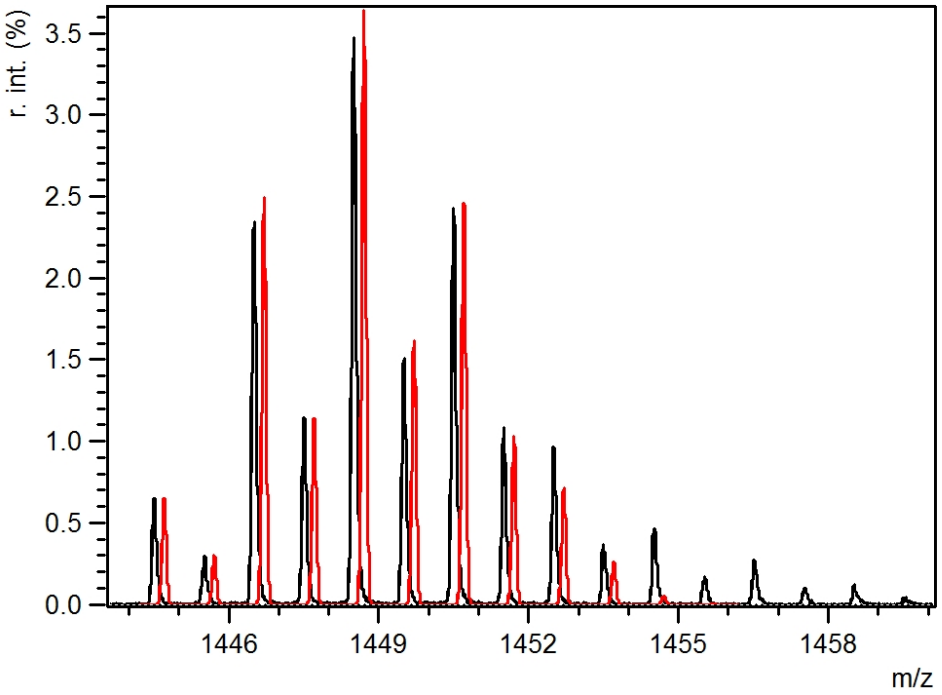



**Figure S 42.** Calculated for $C_{40}H_{44}Ag_3I_2N_8$ [**3b**-AgI-I] (red) and Observed (black).

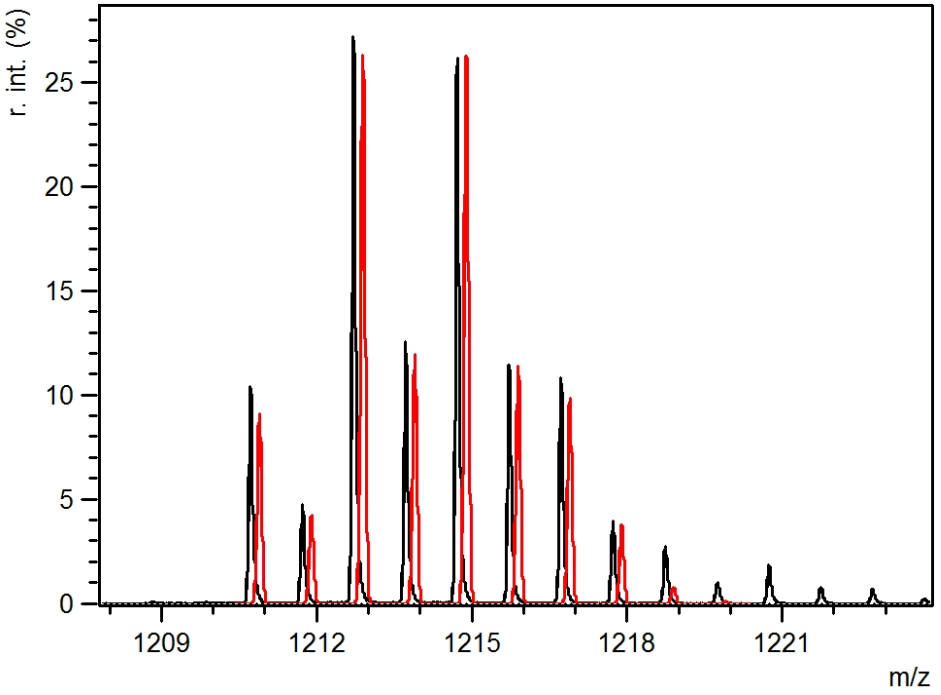


**Figure S 43.** Calculated for $C_{40}H_{44}Ag_2IN_8$ [**3b**-2AgI-I] (red) and Observed (black).

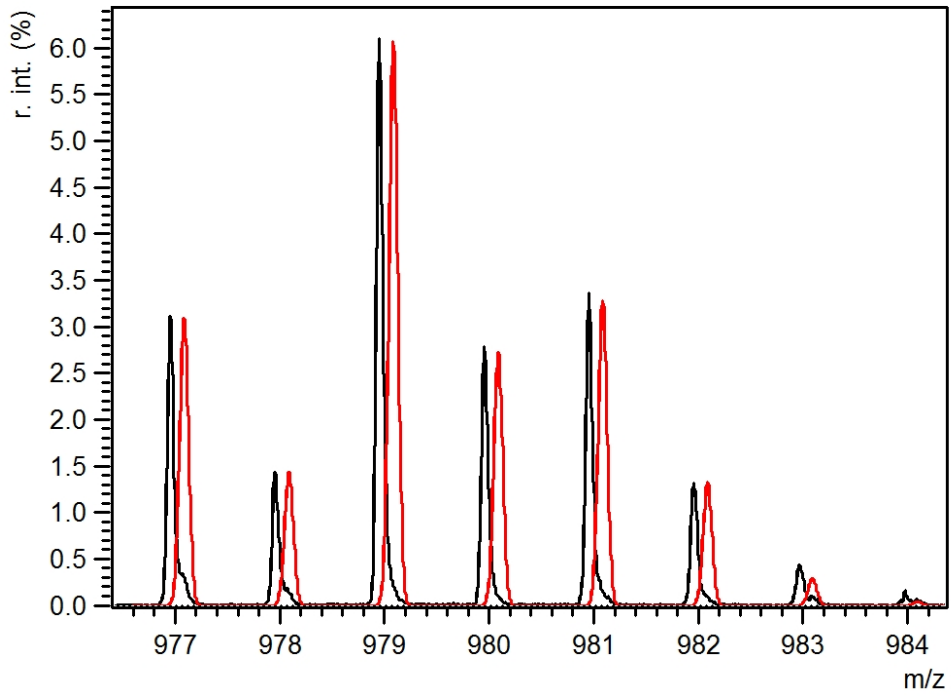



