Gold Complexes with Tridentate Cyclometalating and NHC ligands: A Search for New Photoluminescent Au(III) Compounds

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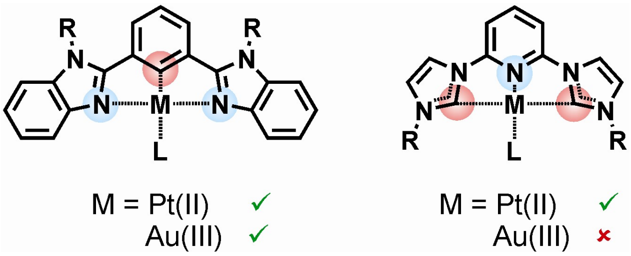
TOC Synopsis



Abstract

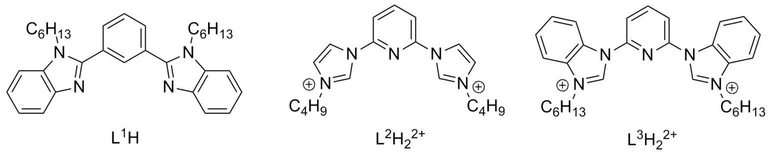
Many square-planar Pt(II) complexes are strongly photoluminescent, particularly when containing cyclometalating and/or NHC ligands which produce strong ligand fields. In this work we investigated the possibility of obtaining isoelectronic Au(III) complexes with favorable luminescence properties. Toward this end, the coordination chemistry of gold with three different (potentially) tridentate ligands was explored: 1,3-bis(1-hexyl-2'-benzimidazoyl)benzene (L^1H), 2,6-bis(3-butylimidazol-1-ium)pyridine ($L^2H_2^{2+}$), and 2,6-bis(3-hexylbenzimidazol-1-ium)pyridine ($L^3H_2^{2+}$). Pt(II) or Pd(II) complexes are known for all of these ligands or closely related analogues and hence we anticipated that similar Au(III) complexes would be synthetically accessible as well. This turned out to be the case only for L^1, despite exploration of different synthetic routes including (i) direct complexation of Au(III), (ii) transmetallation from Ag(I) precursor complexes, and (iii) transmetallation from suitable Hg(II) precursors. Only the mercury procedure was successful (at least in the case of L^1), transmetallation from silver or direct complexation yield other reaction products containing Au(I) in most cases. Likewise, with ligands L^2 and L^3 mainly complexes of Au(I) were obtained, i. e., the propensity of gold for low oxidation states is a major obstacle to obtaining the desired Au(III) compounds. Several new complexes of Au(I) and Au(III) were characterized crystallographically. Our results provide insight into the differences between the coordination chemistry of isoelectronic Pt(II) and Au(III) with tridentate cyclometalating and NHC ligands.

1. Introduction

In purely organic light-emitting diodes (OLEDs) one is confronted with the problem that electrogenerated triplet excited states dissipate their energy to a large extent nonradiatively, leading to lower electroluminescence quantum yields than what is possible with transition metal doped OLEDs. Iridium(III) and platinum(II) complexes have received much attention as so-called triplet harvesters in OLEDs because many of them emit from excited states that have mixed ^{3}MLCT/^{3}IL character (MLCT = metal-to-ligand charge transfer; IL = intraligand), exhibiting high luminescence quantum yields and good color tunability combined with good (photo)chemical stability.[1-5] Complexes with the most favorable properties often contain cyclometalating ligands which induce strong ligand fields, making nonradiative relaxation from d-d excited states inefficient. While numerous Pt(II) complexes of this type exist, there has yet been a limited amount of work on isoelectronic Au(III) complexes as we already noted in a recent review.[6] Over the past few years the groups of Yam,[7-15] Che,[16-21] Venkatesan,[22, 23] and others [24-32] reported on emissive Au(III) complexes containing cyclometalating, N-heterocyclic carbene (NHC), or alkynyl ligands, demonstrating the potential of this new class of compounds for luminescent materials.[6, 11] Several of these previously explored complexes contained nearly identical tridentate ligands, and chemical variation mostly occurred at the fourth coordination site of the Au(III) center. Here, we report our findings from a study in which we explored the coordination chemistry of gold with three different (potentially) tridentate ligands (Scheme 1). While the emphasis of the work reported herein is on exploring possible synthetic pathways to such compounds, the question whether cyclometalated Au(III) complexes can exhibit similarly high luminescence quantum yields as isoelectronic Pt(II) complexes, possibly at even higher emission energies (band maxima shifted further toward the blue) is of fundamental interest.

