Supplementary Information

Defined Tetranuclear Coinage Metal Chains

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Synthesis and analysis[1]

General Procedures:

All manipulations were performed under rigorous exclusion of moisture and oxygen in flame-dried Schlenk-type glassware or in an argon-filled MBraun glovebox. Obtained products after workup can be handled in air if not statet otherwise. Furthermore, for the most part the silver compounds were handled with the exclusion of light by wrapping the compound-containing flasks in aluminium foil.

Prior to use, CH_2Cl_2 and MeCN were distilled under nitrogen from CaH_2. MeOH was distilled under Nitrogen from activated magnesium. Hydrocarbon solvents (THF, diethyl ether, *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). Deuterated solvents were obtained from Carl Roth GmbH (99.5 atom% D).

NMR spectra were recorded on a Bruker Avance II 300 MHz or Avance 400 MHz. Chemical shifts are referenced to the residual ^{1}H and ^{13}C resonances of the deuterated solvents and are reported relative to tetramethylsilane.

IR spectra were obtained on a Bruker Tensor 37.

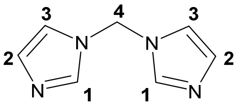
EI-Mass spectra were recorded at 70 eV on a Thermo Scientific DFS.

ESI mass spectra were obtained using a FT-ICR (Fourier transform ion cyclotron resonance) IonSpecUltima mass spectrometer equipped with a 7 T magnet (Cryomagnetics).

Elemental analyses were carried out with an ElementarVario EL or Micro Cube.

[AuCl(tht)],[2] $[Cu(MeCN)_4][ClO_4]$,[3] and 6-chloromethyl-2-,2'-bipyridine[4] were prepared according to literature procedures. Ag_2O was purchased from Alfa-Aesar (99.99 %) and used as received.

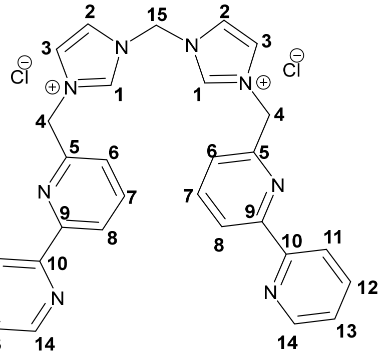
Synthesis of 1,1'-Methylenebis(1H-imidazole) (**I**)



The synthesis was carried out following a literature protocol.[5]

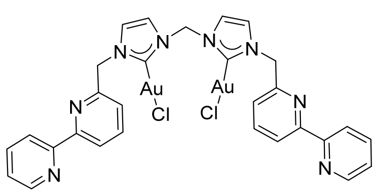
Imidazole (10.0 g, 147 mmol, 2.0 eq.), tetrabutylammoniumbromide (1.42 g, 4.40 mmol, 0.06 eq.) and KOH powder (16.5 g, 294 mmol, 4.0 Äq.) are stirred at room temperature for ca. 1 h until a slurry is formed. Then, dibromoethane (12.8 g, 5.11 mL, 73.5 mmol, 1.0 eq.) is added dropwise over a period of 2 h. At the end of addition, the mixture becomes a solid. The product is separated by sublimation (ca. $6 \cdot 10^{-3}$ mbar, 180 °C). Yield (colourless crystals): 7.80 g, 52.6 mmol, 72 %. **^{1}H NMR** (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 7.62 (s, 2H, *H*1), 7.07 (s, 2H, *H*2), 6.97 (s, 2H, *H*3), 5.99 (s, 2H, *H*4). **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$, 25 °C): δ (ppm) = 136.6 (*C*1), 131.1 (*C*2), 118.2 (*C*3), 56.3 (*C*4).

Synthesis of (**L(**2 HCl**)**)



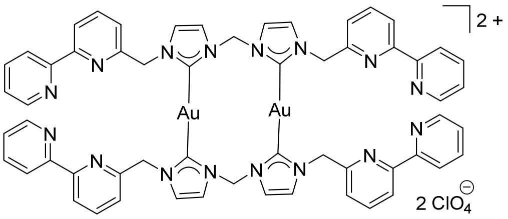
A solution of **I** (181 mg, 1.22 mmol, 1.0 eq.) and 6-chloromethyl-2,2'-bipyridine (500 mg, 2.44 mmol, 2.0 eq.) is heated in dry acetonitrile (5 mL) at 80 °C for 72 h. After cooling down to room temperature, the precipitate is filtered off, washed with small amounts of acetonitrile, thf, and Et_2O and dried under high vacuum. Yield (colourless powder): 532 mg, 0.954 mmol, 78 %. **^{1}H NMR** (300 MHz, DMSO-d_6, 25 °C): δ (ppm) = 10.28 (t, J = 1.6 Hz, 2H, H1), 8.61 (ddd, J = 4.8, 1.8, 0.9 Hz, 2H, H14), 8.49 (t, J = 1.8 Hz, 2H, H3), 8.29 (dd, J = 7.9, 1.0 Hz, 2H, H8), 8.10 (dt, J = 8.0, 1.1 Hz, 2H, H11), 8.07 (t, J = 1.8 Hz, 2H, H2), 7.99 (t, J = 7.8 Hz, 2H, H7), 7.79 (td, J = 7.6, 1.8 Hz, 2H, H12), 7.58 (dd, J = 7.7, 1.0 Hz, 2H, H6), 7.35 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H, H13), 7.13 (s, 2H, H15), 5.78 (s, 4H, H4). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6, 25 °C): δ (ppm) = 155.1 (C9), 154.2 (C10), 152.6 (C5), 149.2 (C14), 138.7 (C1), 138.6 (C7), 137.1 (C12), 124.4 (C13), 124.0 (C2), 122.7 (C6), 122.3 (C3), 120.5 (C11), 120.0 (C8), 57.8 (C15), 53.2 (C4). **ESI-MS** (MeOH): *m/z* (%): 243.11 $[M]^{2+}$ (99.9), 485.22 $[M\text{-}H^+]^+$ (58.4), 317.15 $[M\text{-}MeBipy]^+$ (97.5). **IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 3064 (w), 3030 (w), 2939 (w), 2871 (w), 1579 (s), 1564 (s), 1542 (w), 1475 (w), 1455 (w), 1430 (s), 1420 (s), 1362 (w), 1339 (w), 1300 (w), 1263 (w), 1231 (w), 1216 (w), 1173 (s), 1166 (s), 1156 (s), 1115 (w), 1093 (w), 1079 (w), 1041 (w), 1030 (w), 992 (w), 960 (w), 918 (w), 876 (w), 854 (w), 825 (w), 820 (w), 786 (m), 774 (s), 760 (s), 753 (s), 736 (w), 725 (w), 697 (w), 653 (w), 647 (m), 626 (w), 618 (m), 611 (m), 603 (m), 587 (w), 573 (w), 470 (w). **EA:** $C_{29}H_{26}Cl_2N_8$ (557.48): calculated C 62.48; H 4.70; N 20.10; found C 62.53 H 4.76; N 19.95.

Synthesis of [**L**$[AuCl)_2$] (**1**)



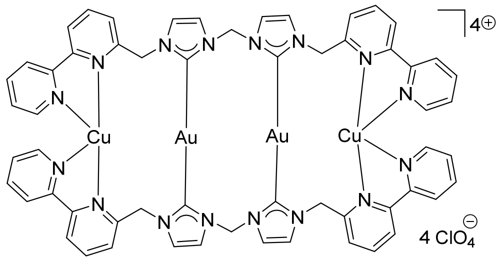
L(2 HCl) (200 mg, 0.359 mmol, 1.0 eq.) and [AuCl(tht)] (230 mg, 0.718 mmol, 2.0 eq.) are dissolved in dimethylformamide (6 mL). To the clear solution, sodium acetate (73.6 mg, 0.897 mmol, 2.5 eq.) is added and the mixture is heated at 80 °C for 2 h. The precipitate is removed by filtration. The volume of the filtrate is reduced under vacuum and the product is precipitated by addition of Et_2O. The solvent is decanted and the residue is dried under vacuum. Single crystals can be obtained by slow evaporation of a dimethylformamide (or dichloromethane) solution. Yield (beige powder): 274 mg, 0.289 mmol, 80 %. **^{1}H NMR** (300 MHz, DMSO-d_6, 25 °C): δ (ppm) = 8.63 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 2H, *H*14), 8.26 (dd, *J* = 7.9, 0.7 Hz, 2H, *H*8), 8.22 (d, *J* = 7.9 Hz, 2H, *H*11), 7.92 (t, *J* = 7.8 Hz, 2H, *H*7), 7.84 (td, *J* = 7.7, 1.8 Hz, 2H, *H*12), 7.79 (d, *J* = 2.0 Hz, 2H, *H*2), 7.75 (d, *J* = 2.0 Hz, 2H, *H*3), 7.40 (dd, *J* = 7.5, 1.0 Hz, 2H, *H*6), 7.39 – 7.35 (m, 2H, *H*13), 6.56 (s, 2H, *H*15), 5.59 (s, 4H, *H*4). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6, 25 °C): δ (ppm) = 171.1 (*C*1), 154.9 (*C*9), 154.7 (*C*10), 154.6 (*C*5), 149.2 (*C*14), 138.4 (*C*7), 137.2 (*C*12), 124.3 (*C*13), 123.3 (*C*3), 122.1 (*C*6), 121.8 (*C*2), 120.7 (*C*11), 119.6 (*C*8), 62.8 (*C*15), 55.6 (*C*4). **IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 3153 (w), 3106 (w), 2953 (w), 2856 (w), 1581 (s), 1565 (s), 1454 (m), 1430 (s), 1418 (s), 1385 (w), 1333 (w), 1262 (w), 1247 (m), 1231 (m), 1192 (w), 1172 (w), 1145 (w), 1097 (w), 1077 (w), 1044 (w), 992 (m), 974 (w), 904 (w), 765 (s), 745 (s), 737 (s), 725 (w), 668 (w), 661 (w), 643 (w), 622 (m), 594 (w), 465 (w). **EA:** $C_{29}H_{24}N_8Au_2Cl_2$ (949.39): calculated C 36.69; H 2.55; N 11.80; found C 36.79; H 2.65; N 11.64.

Synthesis of [(**L**)$_2$Au$_2$][ClO$_4$]$_2$ (**2**)



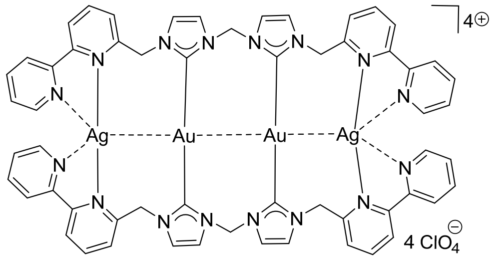
L(2 HCl) (250 mg, 0.448 mmol, 2.0 eq.) and Ag_2O (104 mg, 0.448 mmol, 2.0 eq.) are stirred for 18 h under exclusion of light in methanol (15 mL). A suspension with colourless precipitate is formed. Then, dichloromethane (15 mL) and [Au(tht)$_2$][ClO$_4$] (212 mg, 0.448 mmol, 2.0 eq.) are added and the mixture is stirred for another 3 h. The AgCl precipitate is removed by filtration. After removing all volatiles under vacuum, the residue is dissolved in dichloromethane (15 mL) an stirred with a small amount of activated coal for 18 h. The mixture is filtered and the product is precipitated with pentane. The solid is collected by filtration, washed with pentane and dried under vacuum. Yield (colourless powder): 294 mg, 0.188 mmol, 84%. **^{1}H NMR** (300 MHz, DMSO-d_6, 25 °C): δ (ppm) = 8.57 (ddd, *J* = 4.7, 1.8, 0.9 Hz, 4H, *H*14), 8.09 (dd, *J* = 7.9, 1.0 Hz, 4H, *H*8), 7.99 (d, *J* = 2.0 Hz, 4H, *H*2), 7.93 (dt, *J* = 8.0, 1.1 Hz, 4H, *H*11), 7.76 (d, *J* = 1.9 Hz, 4H, *H*3), 7.65 (td, *J* = 7.7, 2.0 Hz, 8H, *H*7 & *H*12), 7.40 – 7.29 (m, 6H, *H*13 & *H*15a), 7.04 (d, *J* = 7.8 Hz, 2H, *H*6), 6.45 (d, *J* = 13.7 Hz, 2H, *H*15b), 5.44 (d, *J* = 15.6 Hz, 4H, *H*4a), 5.36 (d, *J* = 15.6 Hz, 4H, *H*4b). **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6, 25 °C): δ (ppm) = 183.9 (C1), 154.6 (*C*5/*C*9/*C*10), 154.2 (*C*5/*C*9/*C*10), 149.2 (*C*14), 138.1 (*C*7), 136.9 (*C*12), 124.5 (*C*3), 124.3 (*C*13), 122.0 (*C*2), 121.6 (*C*6), 120.2 (*C*11), 119.6 (*C*8), 62.2 (*C*15), 55.1 (*C*4). At 154.2 ppm two signals of the quarternary carbon atoms *C*5/*C*9/*C*10 are overlapping. **ESI-MS** (CH_2Cl_2): *m/z* (%) = 681.19 $[M]^{2+}$ (100). **IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 3170 (w), 3131 (w), 3051 (w), 3021 (w), 1582 (m), 1564 (m), 1459 (m), 1450 (m), 1430 (s), 1380 (w), 1331 (w), 1288 (w), 1244 (m), 1193 (w), 1171 (w), 1077 (s), 992 (m), 975 (w), 958 (w), 932 (w), 899 (w), 856 (w), 823 (w), 791 (w), 763 (s), 726 (w), 680 (w), 675 (w), 660 (w), 643 (w), 636 (w), 621 (s), 597 (w), 573 (w), 454 (w), 403 (w). **EA:** $C_{58}H_{48}N_{16}Au_2Cl_2O_8$ (1561.94): calculated C 44.60; H 3.10; N 14.35; found C 44.52; H 3.02; N 14.28.