**Figure S 44.** Calculated for $C_{40}H_{44}Ag_2I_2N_8$ [**3b**-2AgI-2I]$^{2+}$ (red) and Observed (black).

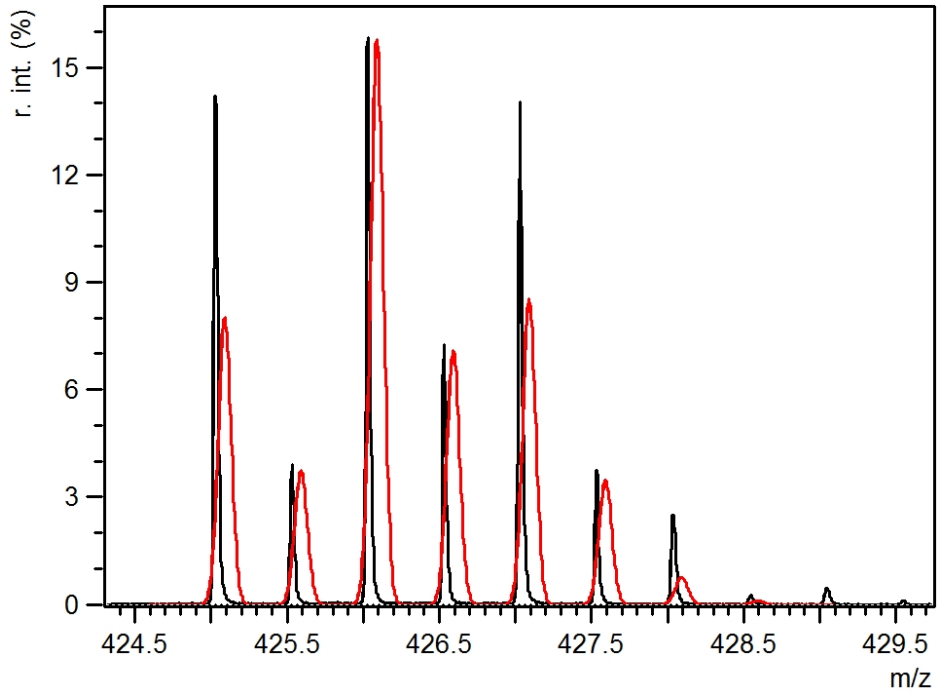


**Figure S 45.** Calculated for $C_{20}H_{44}Ag_2I_2N_8$ [**3b**-2AgI-I]$^{2+}$ (red) and Observed (black).

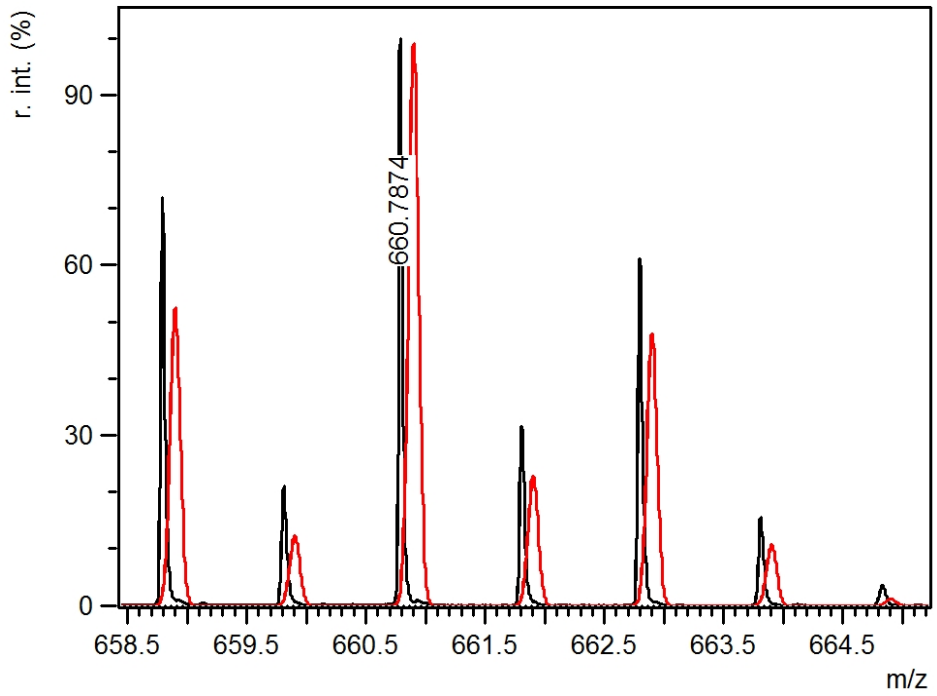