Ligand L^1H is charge-neutral and its analogue with butyl-groups instead of hexyl-chains has been previously used as a tridentate cyclometalating ligand offering N, C, N coordination sites for Pt(II).[33-35] Ligands $L^2H_2^{2+}$ and $L^3H_2^{2+}$ are cationic but lose their acidic carbene H-atoms upon coordination to Pd(II) or Pt(II). L^2 was previously found to act as tridentate C, N, C ligand to Pd(II) or Pt(II), a palladium(II) complex of a modified version of L^3 (with butyl-groups instead of hexyl-chains) is known as well.[36-38] Our goal was to synthesize analogous Au(III) complexes in which L^1 – L^3 are tridentate, and to use phenylethynyl ligands at the fourth coordination site of the expected square-planar complexes because comparable Pt(II) complexes are highly emissive.[1, 34] We wondered to what extent the luminescence properties of these Au(III) compounds would differ from those of the respective Pt(II) complexes. We found that the propensity of gold for low oxidation states leads to a variety of new Au(I) complexes, some of which could be characterized crystallographically. The desired square-planar complex of Au(III) could only be obtained with L^1, but only under carefully selected reaction conditions. Direct cyclometalation of Au(III) by L^1 – L^3 turned out to be impossible under the conditions used. Transmetallation from Ag(I) NHC complexes gave Au(I) compounds, while transmetallation from Hg(II) gave the desired Au(III) complex of L^1. Thus, the coordination chemistry of Au(III) with L^1 – L^3 is significantly different than for Pt(II) or Pd(II), for which direct cyclometalation or transmetallation from Ag(I) precursors is feasible.

Scheme 1. The three potentially tridentate ligands used in this work.



2. Results and discussion

2. 1 Ligand syntheses and strategies for complexation

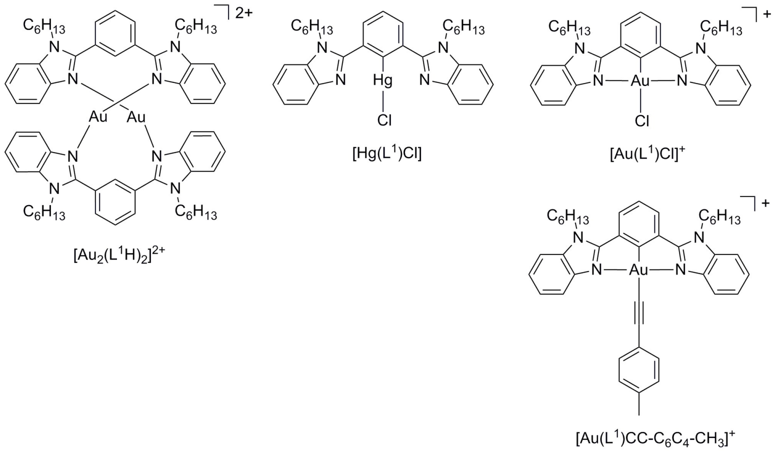
Ligands L^1 – L^3 were synthesized following previously published protocols. Briefly, L^1H was obtained by reacting isophtalic acid and *o*-phenylenediamine in polyphosphoric acid,[39] followed by alkylation with 1-iodohexane.[40] The bromide salt of $L^2H_2^{2+}$ is available in one step from reaction of 2,6-dibromopyridine with 1-butylimidazole.[38] $L^3H_2^{2+}$ was obtained as an iodide salt from reaction of 2,6-dibromopyridine with benzimidazole followed by alkylation with 1-iodohexane.[36] Detailed synthetic protocols and ligand characterization data are given in the supporting information.

Three different strategies were explored for complexation of Au(III) by L^1 – L^3: (i) direct complexation of Au(III) using the free ligand and commercially available gold(III) salts such as $KAuCl_4$ or $Au(OAc)_3$; (ii) synthesis and isolation of a silver(I) precursor complex which is then reacted with one of the abovementioned gold(III) sources in the expectation of a transmetallation reaction; (iii) synthesis and isolation of a mercury(II) precursor complex and subsequent transmetallation to Au(III). The following subjections report our findings with these three strategies for L^1 – L^3.