Synthesis of $[(\mathbf{L})_2Au_2Cu_2][ClO_4]_4$ (**3a**)



$[(\mathbf{L})_2Au_2][ClO_4]_2$ (100 mg, 0.0641 mmol, 1.0 eq.) and $[Cu(MeCN)_4][ClO_4]$ (42.0 mg, 0.128 mmol, 2.0 eq.) are stirred in acetonitrile for 18 h. The solution is filtered if necessary. After reducing the volume under vacuum, the product is precipitated with Et_2O. The solid is collected by filtration, washed with dichloromethane (2 x 10 mL) and Et_2O and dried under vacuum. Yield (red powder): 116 mg, 0.0612 mmol, 96%. **^{1}H NMR** (300 MHz, MeCN-*d₃*, 25 °C): δ (ppm) = 8.88 – 6.11 (m, 40H), 5.51 – 4.74 (m, 8H). **^{13}C{^{1}H} NMR** (75 MHz, MeCN-d_3, 25 °C): δ (ppm) = 185.9 (*C*1), 156.6, 153.2, 152.5, 150.4, 140.7, 139.5, 127.8, 123.7, 123.2, 122.5, 63.8 (*C*15), 56.4 (*C*4). Due to limited solubility and the broadness of the signals, some resonances could not be detected in the ^{13}C{^{1}H} NMR experiment. **IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 3169 (w), 3132 (w), 3113 (w), 1598 (m), 1572 (m), 1453 (m), 1410 (m), 1377 (w), 1331 (w), 1299 (w), 1245 (m), 1171 (w), 1075 (s), 959 (w), 929 (w), 875 (w), 768 (s), 704 (w), 652 (w), 620 (s), 450 (w), 409 (w). **EA:** $C_{58}H_{48}N_{16}Au_2Cu_2Cl_4O_{16} \cdot CH_2Cl_2$ (1972.87): calculated C 35.92; H 2.55; N 11.36; found C 35.66; H 2.65; N 11.44.

Synthesis of $[(\mathbf{L})_2Au_2Ag_2][ClO_4]_4$ (**3b**)



The synthetic procedure is identical to **3a**.

$[(\mathbf{L})_2Au_2][ClO_4]_2$ (100 mg, 0.0641 mmol, 1.0 eq.); $AgClO_4$ (26.6 mg, 0.128 mmol, 2.0 eq.). Yield (colourless powder): 112 mg, 0.0566 mmol, 88 %. Single crystals can be obtained by slow diffusion of Et_2O into an acetonitrile solution. **^{1}H NMR** (300 MHz, MeCN-d_3, 25 °C): δ (ppm) = 8.41 – 8.29 (m, 8H), 8.12 (t, *J* = 7.9 Hz, 4H), 8.09 – 8.01 (m, 8H), 7.52 – 7.40 (m, 16H), 6.07 (d, *J* = 13.9 Hz, 2H, *H*15a), 5.61 (d, *J* = 15.5 Hz, 4H, *H*4a), 5.54 (d, *J* = 15.5 Hz, 4H, *H*4b), 5.33 (d, *J* = 14.0 Hz, 2H, *H*15b). **^{13}C{^{1}H} NMR** (75 MHz, MeCN-d_3, 25 °C): δ (ppm) = 183.0 (*C*1), 155.9, 153.3, 152.3, 151.3, 141.7, 140.4, 126.9, 125.9, 125.1, 124.5, 124.1, 123.7, 63.2 (*C*15), 58.3 (*C*4). **IR** (ATR): $\tilde{\nu}$ (cm^{-1}) = 3167 (w), 3132 (w), 3112 (w), 1592 (m), 1576 (m), 1484 (w), 1454 (w), 1413 (w), 1382 (w), 1330 (w), 1249 (m), 1180 (w), 1159 (w), 1077 (s), 1008 (m), 930 (w), 877 (w), 827 (w), 772 (s), 705 (w), 675 (w), 667 (w), 649 (w), 621 (s). **EA:** $C_{58}H_{48}N_{16}Ag_2Au_2Cl_4O_{16}$ (1976.58): calculated C 35.24; H 2.45; N 11.34; found C 35.05; H 2.71; N 11.41.

NMR spectra

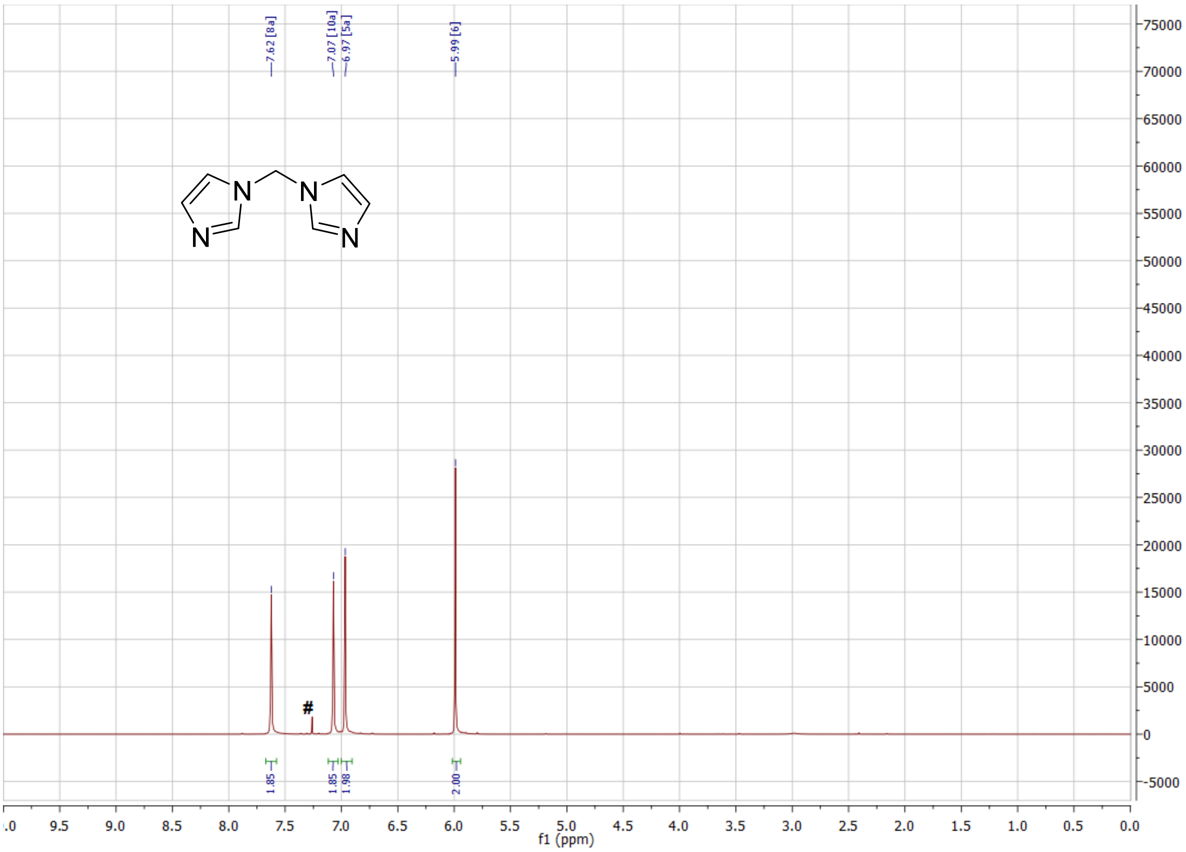


Figure S 1: ^{1}H NMR spectrum of **I** in $CDCl_3$ (#: solvent peak)

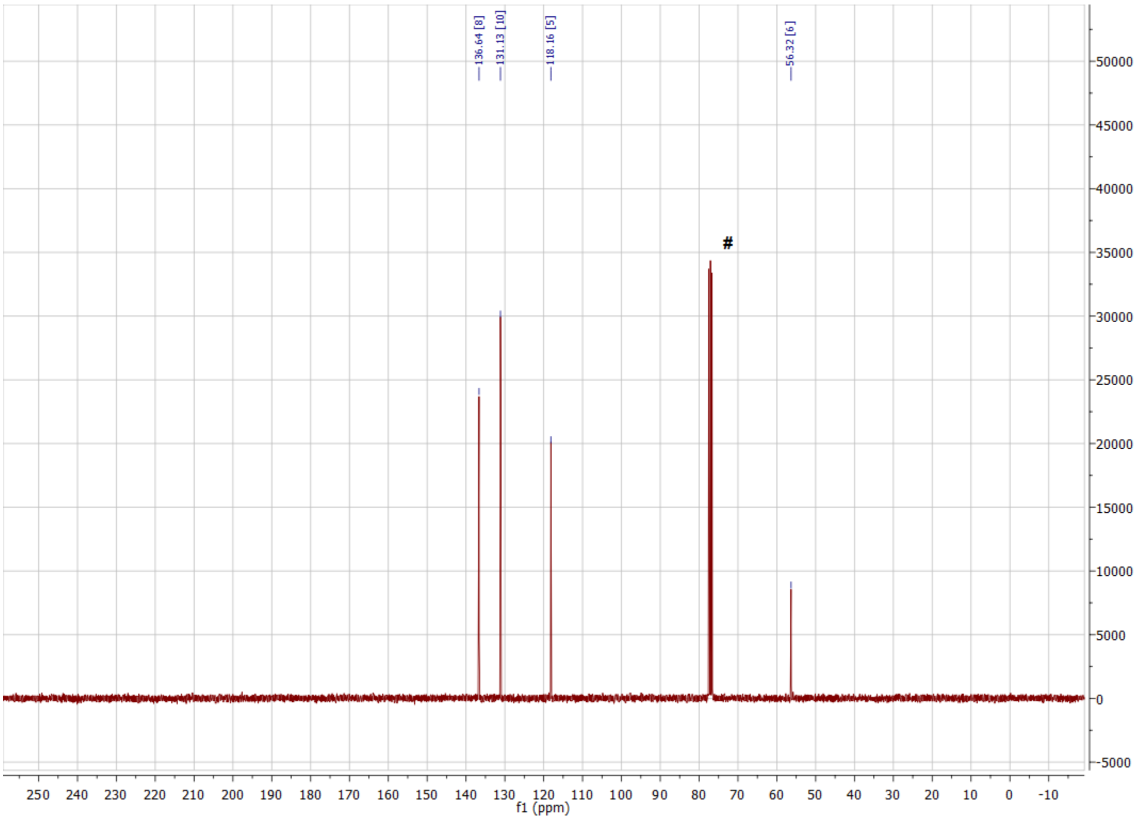


Figure S 2: $^{13}C\{^{1}H\}$ NMR spetrum of **I** in $CDCl_3$. (#: solvent peak)