**Figure S 46.** Mass Spectrum of Complex **3c**.

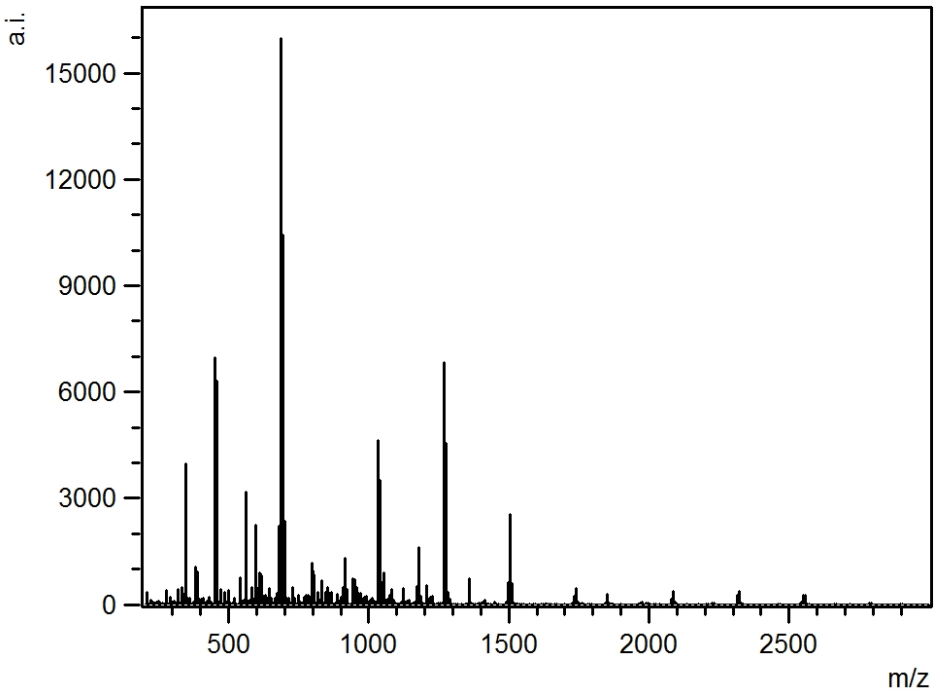



**Figure S 47.** Calculated for $C_{44}H_{52}Ag_4I_4N_8$ [**3c**+H] (red) and Observed (black).

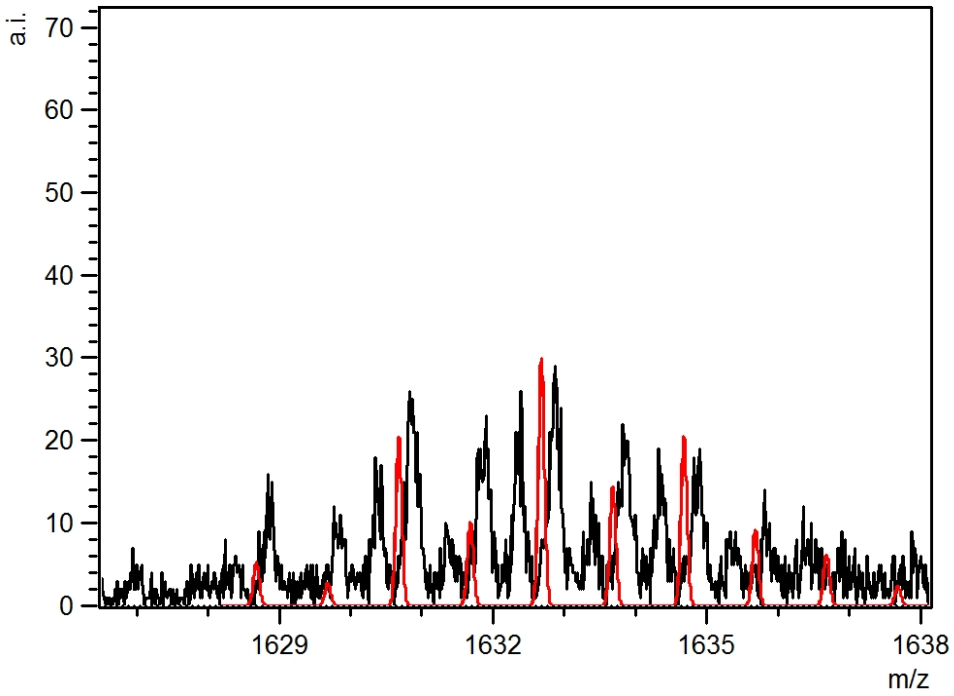


**Figure S 48.** Calculated for $C_{44}H_{52}Ag_4I_3N_8$ [**3c**-I] (red) and Observed (black).