2.2 Complexation attempts with 1,3-bis(1-hexyl-2'-benzimidazoyl)benzene (L^1H)

For direct cyclometalation of Pt(II) using K_2PtCl_4 as a starting material acetonitrile/water mixtures are a common choice as a solvent.[1, 41, 42] Our attempts to form a complex of Au(III) with L^1 under analogous conditions using $KAuCl_4$ failed, similar experiences had been made earlier with $NaAuCl_4$ / $HAuCl_4$ and 2-phenylpyridine.[43] We also explored the possibility of enforcing the desired cyclometalation by heating the neat precipitate obtained after acetonitrile removal from the abovementioned CH_3CN/H_2O mixtures to 150 °C. In two independent attempts we were able to isolate in ~20% yield a product whose elemental analysis is compatible with the formulation $C_{64}H_{76}N_8Au_4Cl_6$, implying two molecules of L^{1}H per formula unit. $^1H/^{13}C$ NMR and high-resolution mass spectroscopy data of this material are consistent with a gold(I) dimer cation ($[Au_2(L^1H)_2]^{2+}$) as shown in Scheme 2; from the NMR data it is obvious that cyclometalation has not occurred. To account for the elemental analysis data one has to invoke one $[AuCl_2]^-$ and one $[AuCl_4]^-$ counter-anion, which seems to make chemical sense. Given the preference of Au(I) for linear coordination we assume that each gold(I) center is ligated to two N atoms of different ligands giving a dimer structure as it has been reported previously for dinuclear Ag(I) or Au(I) complexes with comparable ligands.[36, 44-46]

Scheme 2. Complexes obtained with L^1.



Transmetallation from Hg(II) precursor complexes has previously been identified as an efficient method for complexation of Au(III) and other d^8 metals,[6, 43, 47, 48] hence in a first step it seemed promising to react L^1H with $Hg(OAc)_2$ in ethanol in presence of LiCl. The reaction product, obtained in 27% yield, is unequivocally the expected $Hg(L^1)Cl$ complex (Scheme 2). Subsequent reaction of $Hg(L^1)Cl$ with $HAuCl_4$ in ethanol in presence of $NaHCO_3$ gave the desired $[Au(L^1)Cl]^+$ complex (Scheme 2) in good yields (73 – 84%). When reacting $Hg(L^1)Cl$ and $HAuCl_4$ in 1:1 molar ratio, the $[Au(L^1)Cl]^+$ complex is obtained as a tetrachloromercurate(II) salt ($[Au(L^1)Cl]_2[HgCl_4]$) whereas a molar ratio of 1:2 between $Hg(L^1)Cl$ and $HAuCl_4$ yields the tetrachloroaurate salt ($[Au(L^1)Cl][AuCl_4]$). Both salts were fully characterized (see experimental section), and we obtained X-ray diffraction data from single crystals for both salts. The cation of $[Au(L^1)Cl][AuCl_4]$ is shown in Figure 1.

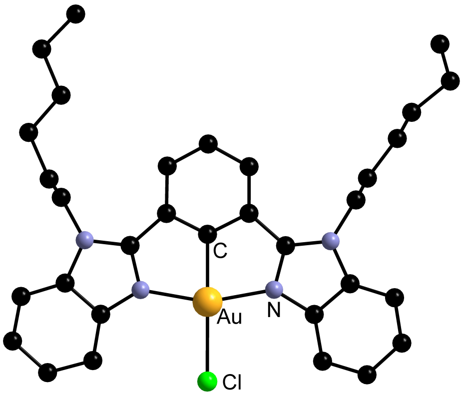


Figure 1. Crystal structure of the $[Au(L^1)Cl]^+$ cation in $[Au(L^1)Cl][AuCl_4]$. Hydrogen atoms are omitted for clarity.