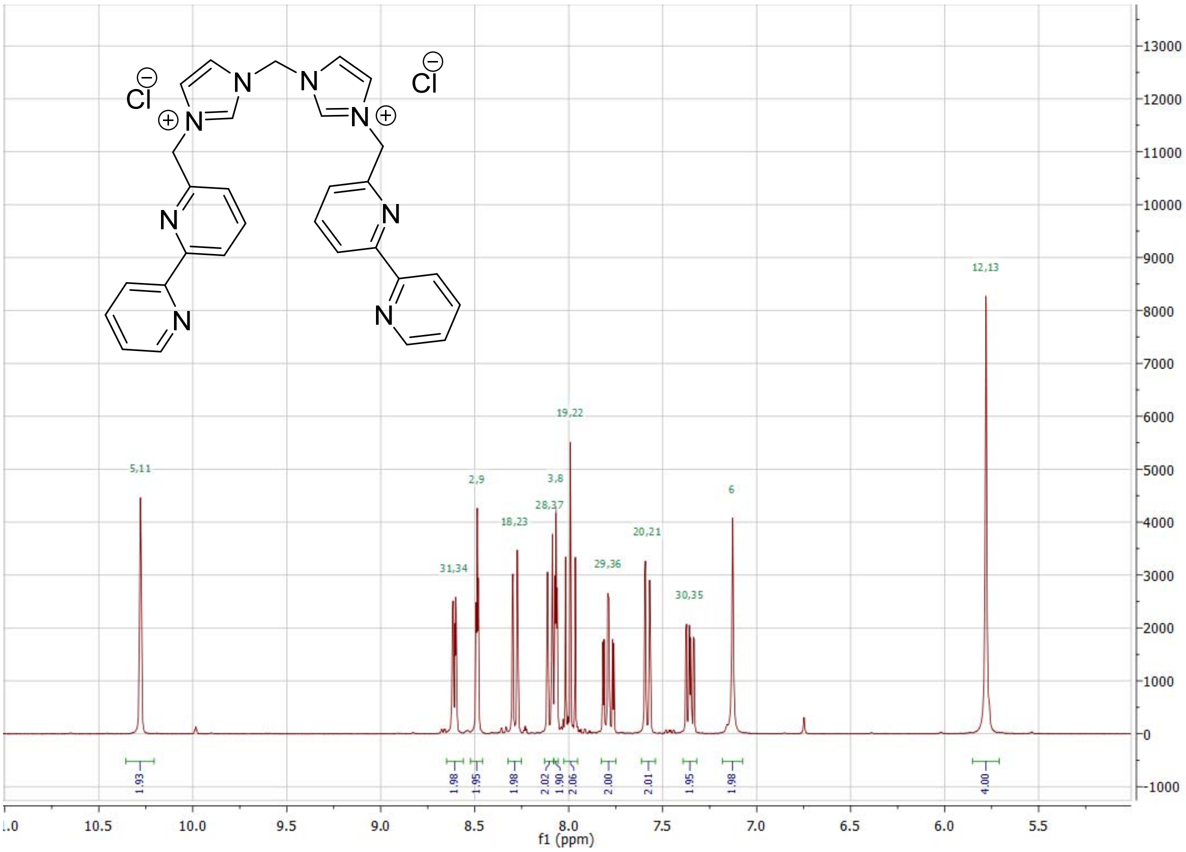


Figure S 3: ^{1}H NMR spectrum of **L(2 HCl)** in DMSO-d$_6$.

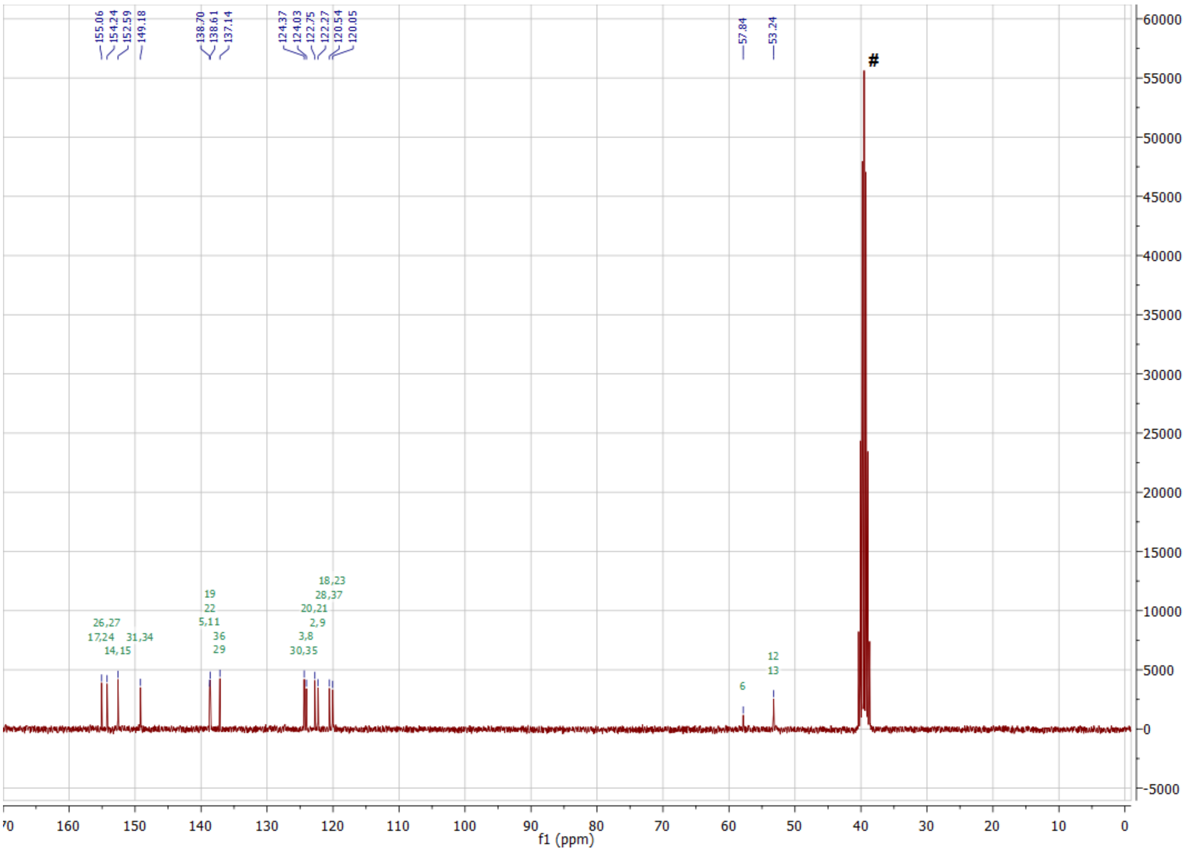


Figure S 4: ^{13}C{^{1}H} NMR spectrum of **L(2 HCl)** in DMSO-d$_6$. (#: solvent peak)

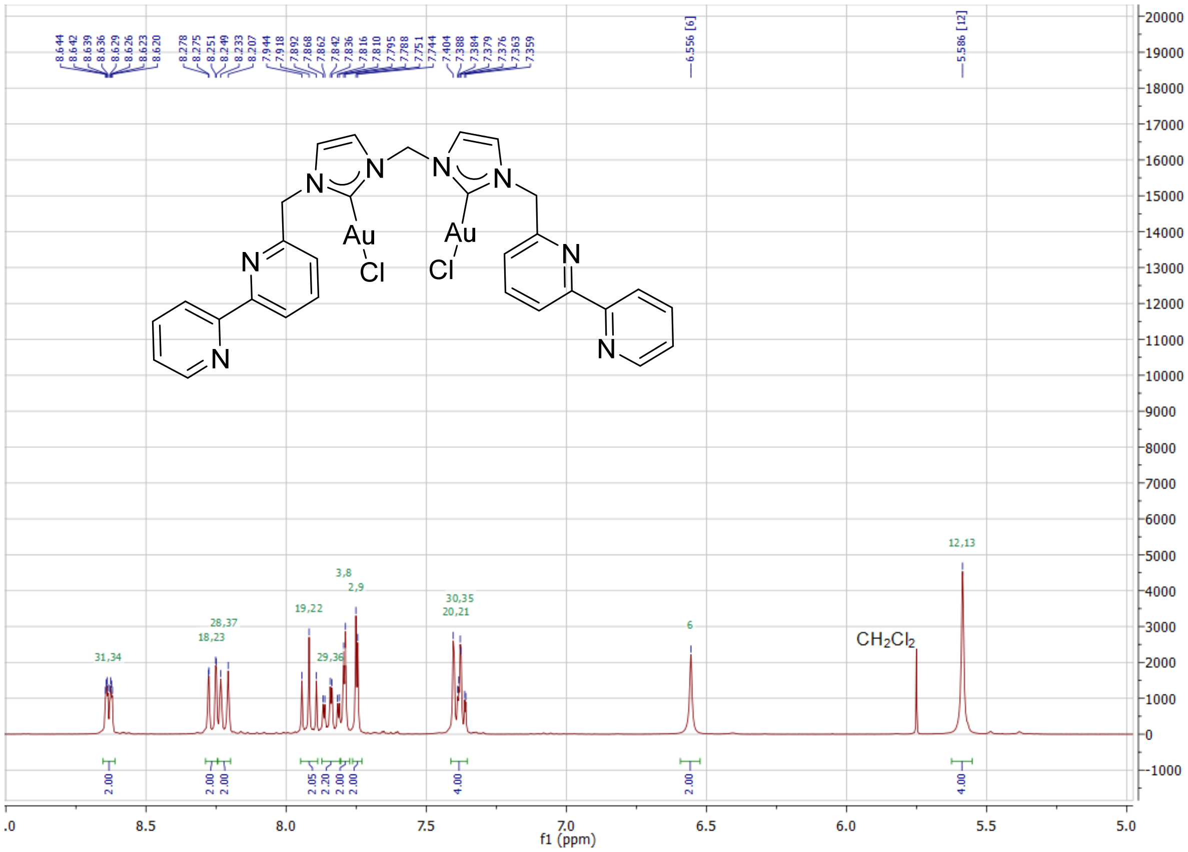


Figure S 5: ^{1}H NMR spectrum of **1** in DMSO-d$_6$.

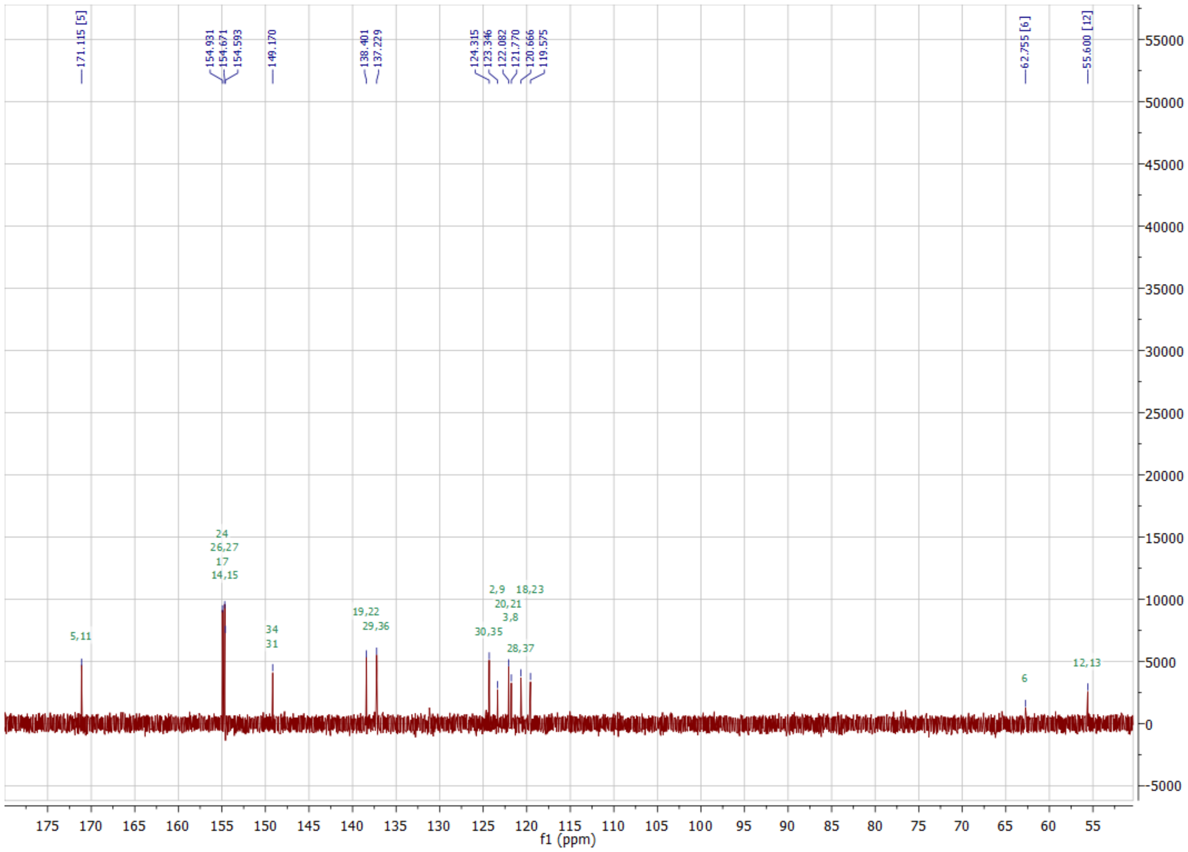


Figure S 6: ^{13}C{^{1}H} NMR spectrum of **1** in DMSO-d$_6$.