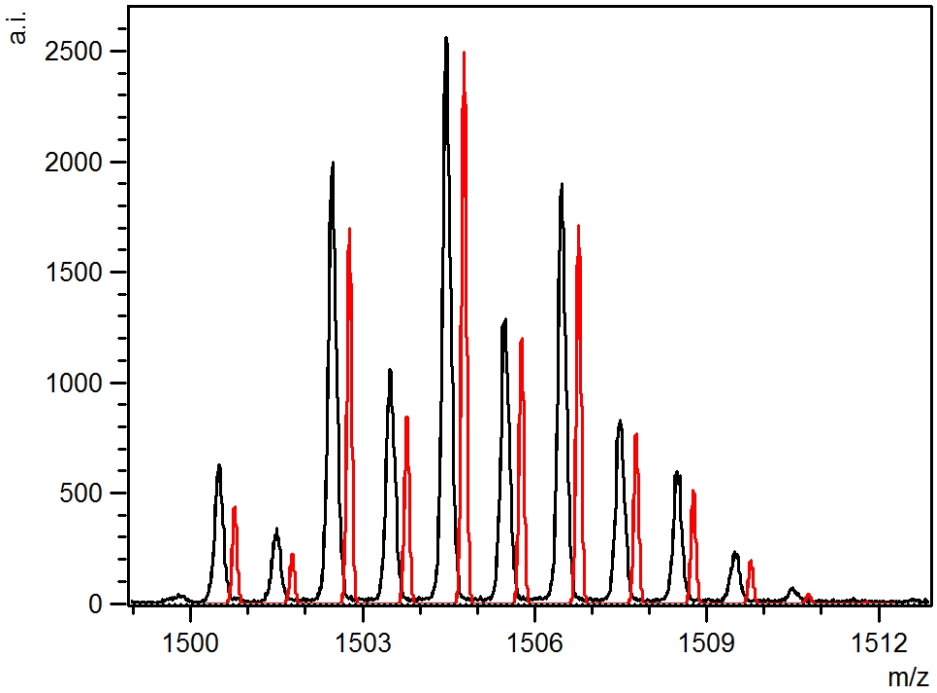



**Figure S 49.** Calculated for $C_{44}H_{52}Ag_3I_2N_8$ [**3c**-AgI-I] (red) and Observed (black).

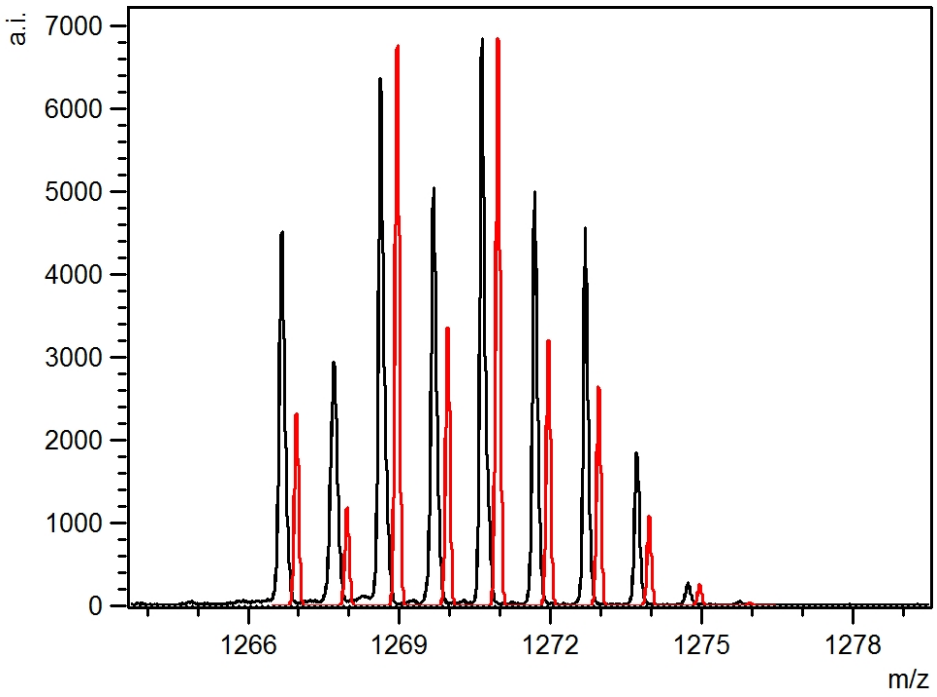


**Figure S 50.** Calculated for $C_{44}H_{52}Ag_2IN_8$ [**3c**-2AgI-I] (red) and Observed (black).

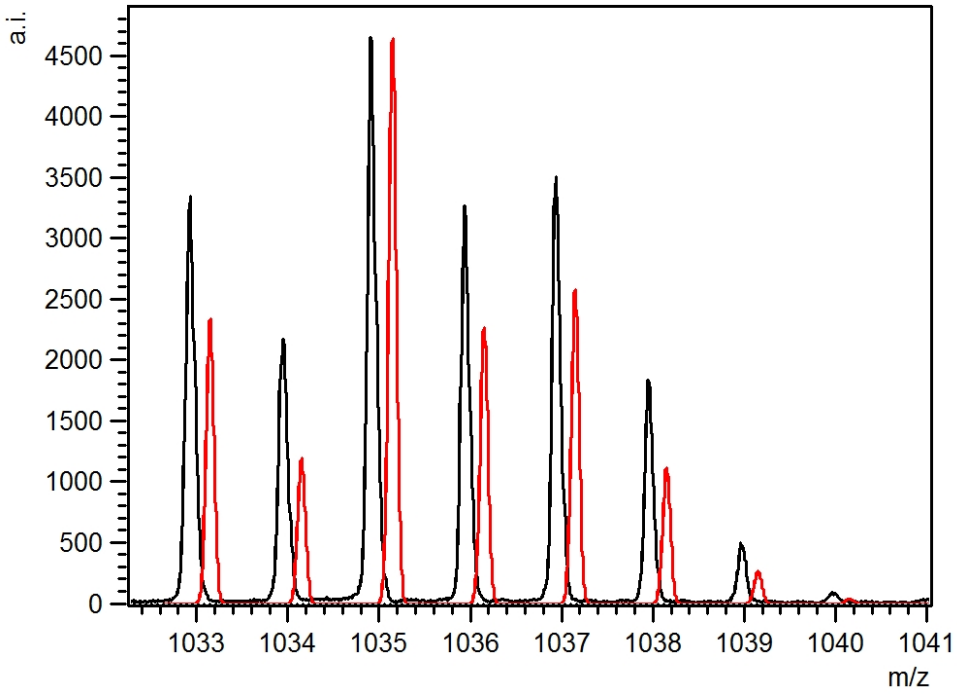