A third crystal structure with $AuCl_2^-$ as a counter anion ($[Au(L^1)Cl][AuCl_2]$) was also accidently obtained (see supporting information). There are no unusual features in the $[Au(L^1)Cl]^+$ cation structures as most of the bond lengths and angles around the metal center are similar to those previously reported for an analogous chloroplatinum(II) complex with a modified version of tridentate L^1 (butyl-groups instead of hexyl-chains).[34] One noticeable difference is that the Au(III)-Cl bond distance in our three structures is shorter (2.350(3) – 2.359(2) Å) than the Pt(II)-Cl distance (2.4046(11) Å). By contrast, the Au(III)-C distance (1.972(13) – 2.005(10) Å) is longer than the Pt(II)-C distance (1.932(4) Å) in the abovementioned Pt(II) complex. In $[Au(L^1)Cl][HgCl_4]$ parts of the hexyl chains were found to be disordered over two positions with equal occupancy. More interesting are the differences in packing between the three different salts of the $[Au(L^1)Cl]^+$ complex, particularly in view of the possibility of d^8-d^8 interactions as observed for many square-planar Pt(II) complexes.[49-51] In the tetrachloromercurate(II) and dichloroaurate(I) salts, the cations form linear chains along the crystallographic a-axis with individual complexes oriented in head-to-tail fashion (Figures S2 / S3 of the supporting information). These chains form as a result of π–stacking between benzimidazole rings of the cationic complexes with interplanar distances ranging from ca. 3.2 Å to 3.6 Å.[52] Within the chains, in the tetrachloromercurate salt, there are alternatively short-long-short-medium intermetallic distances (d_{Au-Au} = 3.920(1) / 4.417(1) / 3.920(1) / 4.009(1) Å), whereas in the dichloroaurate salt the intermetallic distances (d_{Au-Au}) alternate between 4.198(2) and 4.389(2) Å. These Au(III)-Au(III) contacts are clearly too long to speak of significant metal-metal interactions. For reference, a recent study reported an Au(III)-Au(III) separation as short as 3.495 Å,[16] a distance of 3.846 Å was found for another material with square-planar gold(III).[14] The cationic chains along the a-axis are separated from each other by the counter-anions and by space taken up by the hexyl chains (Figure S2 / S3). These chains stack in a parallel fashion with interchain distances of 15.6412(15) Å and 16.3321(14) Å in the tetrachloromercurate salt, and 15.2847(11) Å and 15.1948 Å in the dichloroaurate(I) salt.

In the tetrachloroaurate(III) salt the crystal packing is very different with cations oriented both along the a- and c-axes (Figure S1). Here, too, the cationic complexes are π-stacked (interplane distance of ca. 3.5 Å) and oriented in head-to-tail fashion to form pairs with short Au(III)-Au(III) distances of 3.622(1) Å. Each $[Au(L^1)Cl]^+$ cation pair is surrounded by two $AuCl_4^-$ anions to form a charge-neutral tetranuclear unit with Au(III)-Au(III) distances of 4.016(1) Å between cationic and anionic units. The $[Au(L^1)Cl][AuCl_4]$ and $[Au(L^1)Cl]_2[HgCl_4]$ compounds both emit in the solid state with λ_{max} at 427 nm at room temperature, and they luminesce in frozen 2-methyltetrahydrofuran at 77 K (Figure 2). It thus appears that the counter-anion has little influence on the luminescence properties of these two materials. This observation is noteworthy because many square-planar d^8 complexes exhibit strongly counter-ion dependent emission properties,[53] sometimes even in dilute solution.[54, 55] In room temperature solution the $[Au(L^1)Cl][AuCl_4]$ and $[Au(L^1)Cl]_2[HgCl_4]$ compounds are non-emissive.

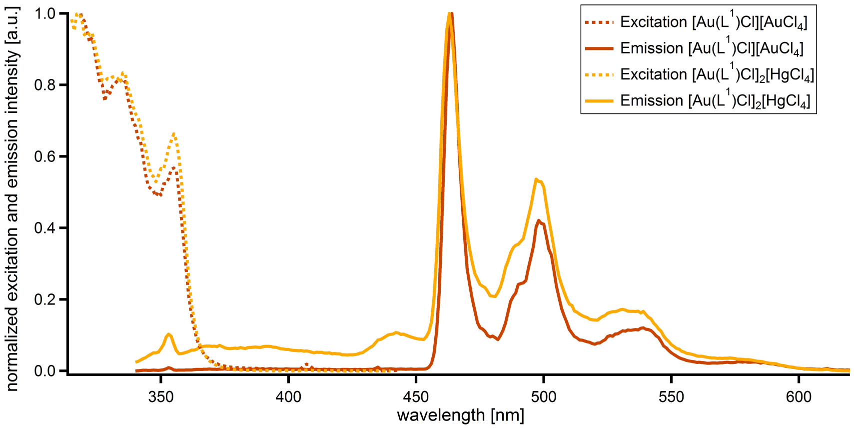


Figure 2. Excitation (dashed lines) and emission (solid lines) spectra of $[Au(L^1)Cl][AuCl_4]$ and $[Au(L^1)Cl]_2[HgCl_4]$ in frozen 2-methyltetrahydrofuran at 77 K. For the excitation spectra detection occurred at 487 nm, for the emission spectra excitation was at 345 nm.

There is a fairly large shift between absorption and emission maxima in Figure 2 which we attribute to the fact that in absorption singlet-singlet transitions are observed while the emission occurs from a triplet excited state.