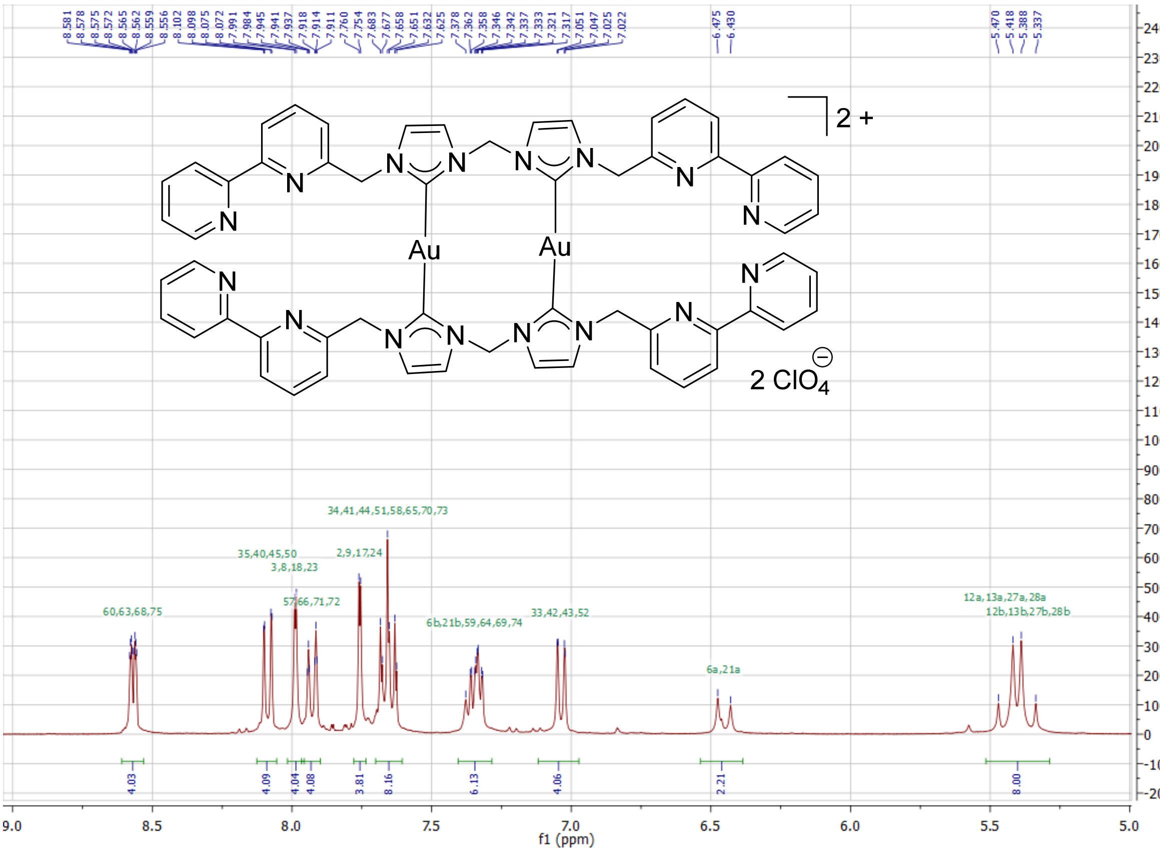


Figure S 7: ^{1}H NMR spectrum of **2** in DMSO-d$_6$.

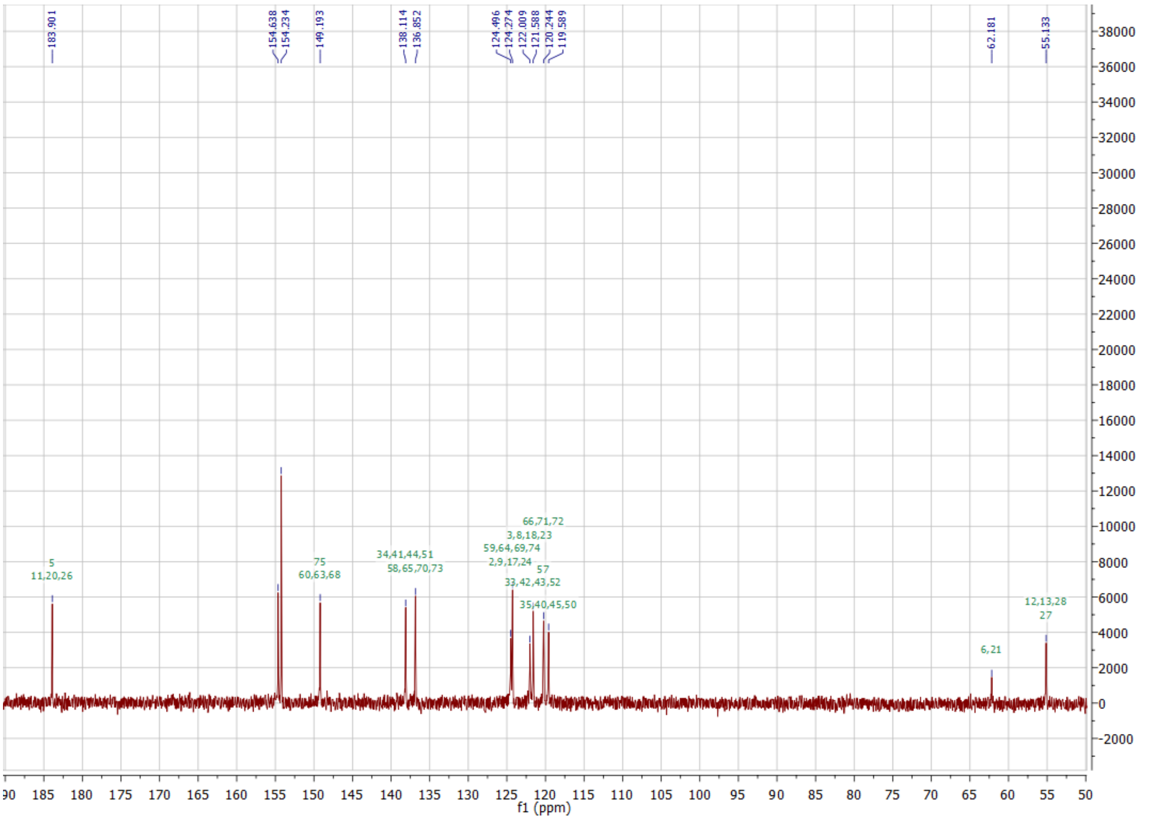


Figure S 8: ^{13}C{^{1}H} NMR spectrum of **2** in DMSO-d$_6$.

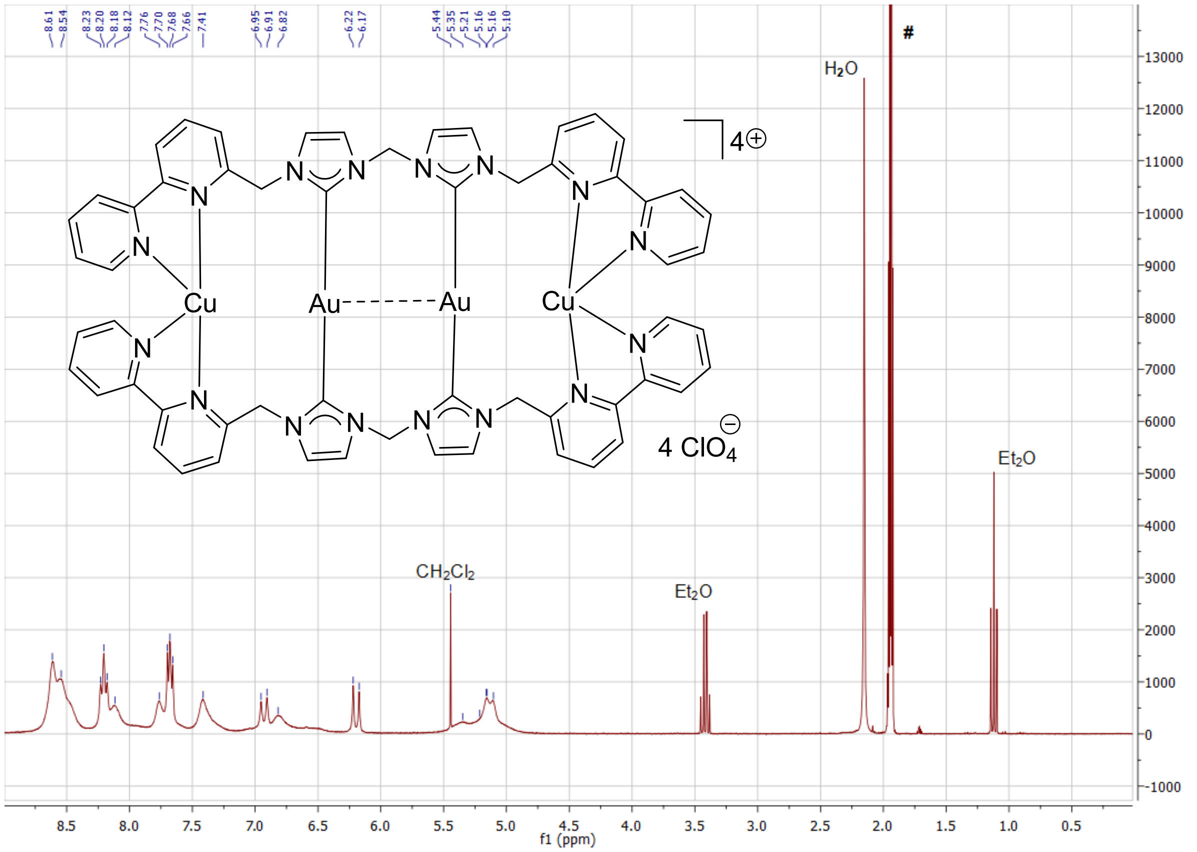


Figure S 9: ^{1}H NMR spectrum of **3a** in MeCN-d_3. (#: solvent peak)