**Figure S 51.** Calculated for $C_{66}H_{78}Ag_7I_6N_8$ [**3c**+$C_{22}H_{26}N_4$+3Ag+2I ] (red) and Observed (black).

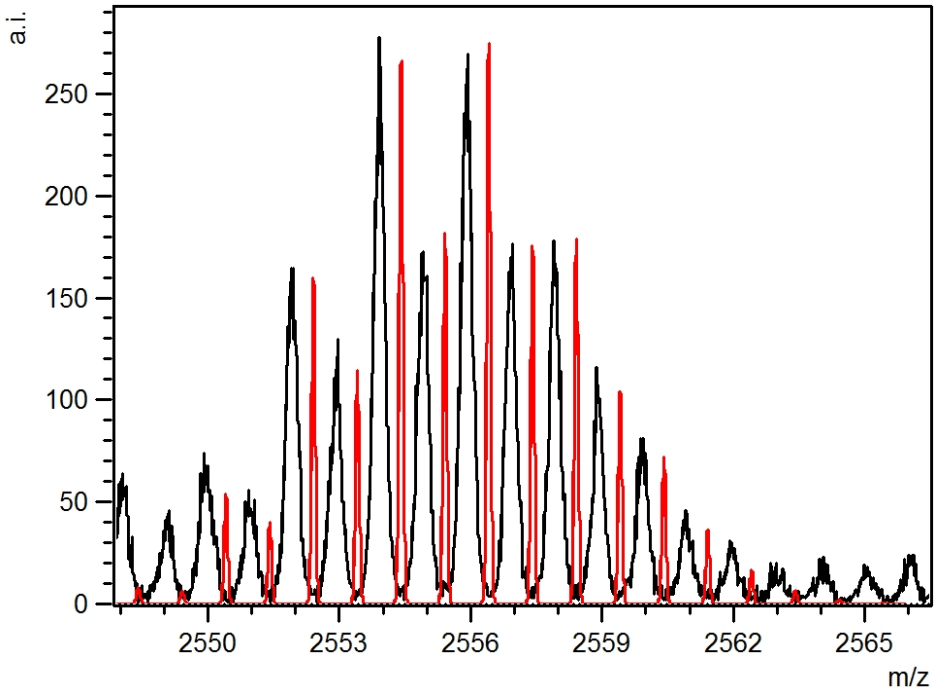


**Figure S 52.** Calculated for $C_{66}H_{78}Ag_6I_5N_8$ [**3c**+$C_{22}H_{26}N_4$+2Ag+I ] (red) and Observed (black).

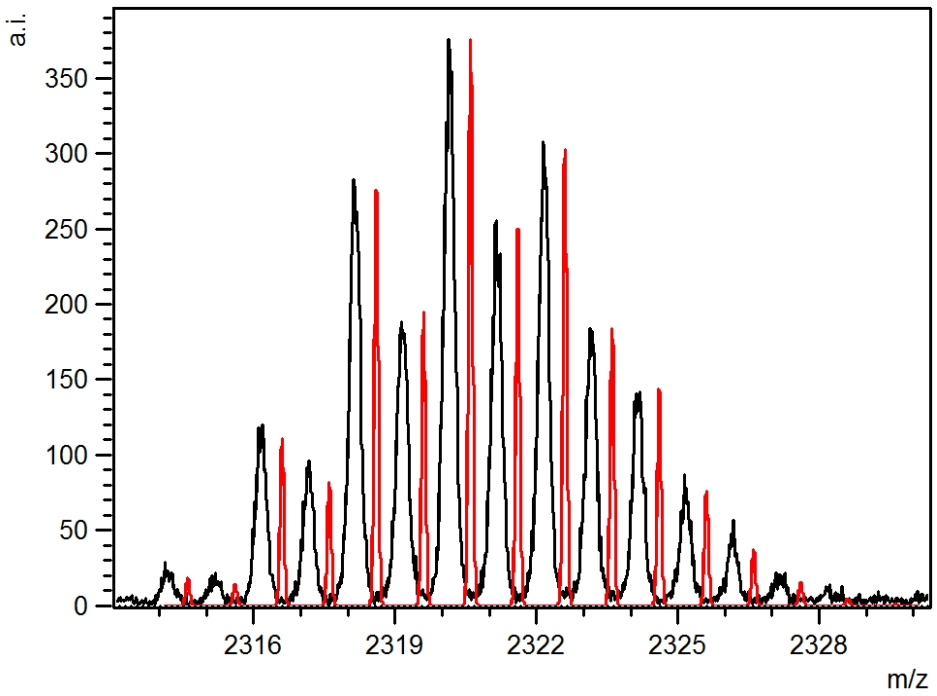