Given the prior observation that alkynylplatinum(II) and alkynylgold(III) compounds exhibit enhanced luminescence properties with respect to chloroplatinum(II) and chlorogold(III) complexes we were interested in replacing the chloro-ligand of $[Au(L^1)Cl]^+$ by a 4-ethynyltoluene ligand. A common method for introducing alkynyl ligands to Pt(II) and Au(III) complexes is the use of Sonogashira coupling conditions,[14, 56] but our attempts to perform ligand exchange in dichloromethane in presence of CuI and triethylamine or diisopropylamine were unsuccessful. A method previously used for introduction of an ethynyl ligand to a gold(III) center seemed to yield the desired $[Au(L^1)(C{\equiv}CC_6H_4\text{-}CH_3)]^+$ complex in very modest yields.[15] This method makes use of *n*-butyllithium in THF at -78°C to deprotonate 4-ethynyltoluene before exposing it to $[Au(L^1)Cl]^+$. However, while we were able to detect the $[Au(L^1)(C{\equiv}CC_6H_4\text{-}CH_3)]^+$ cation in high-resolution mass spectrometry, we were unable to obtain satisfactory elemental analysis data, i. e., the compound could not be properly characterized. It seems interesting to note that acetonitrile solutions of this compound are emissive at room temperature (Figure S4), but more detailed investigations of this compound are not appropriate under these circumstances. The key point is here that the synthesis of the $[Au(L^1)(C{\equiv}CC_6H_4\text{-}CH_3)]^+$ complex is significantly more delicate than the synthesis of analogous Pt(II) alkynyls.

2.3 Complexation attempts with 2,6-bis(3-butylimidazol-1-ium)pyridine ($L^2H_2^{2+}$) and 2,6-bis(3-hexylbenzimidazol-1-ium)pyridine ($L^3H_2^{2+}$)

Reaction of $KAuCl_4$ with $L^2H_2^{2+}$ or $L^3H_2^{2+}$ in CH_3CN/H_2O mixtures does not lead to any complexation of the organic ligands. From the reaction with $L^2H_2Br_2$ a material with the stoichiometry $[L^2H_2][AuBr_2][AuBr_4]$ crystallized (Figure 3). The first observation is that chloro-ligands of $AuCl_4^-$ have been exchanged by bromo-ligands, but Br^-/Cl^- ligand exchange reactions on the $AuCl_4^-$ complex are known.[57] In our case the source of Br^- must be the $L^2H_2Br_2$ starting material. We note that full exchange of Cl^- by Br^- is only complete in the small fraction (~16%) of the reaction mixture which crystallized; mass spectrometry of the supernatant provides evidence for $AuCl_2^-$, $AuClBr^-$, and $AuCl_4^-$ anions (see supporting information). The second observation is that one of the two involved gold centers has been reduced to the monovalent state. The Au-Br distances in the tetrabromoaurate(III) anion range from 2.3500(12) to 2.4143(10) Å, while in the dibromoaurate(I) they are 2.3688(15) and 2.3700(13) Å. The two imidazolium rings of the uncoordinated organic ligand are almost perfectly coplanar with the central pyridine ring, whereas the *n*-butyl chains are bent with maximum angles of *ca.* 104° and 138° with respect to the average plane of the aromatic core. One of the two butyl chains was found to be disordered over two positions in a 3:1 ratio. The uncoordinated organic ligand interacts with the tetrabromoaurate anions through weak C-H…Br hydrogen bonds (d_{C-Br} = 3.620(1) and 3.777(1) Å).[58]

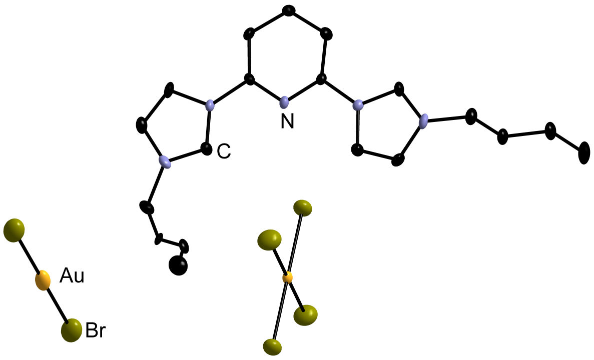


Figure 3. Crystal structure of $[L^2H_2][AuBr_4][AuBr_2]$. Note that only one of the two positions of the disordered *n*-butyl chains is shown. Anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms are omitted for clarity.