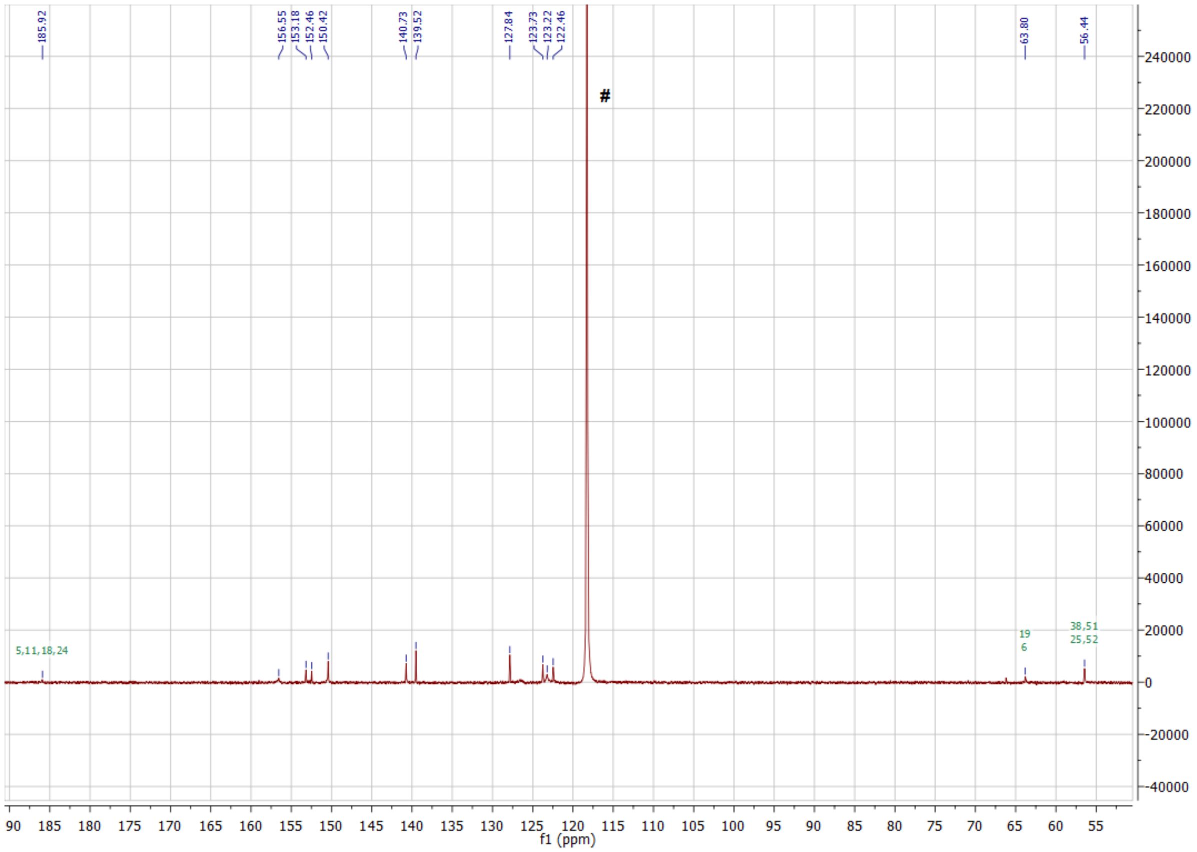


Figure S 10: ^{13}C{^{1}H} NMR spectrum of **3a** in MeCN-d_3. (#: solvent peak)

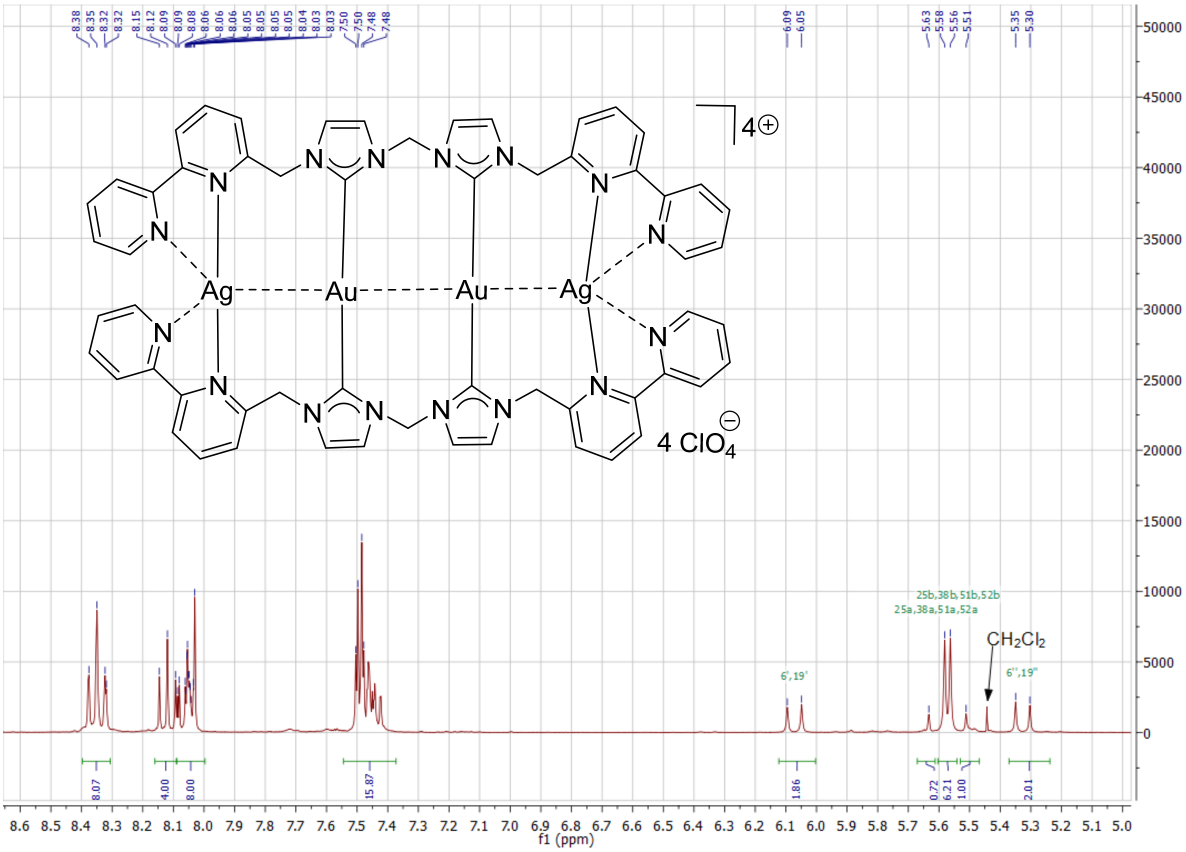


Figure S 11: ^{1}H NMR spectrum of **3b** in MeCN-d$_3$.

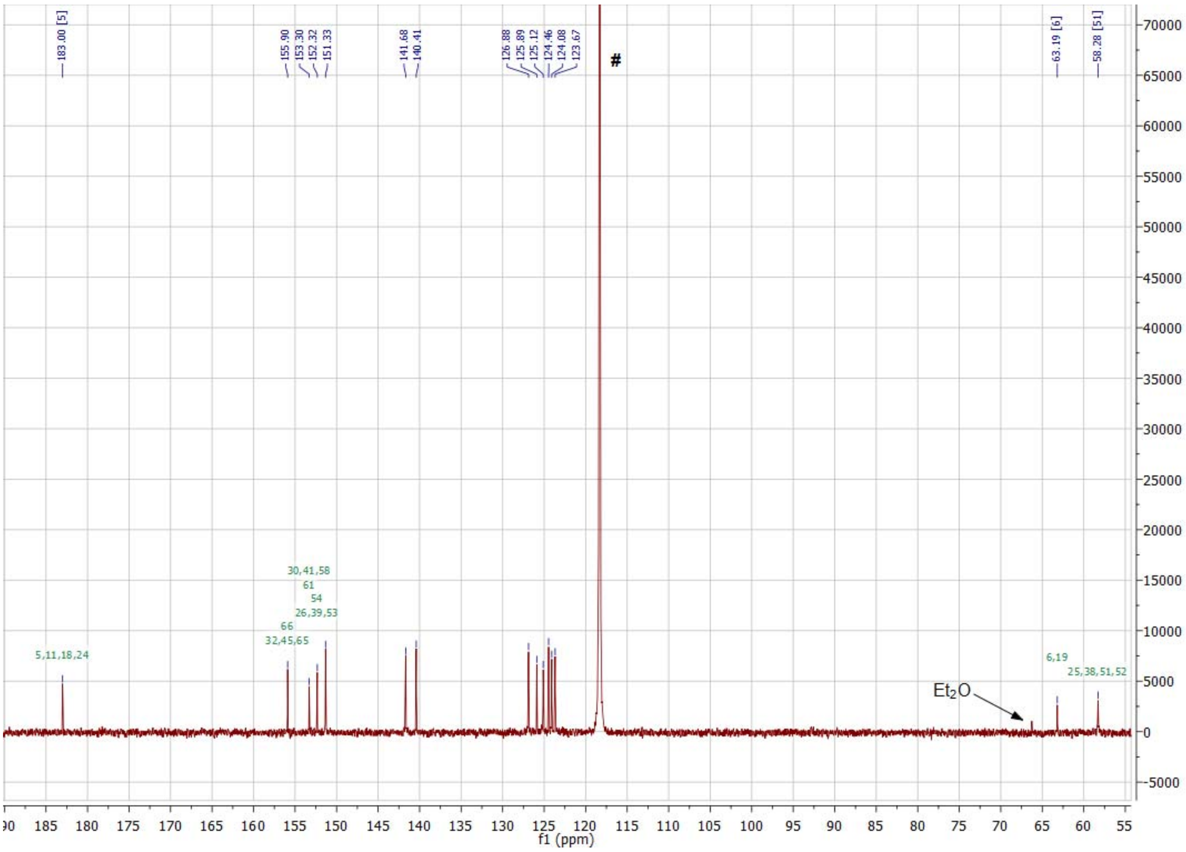


Figure S 12: ^{13}C{^{1}H} NMR spectrum of **3b** in MeCN-d$_3$. (#: solvent peak)

Crystallographic appendix

X-ray crystallographic studies: A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or a STOE StadiVari diffractometer. All structures were solved by direct methods or by the Patterson method (SHELXS-2013)[6] using the OLEX2 GUI.[7] The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_0 - F_c)^2$, where the weight is defined as $4F_0^2/2(F_0^2)$ and F_0 and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-2013.[8] Carbon-bound hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. In some structures, highly disordered solvent molecules were removed using the PLATON[9] SQEEZE[10] routine.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 1556510-1556513. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Compound	**L**(2 HCl)	**1**	**3a**	**3b**
ID code	**CCK266-4**	**CCK274-5**	**CCK333-1**	**CCK334-1**
Formula	$C_{29}H_{26}Cl_2N_8$	$C_{29}H_{24}Au_2Cl_2N_8$	$C_{58}H_{48}Au_2Cl_4Cu_2N_{16}O_{16}$	$C_{60}H_{51}Ag_2Au_2Cl_4N_{17}O_{16}$
$D_{calc.}$/ g cm^{-3}	1.370	1.901	1.720	1.857
μ/mm^{-1}	0.276	9.027	4.806	4.812
Formula Weight	557.48	949.39	1887.93	2017.65
Colour	clear colourless	clear colourless	clear red	clear colourless
Shape	fragment	prism	plate	prism
Size/mm^3	0.41×0.24×0.14	0.27×0.20×0.11	0.21 × 0.111 × 0.046	0.415 × 0.314 × 0.144
T/K	210(2)	210(2)	110(2)	210(2)
Crystal System	triclinic	orthorhombic	monoclinic	triclinic
Space Group	*P*-1	*Fddd*	*C*2/*c*	*P*-1
a/Å	11.9504(9)	10.5556(6)	44.7148(14)	14.6489(5)
b/Å	12.7279(10)	28.004(2)	13.6599(3)	19.5901(7)
c/Å	17.9011(13)	44.889(3)	25.8961(8)	26.9914(10)
α/°	92.009(6)	90	90	91.502(3)
β/°	96.335(6)	90	112.789(2)	101.697(3)
γ/°	92.319(6)	90	90	107.160(3)
V/Å^3	2701.8(4)	13269.1(15)	14582.6(7)	7216.6(5)
Z	4	16	8	4
Z'	2	0.5	1	2
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Radiation type	MoK$_a$	MoK$_a$	MoK$_a$	MoK$_a$
Θ_{min}/°	1.602	1.714	1.570	1.521
Θ_{max}/°	26.221	25.173	26.092	26.128
Measured Refl.	20969	8670	34765	54370
Independent Refl.	10600	2964	14227	28168
Reflections Used	6315	1907	9443	18905
R_{int}	0.0356	0.0412	0.0677	0.0401
Parameters	703	186	910	1851
Restraints	0	0	138	169
Largest Peak	0.191	0.958	2.153	1.839
Deepest Hole	-0.182	-0.925	-1.730	-1.489
GooF	0.925	0.887	0.952	0.998
wR_2 (all data)	0.0844	0.0750	0.1566	0.1234
wR_2	0.0778	0.0706	0.1418	0.1141
R_1 (all data)	0.0775	0.0548	0.0867	0.0781
R_1	0.0372	0.0317	0.0563	0.0454

1: One molecule of dichloromethane in the asymmetric unit was found to be disordered over multiple positions and could therefore not be modelled satisfactorily. It was removed from the electron density map using the OLEX solvent mask command.