**Figure S 53.** Calculated for $C_{66}H_{78}Ag_5I_4N_8$ [**3c**+$C_{22}H_{26}N_4$+Ag ] (red) and Observed (black).

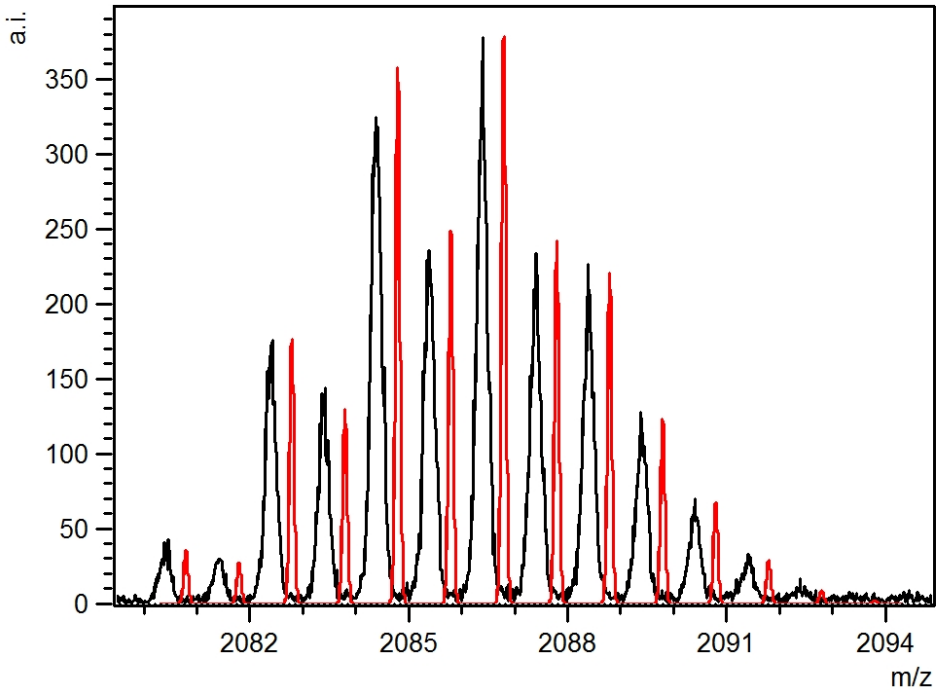


**Figure S 54** Mass Spec of Triazole Complex **3e**.

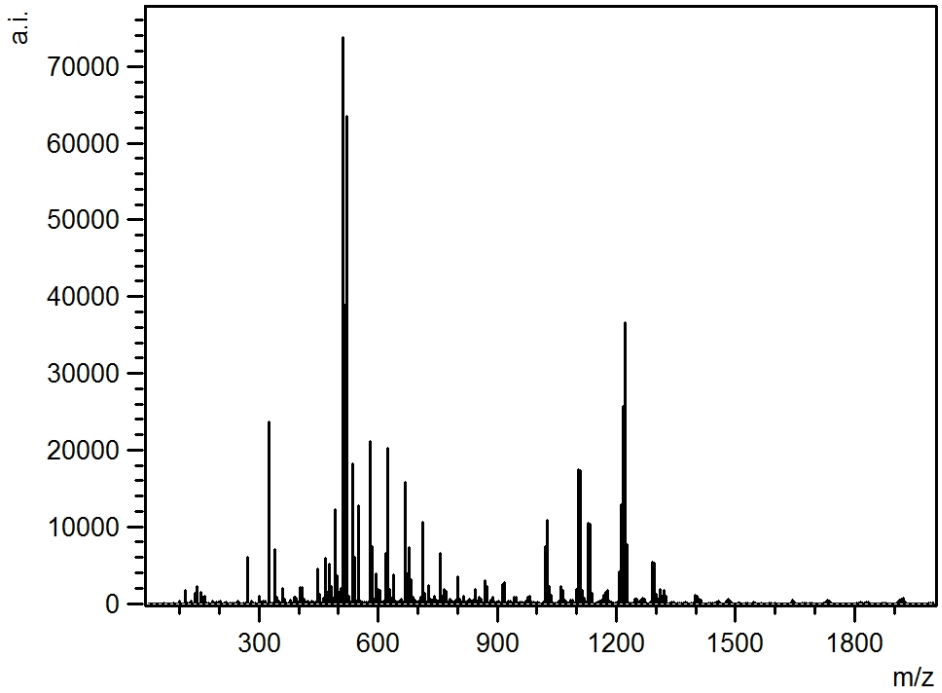