For the synthesis of NHC complexes the use of transmetallation reactions from silver(I) precursor complexes is common practice, at least when aiming at gold(I) complexes.[59, 60] We explored whether this would also be a viable procedure for obtaining a $[Au(L^2)Cl]$ complex in which the L^2 ligand is tridentate to Au(III). Reaction of $L^2H_2Br_2$ with Ag_2O in dry methanol at room temperature and subsequent treatment with KPF_6 afforded the $[Ag_2(L^2)_2](PF_6)_2$ complex which has a similar formula as a previously characterized dinuclear silver(I) complex;[36] probably its structure is similar but we have no crystallographic data to prove this. $[Ag_2(L^2)_2](PF_6)_2$ was then reacted with $Au(OAc)_3$ in 2-methoxyethanol at 110 °C yielding a structurally analogous dinuclear Au(I) complex, similar to a recently published gold(I) dimer.[59] $[Au_2(L^2)_2](PF_6)_2$ could be crystallized from acetone solution, and X-ray diffraction gave the structure shown in Figure 4.

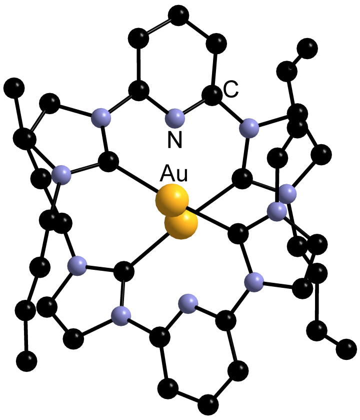


Figure 4. Crystal structure of the cation of $[Au_2(L^2)_2](PF_6)_2$. Hydrogen atoms are omitted for clarity.

The bis-NHC ligands are arranged in a helical fashion, yielding a C-Au-C angle of 173.9(2)°. Due to this helicity, $[Au_2(L^2)_2][PF_6]_2$ was found to crystallize in a chiral space group ($P6_522$). The Flack parameter was found to be 0.011(11), indicating that the measured crystal is enantiopure. We did not try to isolate crystals of the other enantiomeric form.

The intramolecular Au(I)-Au(I) distance is 3.3000(4) Å, i. e., close to what may be called an aurophilic interaction.[61] The distance between gold(I) centers of two related dimers is similar (3.2971(4) and 3.2797(9) Å, respectively).[44, 59] Given the relatively short distance between metal centers we were interested in the emission properties of the $[Au_2(L^2)_2]^{2+}$ complex but found evidence that it might not be stable in solution, at least not in CH_3CN. From DOSY NMR experiments a diffusion coefficient of $8.5 \cdot 10^{-10}$ m^2/s was determined which translates to a molecular radius of 6.96 Å using the Stokes-Einstein relation for spherical particles. For reference, for the free $L^2H_2^{2+}$ ligand we found a diffusion coefficient of $1.01 \cdot 10^{-9}$ m^2/s, translating to a molecular radius of 5.86 Å. The small increase (~19%) in molecular radius between free ligand and complex does not appear to be compatible with a dimer structure in CH_3CN. Whether or not the $[Au_2(L^2)_2]^{2+}$ complex is stable in non-coordinating solvents is a separate question that we did not explore further. Under a hand-held UV lamp the solid $[Au_2(L^2)_2](PF_6)_2$ material did not exhibit any emission which is readily visible by naked eye.

Given the result of Au(I) coordination with L^2 via the silver(I) transmetallation procedure and our interest in Au(III) complexes, with ligand L^3 we decided to explore transmetallation from mercury(II) complexes. In a first step, $L^3H_2I_2$ was reacted with $Hg(OAc)_2$ in ethanol at reflux, and this resulted in a material (~ in 55% yield) whose elemental analysis, NMR and mass spectrometry data are consistent with formulation as $[Hg_2(L^3)_2][HgI_4]_2$.

Reaction of the mercury transmetallation product with $KAuCl_4$ in refluxing acetonitrile gives in 25% yield a dinuclear Au(III) complex with formulation $[(AuI_2Cl)_2(L^3)]$. In this complex the two NHC functions of L^3 ligate to two different Au(III) centers each of which is additionally coordinated by one chloro- and two iodo-ligands; an X-ray crystal structure of this compound is shown in Figure 5. Evidently square-planar Au(III) is present, and the Au(III)-C(carbene) bond lengths are somewhat shorter (1.995(6) Å and 2.000(7) Å, respectively) than what was observed above for the Au(I)-C(carbene) bond lengths of $[Au_2(L^2)_2]^{2+}$ (2.008(7) – 2.021(6) Å). In the structure from Figure 5 ligand L^3 seems to be distorted in such a way as to maximize the distance between the two AuI_2Cl moieties. The extremity of one of the two hexyl chains was found to be disordered over two positions with equal occupancy.