3a: One molecule of diethylether could not be modelled satisfactorily and was therefore removed from the electon density map using the OLEX2 solvent mask command. One $[ClO_4]^-$ anion was disordered over two positions and each part was refined with 50 % occupancy using rigid group model.

3b: Two molecules of acetonitrile could not be modelled satisfactorily and were therefore removed from the electron density map using the SQEEZE command in PLATON. One molecule of acetonitrile as well as one $[ClO_4]^-$ anion were disordered over two positions and each part was refined with 50 % occupancy using a rigid group model.

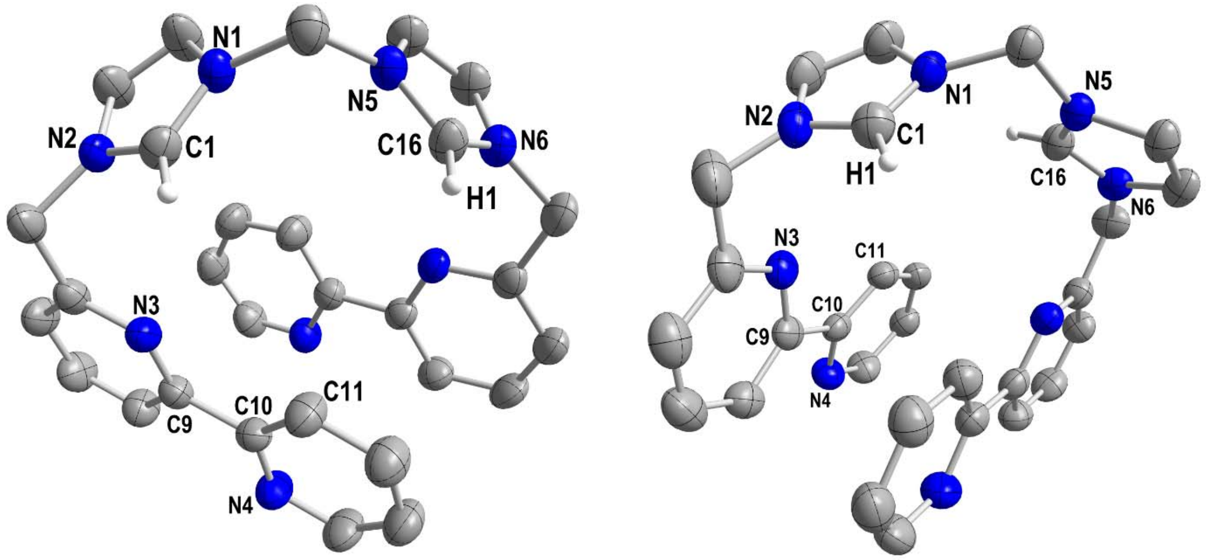


Figure S 13: Molecular structure of the cation of **L(**2 HCl**)** in the solid-state. Hydrogen atoms except for H1 & H16 are omitted for clarity. Ellipsoids displayed at 50 % probability. **Left:** Selected bond lengths [Å] and angles [°]: N1-C1 1.331(2), N2-C1 1.379(2), N6-C16 1.311(2), N5-C16 1.324(2); N1-C1-N2 108.3(2), N5-C16-N6 108.4(2), N3-C9-C10-C11 5.3(1), N7-C24-C25-C26 0.7(1). **Right:** Selected bond lengths [Å] and angles [°]: N1-C1 1.331(2), N2-C1 1.316(2), N6-C16 1.311(2), N5-C16 1.326(2); N1-C1-N2 108.2(2), N5-C16-N6 108.4(1), N3-C9-C10-C11 13.3(1), N7-C24-C25-C26 2.7(1).

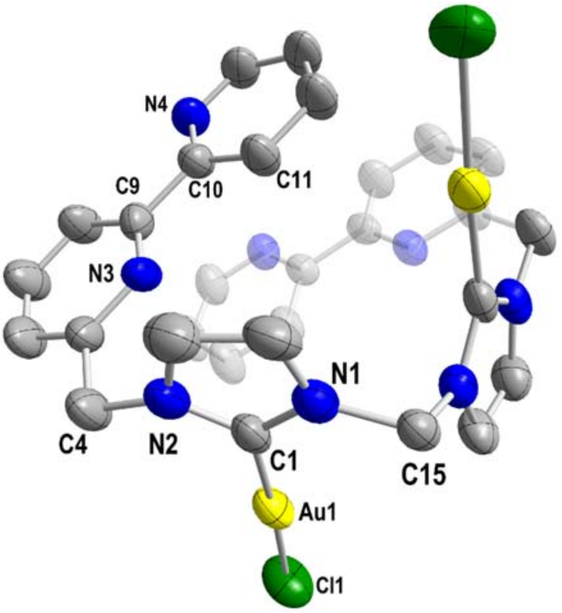


Figure S 14: Molecular structure of **1** in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50 % probability. Selected bond lengths [Å] and angles [°]: Au1-Au1‘ 5.9786(3), Au1-C1 1.973(7), Au1-Cl1 2.269(2), N1-C1 1.354(7), N2-C1 1.372(8); C1-Au1-Cl1 176.6(2), N1-C1-Au1 127.4(5), N2-C1-Au1 127.8(5), N1-C1-N2 104.7(6), N3-C9-C10-C11 2.6(1).

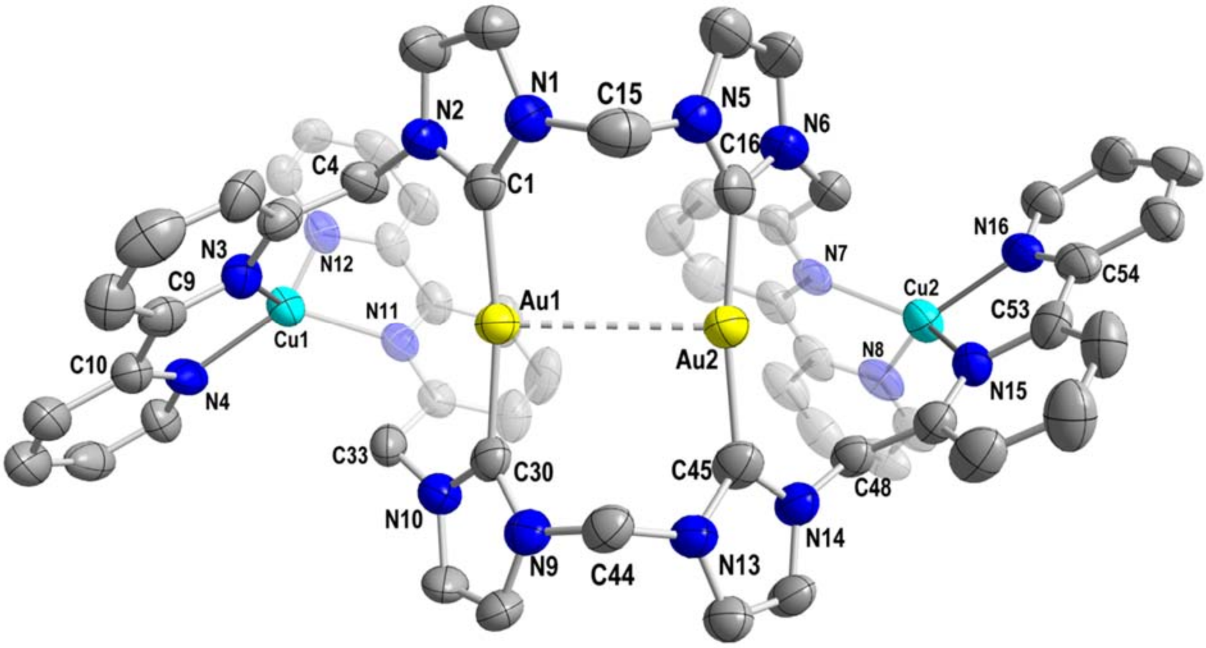


Figure S 15: Molecular structure of the cation of **3a** in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50 % probability. Selected bond lengths [Å] and angles [°]: Au1-Au2 3.3828(1), Au1-Cu1 4.9493(1), Au2-Cu2 4.9476(1), Au1-C1 2.018(9), Au1-C30 2.041(9), Au2-C16 2.021(10), Au2-C45 2.057(10), Cu1-N3 2.032(7), Cu1-N4 2.006(7), Cu1-N11 2.047(7), Cu1-N12 1.991(7), Cu2-N7 2.052(8), Cu2-N8 2.007(8), Cu2-N15 2.048(7), Cu2-N16 2.012(7), N1-C1 1.357(10), N2-C1 1.356(11), N5-C16 1.352(13), N6-C16 1.367(13); C1-Au1-C30 172.0(3), C16-Au2-C45 171.9(4), N1-C1-Au1 131.5(1), N2-C1-Au1 124.6(1), N3-Cu1-N4 81.4(3), N3-Cu1-N11 116.1(3), N3-Cu1-N12 123.0(3), N4-Cu1-N11 126.1(3), N4-Cu1-N12 132.9(3), N11-Cu1-N12 81.9(3), N7-Cu2-N8 81.8(4), N7-Cu2-N15 117.9(3), N7-Cu2-N16 122.4(3), N8-Cu2-N15 127.2(3), N8-Cu2-N16 131.5(3), N15-Cu2-N16 81.2(3), N1-

C1-N2 103.6(1), N5-C16-N6 104.4(1), N1-C1-C30-N9 9.2(1), N5-C16-C45-N13 7.1(1), N3-C9-C10-N4 3.6(1), N15-C53-C54-N16 4.7(1).

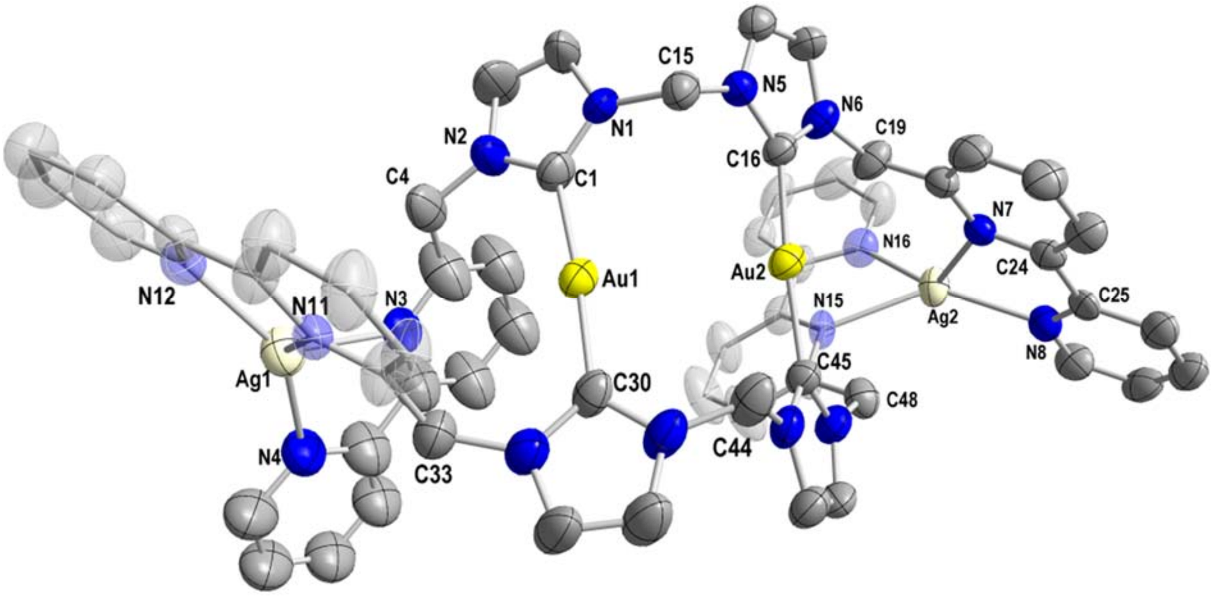


Figure S 16: Molecular structure of the cation of **3b (V-shaped)** in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50 % probability. Selected bond lengths [Å] and angles [°]: Au1-Au2 3.8054(2), Au1-Ag1 5.1364(2), Au2-Ag2 5.1789(2), Au1-C1 2.026(7), Au1-C30 2.009(8), Au2-C16 2.015(7), Au2-C45 2.021(7), Ag1-N3 2.356(7), Ag1-N4 2.267(8), Ag1-N11 2.434(8), Ag1-N12 2.243(8), Ag2-N7 2.423(6), Ag2-N8 2.269(6), Ag2-N15 2.434(6), Ag2-N16 2.224(7), N1-C1 1.351(10), N2-C1 1.332(10), N5-C16 1.385(9), N6-C16 1.338(9); C1-Au1-C30 174.8(3), C16-Au2-C45 174.2(3), N1-C1-Au1 129.445(2), N2-C1-Au1 125.145(2), N3-Ag1-N4 72.2(3), N3-Ag1-N11 108.5(2), N3-Ag1-N12 132.1(3), N4-Ag1-N11 129.7(3), N4-Ag1-N12 146.2(3), N11-Ag1-N12 71.0(2), N7-Ag2-N8 71.5(2), N7-Ag2-N15 104.3(2), N7-Ag2-N16 125.3(2), N8-Ag2-N15 134.0(2), N8-Ag2-N16 148.8(3), N15-Ag2-N16 71.8(3), N1-C1-N2 105.406(3), N5-C16-N6 103.993(3), N1-C1-C30-N9 11.8757(7), N5-C16-C45-N13 18.228(1), N11-C38-C39-N12 10.6520(6), N7-C24-C25-N8 5.4773(3).