**Figure S 55.** Calculated for $C_{36}H_{49}Ag_4Br_4N_{12}$ [**3e**+H] (red) and Observed (black).

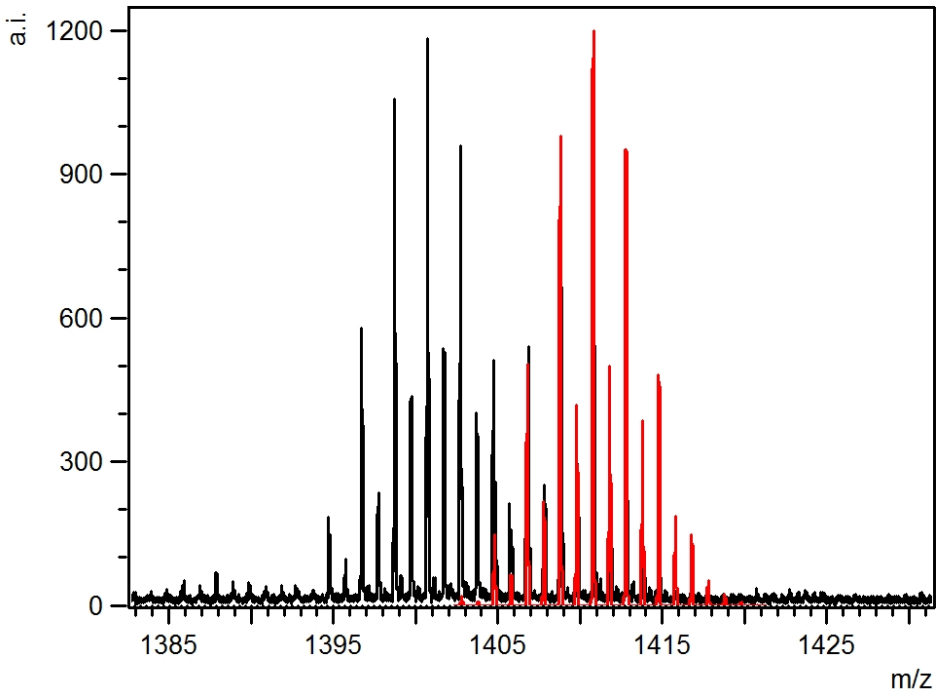


**Figure S 56.** Calculated for $C_{36}H_{48}Ag_4Br_3N_{12}$ [**3e**-Br] (red) and Observed (black).

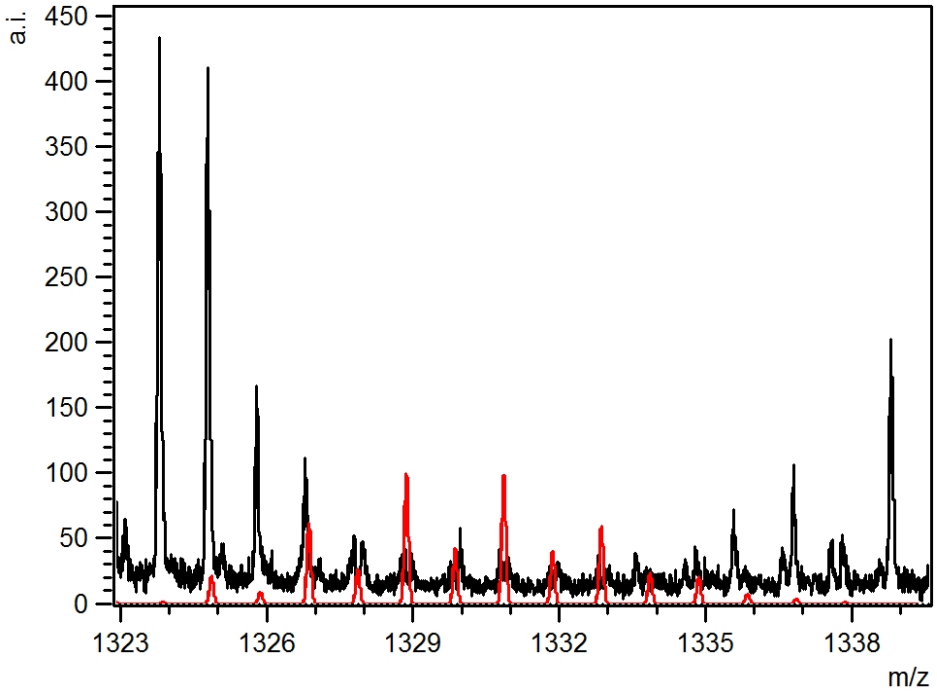