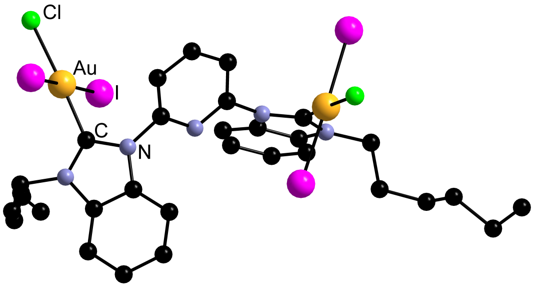


Figure 5. Crystal structure of the $[(AuI_2Cl)_2(L^3)]$ complex as found in $[(AuI_2Cl)_2(L^3)]\cdot(Et_2O)$. Note that only one of the two positions of the disordered *n*-hexyl chains is shown. Hydrogen atoms are omitted for clarity.

Clearly, this is not the product we intended to make, but at least in this case the transmetallation occurred to Au(III) rather than Au(I). Therefore we decided to react the $[(AuI_2Cl)_2(L^3)]$ compound with 1 equivalent of the $[Hg_2(L^3)_2]^{4+}$ precursor material from above. The idea was to use the $[(AuI_2Cl)_2(L^3)]$ compound as an alternative gold source (instead of $KAuCl_4$), in which the two Au(III) centers are already ligated to a carbene, and it was hoped that the iodo- and chloro-ligands of each AuI_2Cl entity would be replaced by tridentate L^3. However, reaction in refluxing CH_3CN produced a dinuclear gold(I) complex of formulation $[Au_2(L^3)_2]^{2+}$ (~42% yield) in which each Au(I) center is coordinated by an NHC moiety from two different molecules of L^3; slow evaporation of CH_3CN afforded single crystals suitable for X-ray diffraction, and the obtained structure of the cation is shown in Figure 6 (the counter-anion is $Hg_2I_6^{2-}$). The pyridine moieties of two different ligands L^3 point to opposite sides of the cationic complex, and they are tilted relative to the benzimidazole rings by 49°-77°. The metal centers are well separated with an Au-Au distance of 6.562(2) Å. The Au-C bond distances range from 2.007(9) to 2.027(7) Å and are consistent with an Au(I) oxidation state; one of the two gold(I) coordination geometries deviates significantly from linearity with a C-Au-C angle of 168.8(3)°, due to a weak Au-I interaction with the $Hg_2I_6^{2-}$ anion (d_{Au-I} = 3.372(7) Å). The counter-anion contains two Hg(II) centers in distorted tetrahedral environments with two bridging iodine atoms.

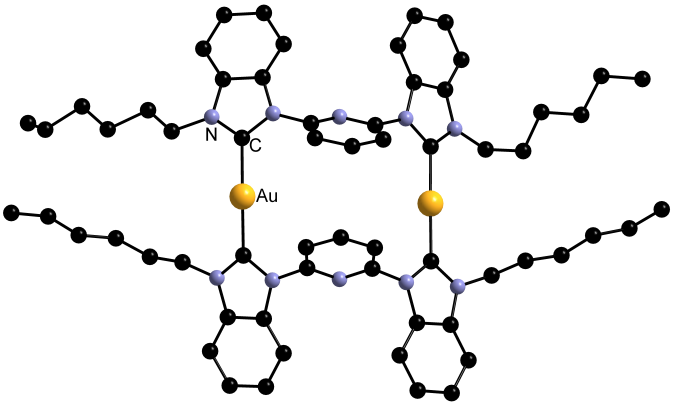


Figure 6. Crystal structure of the cation from $[Au_2(L^3)_2][Hg_2I_6]$. Hydrogen atoms are omitted for clarity.

3. Summary and conclusions

The desired square-planar complexation of Au(III) by a tridentate ligand backbone could only be achieved with L^1, a transmetallation reaction from a mercury(II) precursor being the only viable synthetic route. The obtained $[Au(L^1)(C{\equiv}CC_6H_4\text{-}CH_3)]^+$ complex exhibits promising emission properties, and in the future it may be interesting to perform a comparative photophysical study of such complexes with variable alkynyl ligands. With ligands L^2 and L^3 only Au(I) complexes were obtained irrespective of whether transmetallation occurred from Ag(I) or Hg(II). Thus, we have found no experimental evidence that L^2 and L^3 can indeed act as tridentate ligands to Au(III), despite the fact that closely related analogues are known to ligate to isoelectronic Pt(II) in a tridentate fashion.[36-38] In future work it might be worthwhile to explore the use of gold sources other than $KAuCl_4$ or $Au(OAc)_3$. The tetrabutylammonium salt of $AuCl_4^-$ would represent an interesting choice for organic solvents. For Pt(II) chemistry the $[Pt(CH_3CN)_4]^{2+}$ complex is a highly useful starting material, and similar gold(III) complexes would be promising.