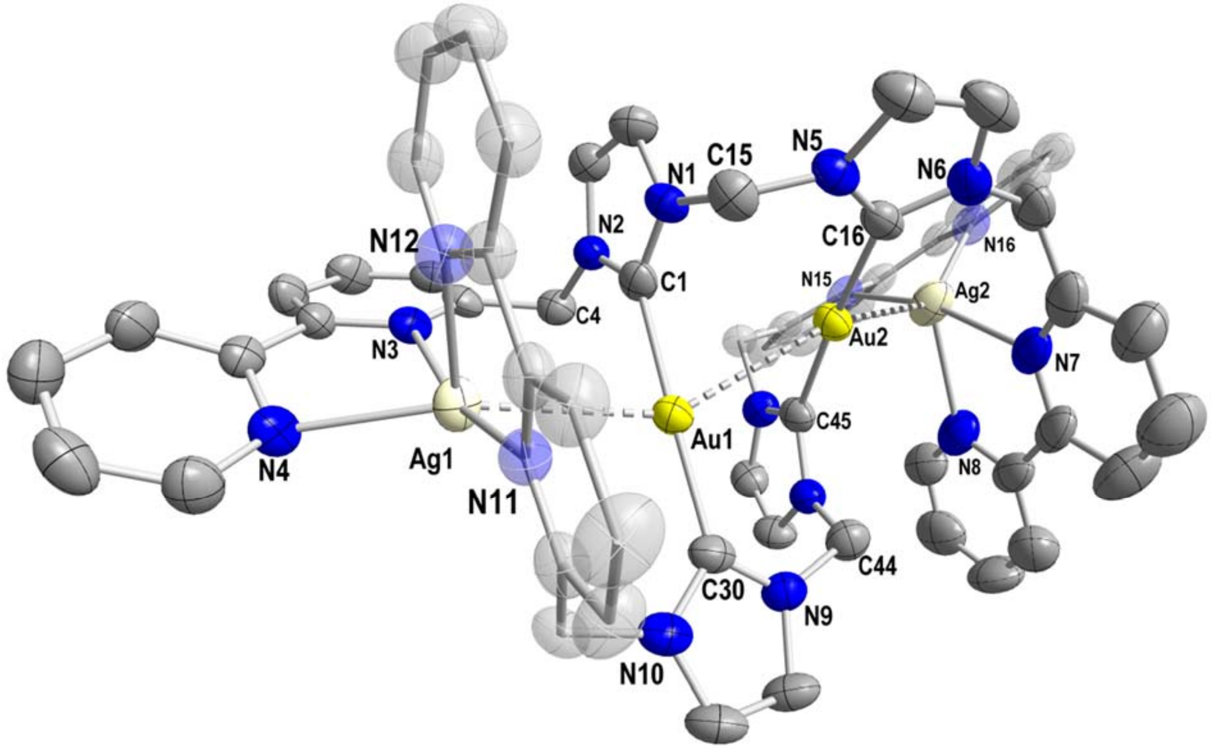


Figure S 17: Molecular structure of the cation of **3b (linear)** in the solid-state. Hydrogen atoms are omitted for clarity. Ellipsoids displayed at 50% probability. Selected bond lengths [Å] and angles [°]: Au1-Au2 3.0501(5), Au1-Ag1 2.9894(7), Au2-Ag2 2.9585(8), Au1-C1 2.032(7), Au1-C30 2.016(7), Au2-C16 2.035(7), Au2-C45 2.035(7), Ag1-N3 2.419(5), Ag1-N4 2.396(6), Ag1-N11 2.386(5), Ag1-N12 2.402(6), Ag2-N7 2.337(7), Ag2-N8 2.397(8), Ag2-N15 2.382(6), Ag2-N16 2.331(7), N1-C1 1.336(9), N2-C1 1.343(8), N5-C16 1.362(9), N6-C16 1.345(10); Ag1-Au1-Au2 147.57(2), Au1-Au2-Ag2 152.71(2), C1-Au1-C30 178.9(3), C16-Au2-C45 175.1(3), N1-C1-Au1 125.110(2), N2-C1-Au1 129.390(2), N3-Ag1-N4 70.2(2), N3-Ag1-N11 165.9(2), N3-Ag1-N12 98.0(2), N4-Ag1-N11 114.8(2), N4-Ag1-N12 98.0(2), N11-Ag1-N12 68.5(2), N7-Ag2-N8 70.0(3), N7-Ag2-N15 166.1(3), N7-Ag2-N16 117.7(2), N8-Ag2-N15 96.4(2), N8-Ag2-N16 115.5(2), N15-Ag2-N16 70.5(2), N1-C1-N2 105.480(3), N5-C16-N6 105.250(4), N1-C1-C30-N9 87.603(3), N5-C16-C45-N13 85.014(3), N3-C9-C10-N4 26.542(2), N11-C38-C39-N12 9.6638(6), N7-C24-C25-N8 2.2757(2), N15-C53-C54-N16 14.5813(8),

Photoluminescence measurements

PL measurements were performed with a Horiba JobinYvon Fluorolog-322 spectrometer equipped with a closed-cycle optical cryostat (Leybold) operating at ~16-300K. Hamamatsu R9910 and R5508 photomultipliers were used as detectors covering the emission spectral range of ~300-800 and ~450-1400 nm, respectively. Solid samples (crystalline powders) were measured as dispersions in a thin layer of polyfluoroester oil (ABCR GmbH) between two 1 mm thin quartz plates. The latter were then fixed on a cold finger of the cryostat. All emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). Emission decay traces were recorded by connecting a photomultiplier to an oscilloscope (typically via a 500 or 50 Ohm load). A frequency-quadrupled Nd:YAG laser at 266 nm (~8 ns, ~10 μJ per pulse) and a N_2–laser at 337 nm (~2 ns, ~5 μJ per pulse) were used for pulsed excitation of complexes **1** and **2**, **3a**,**b**, respectively. Figure S 18 shows exemplary PL decay traces for **1** and **3b**.

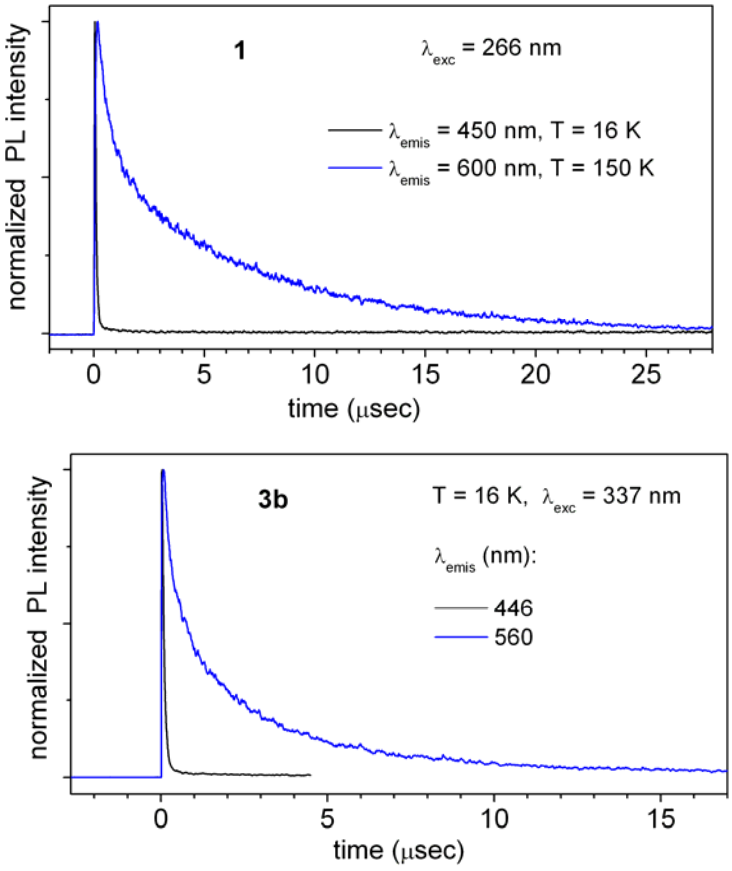


Figure S 18: PL decay curves recorded for solid compounds **1** and **3b** at different emission wavelengths and temperatures (cf. Figure 5 in text).

Absorption spectra of solid complexes **3a**,**b** (Figure S 19) were obtained at ambient temperature for the same sample preparations as for the PL measurements, using an integrating sphere which was placed into the sample chamber of the Fluorolog spectrometer. A tungsten halogen lamp light source was applied as providing a smooth and stable excitation spectral curve. The absorption spectra were referenced to those obtained with the empty integrating sphere.