**Figure S 57.** Calculated for $C_{36}H_{48}Ag_3Br_2N_8$ [**3e**-AgBr- Br] (red) and Observed (black).

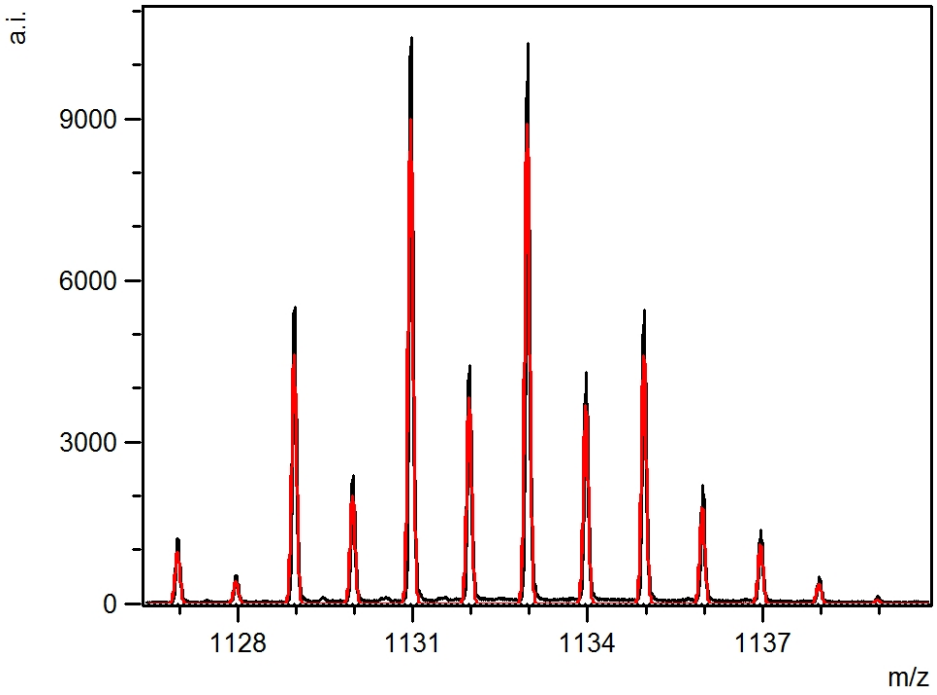
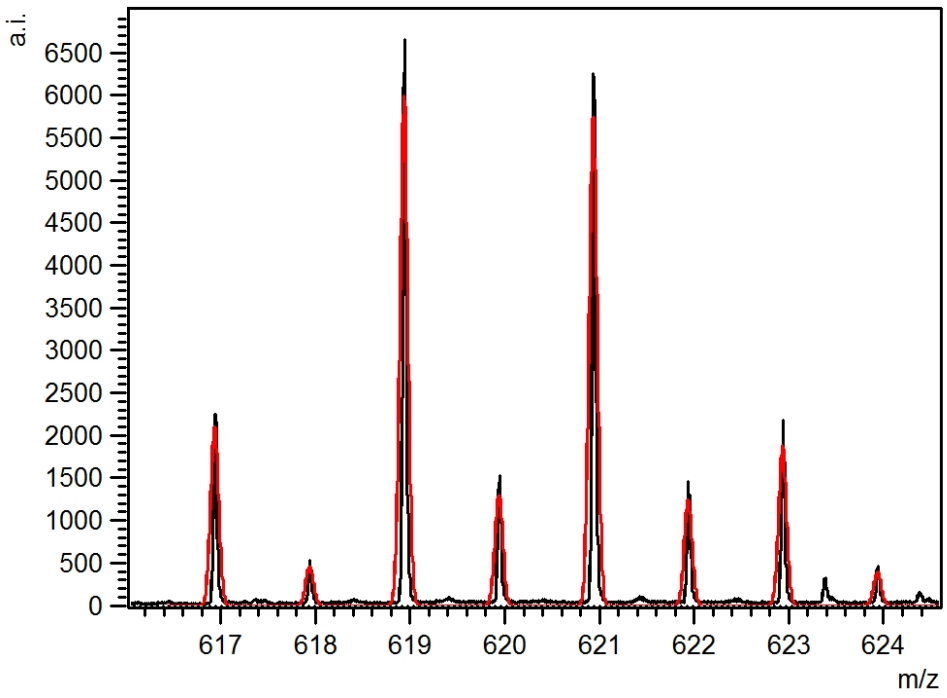


**Figure S 58.** Calculated for $C_{18}H_{24}Ag_2BrN_6$ [**3e**- $C_{18}H_{24}N_6$-2Ag-3Br] (red) and Observed (black).

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