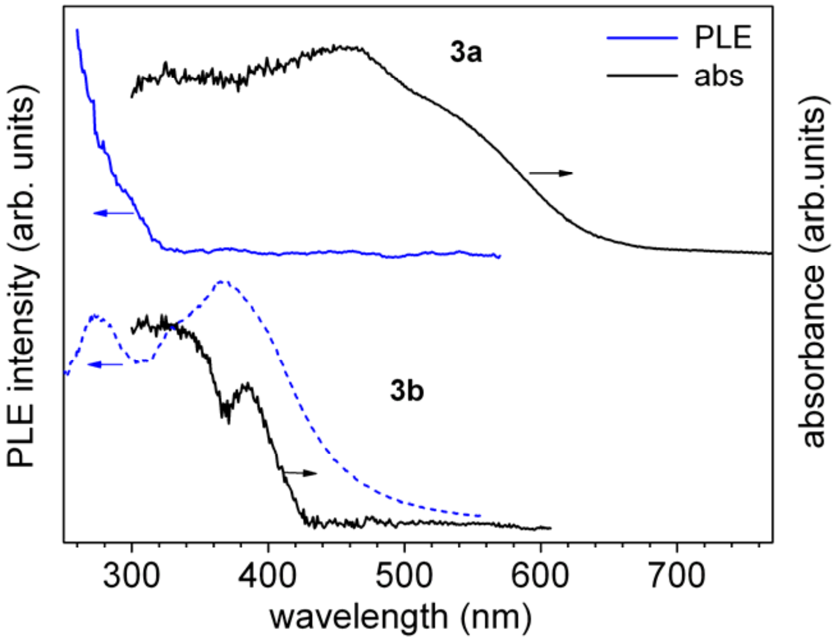
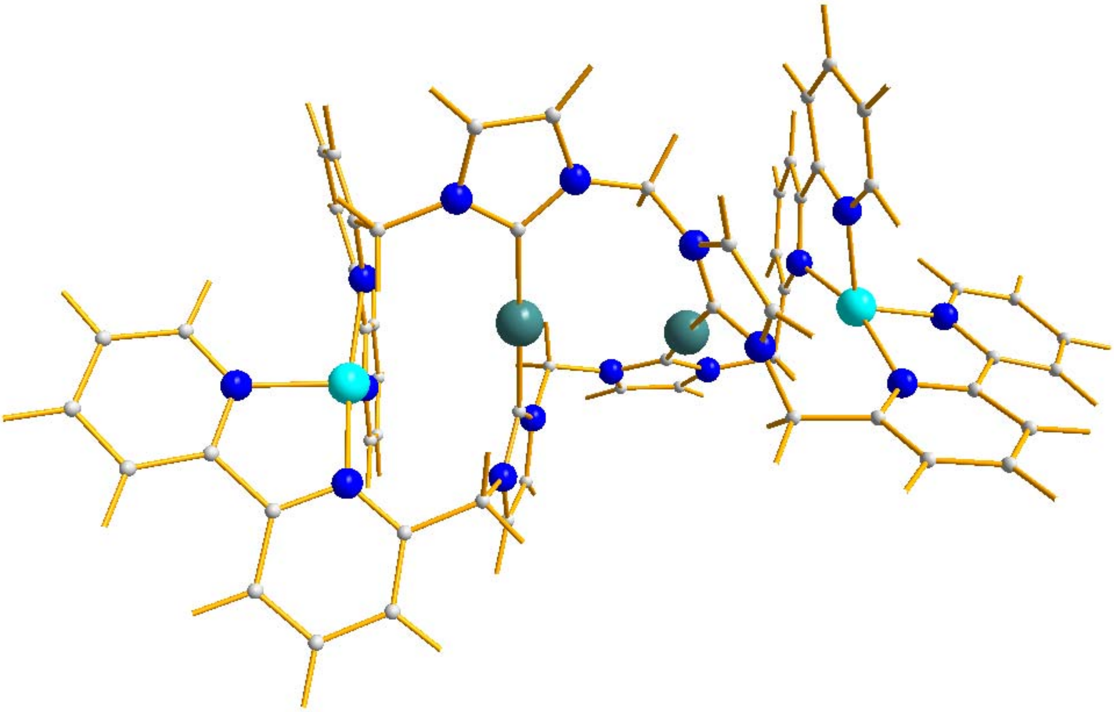
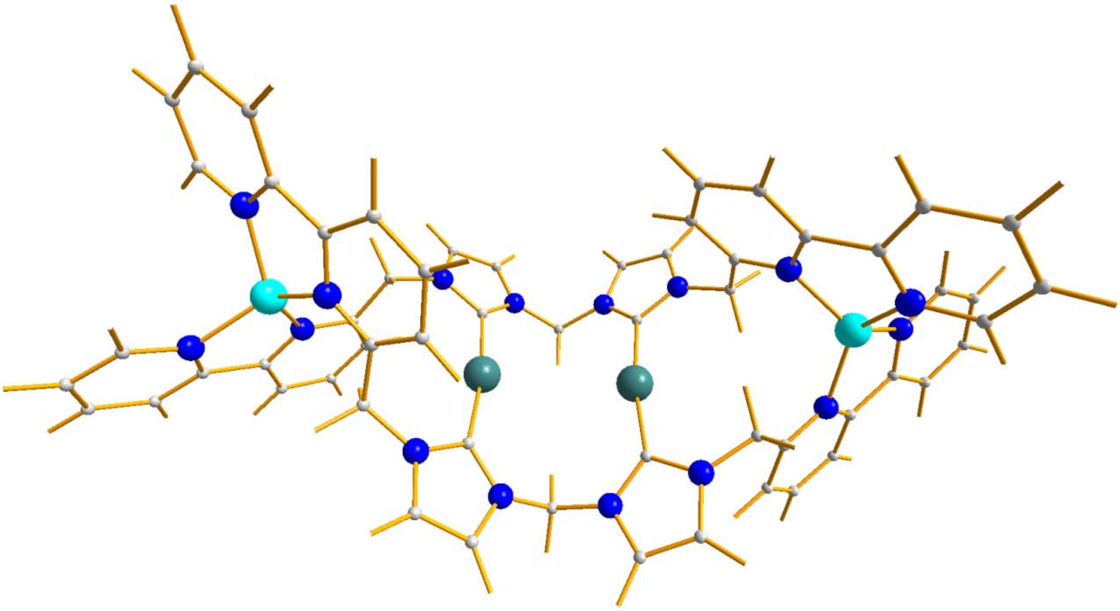


Figure S 19: Absorption and photoluminescence excitation (PLE) spectra of solid compounds **3a**,**b** at ambient temperature. The absorption spectra were measured using an integrating sphere. The PLE spectra were recorded at the emission wavelength of 750 and 600 nm for **3a** and **3b**, respectively.

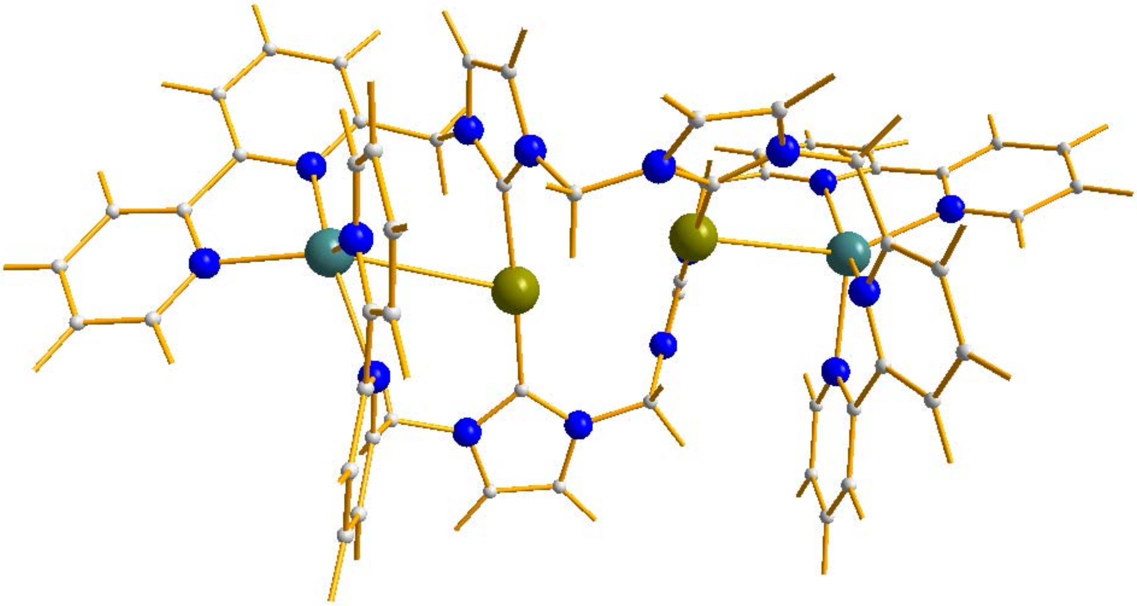
DFT Calculations



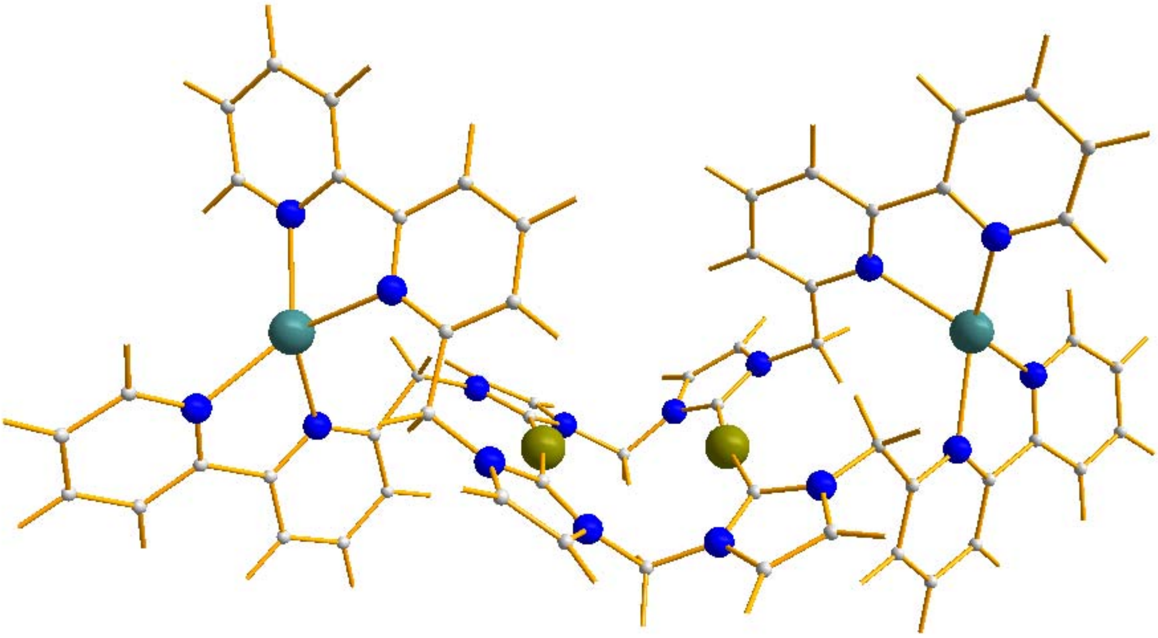
Cu2Au2_twist
3 cu -- 11 n = 202.14 pm
4 cu -- 13 n = 202.18 pm
3 cu -- 30 n = 204.04 pm
3 cu -- 15 n = 204.05 pm
4 cu -- 35 n = 204.06 pm
4 cu -- 29 n = 204.08 pm
3 cu -- 10 n = 205.13 pm
4 cu -- 23 n = 205.16 pm
2 au -- 26 c = 203.97 pm
2 au -- 36 c = 203.99 pm
1 au -- 44 c = 204.00 pm
1 au -- 32 c = 204.04 pm
1 au -- 2 au = 352.10 pm
2 au -- 4 cu = 337.62 pm
1 au -- 3 cu = 338.05 pm



Cu2Au2_coplanar
4 cu -- 37 n = 200.81 pm
3 cu -- 12 n = 200.87 pm
3 cu -- 15 n = 200.89 pm
4 cu -- 20 n = 200.93 pm
4 cu -- 10 n = 201.78 pm
3 cu -- 5 n = 201.80 pm
3 cu -- 25 n = 202.10 pm
4 cu -- 14 n = 202.20 pm
2 au -- 31 c = 203.73 pm
1 au -- 16 c = 203.75 pm
2 au -- 22 c = 203.75 pm
1 au -- 18 c = 203.78 pm
1 au -- 2 au = 369.43 pm
1 au -- 3 cu = 511.47 pm
2 au -- 4 cu = 511.47 pm



Ag2Au2_twist
3 ag -- 15 n = 229.95 pm
4 ag -- 23 n = 230.12 pm
4 ag -- 29 n = 230.18 pm
3 ag -- 10 n = 230.21 pm
3 ag -- 11 n = 232.11 pm
4 ag -- 13 n = 232.31 pm
3 ag -- 30 n = 240.99 pm
4 ag -- 35 n = 241.41 pm
2 au -- 36 c = 203.76 pm
1 au -- 32 c = 203.88 pm
2 au -- 26 c = 204.34 pm
1 au -- 44 c = 204.42 pm
1 au -- 2 au = 343.35 pm
1 au -- 3 ag = 344.67 pm
2 au -- 4 ag = 346.60 pm



Ag2Au2_coplanar
4 ag -- 37 n = 4.2538 au = 225.10 pm
3 ag -- 15 n = 4.2562 au = 225.23 pm
3 ag -- 12 n = 4.2676 au = 225.83 pm
4 ag -- 20 n = 4.2695 au = 225.93 pm
4 ag -- 10 n = 4.4574 au = 235.88 pm
3 ag -- 5 n = 4.4628 au = 236.16 pm
3 ag -- 25 n = 4.5070 au = 238.50 pm
4 ag -- 14 n = 4.5123 au = 238.78 pm
1 au -- 16 c = 3.8491 au = 203.68 pm
2 au -- 22 c = 3.8496 au = 203.71 pm
2 au -- 31 c = 3.8496 au = 203.71 pm
1 au -- 18 c = 3.8498 au = 203.72 pm
1 au -- 2 au = 6.9759 au = 369.15 pm
2 au -- 4 ag = 10.1370 au = 536.43 pm
1 au -- 3 ag = 10.1375 au = 536.46 pm

Theoretical calculations:
BP86/def2-TZVP

Cu2Au2_coplanar	-6669.2120977830 a.u.
Cu2Au2_twist	-6669.2114581770 a.u.
Ag2Au2_coplanar	-3681.7485575840 a.u.
Ag2Au2_twist	-3681.7507864920 a.u.

Cu2Au2_coplanar = Cu2Au2_twist ΔE= +1.7 kJ/mol
Ag2Au2_coplanar = Ag2Au2_twist ΔE= -5.9 kJ/mol

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