Experimental Section

Thin layer chromatography was performed using Polygram SIL G/UV254 plates from Machery-Nagel, and for column chromatography silica gel 60 from the same company was employed. Reaction products were characterized by ^1H NMR spectroscopy on a Bruker Avance DRX 300 spectrometer, by mass spectrometry using a Finnigan MAT 8200 (electron ionization, EI) and an Applied Biosystems API 2000 (electrospray ionization, ESI) instrument, and by elemental analysis (Vario EL III CHNS analyzer from Elementar). Optical absorption spectroscopy was performed using an Agilent Cary 300 spectrophotometer, and steady-state luminescence spectra were measured on a Fluorolog-3 instrument (FL322) from Horiba Jobin-Yvon.

Synthesis of compound $[Au_2(L^1H)_2](AuCl_4)(AuCl_2)$. A mixture of $K[AuCl_4]$ (0.079 g, 0.21 mmol, 1.0 eq.) in H_2O (4 ml) and 1,3-bis(1-hexyl-2′-benzimidazoyl)benzene (0.10 g, 0.21 mmol, 1.0 eq.) in CH_3CN (4 ml) was stirred at room temperature overnight. Then the CH_3CN was evaporated and the precipitate was collected. The solid was heated to 150°C under nitrogen atmosphere (without any solvent) overnight. Then the solid was cooled to room temperature. The crude product was purified by column chromatography (silica, ethyl acetate + 1% NEt_3, $R_f = 0.82$). After drying in air $C_{64}H_{76}Au_4Cl_6N_8$ was obtained as a red solid (58.5 mg, 0.04 mmol, 20%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (s, 12 H, 4×C*H*$_3$), 1.21–1.25 (m, 24 H, 12×C*H*$_2$), 1.85–1.96 (m, 8 H, 4×C*H*$_2$), 4.46 (t, *J* = 7.3 Hz, 8 H, 4×NC*H*$_2$), 7.50–7.54 (m, 8 H, C*H*$_{Ar}$), 7.57–7.62 (m, 4 H, C*H*$_{Ar}$), 7.85–7.92 (m, 2 H, C*H*$_{Ar}$), 7.98–8.06 (m, 8 H, C*H*$_{Ar}$), 8.18 (d, *J* = 1.8 Hz, 2 H, C*H*$_{Ar}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.3, 22.5, 26.4, 31.2, 46.8, 60.5, 111.7, 119.1, 130.5, 140.0 ppm. ESI-HRMS: m/z 675.2762 $[M]^{2+}$ (calcd for $[C_{64}H_{76}Au_2N_8]^{2+}$: 675.2756). Anal. calcd (%) for $C_{64}H_{76}N_8Au_4Cl_6$: C 39.30, H 3.92, N 5.73. Found C 39.41, H 3.96, N 5.44.

Synthesis of complex Hg[L^1]Cl. 1,3-bis(1-hexyl-2′-benzimidazoyl)benzene (200 mg, 0.418 mmol, 1.0 eq.) and $Hg(OAc)_2$ (146.6 mg, 0.460 mmol, 1.1 eq.) were dissolved in ethanol (7 ml) and then heated to 88°C for 3 days. The reaction was cooled to room temperature and LiCl (39 mg, 0.92 mmol, 2.2 eq.) in methanol (6 ml) was added. Then the reaction mixture was heated to reflux for 20 minutes and cooled back to room temperature again. After pouring the solution in water, the aqueous mixture was extracted with ethyl acetate, dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography (silica gel, ethyl acetate/pentane/CH_2Cl_2 4:4:2). After drying under vacuum, Hg[L^1]Cl was obtained as a white solid (80.1 mg, 0.11 mmol, 27%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ 0.75–0.83 (m, 6 H, 2×C*H*$_3$), 1.18 (d, *J* = 3.1 Hz, 12 H, 4×C*H*$_2$), 1.75 (t, *J* =7.2 Hz, 4 H, 2×C*H*$_2$), 4.39 (t, *J* = 7.6 Hz, 4 H, 2×NC*H*$_2$), 7.26–7.38 (m, 4 H, C*H*$_{Ar}$), 7.67–7.74 (m, 5 H, C*H*$_{Ar}$), 8.02 (d, *J* = 7.7 Hz, 2 H, C*H*$_{Ar}$) ppm. ^{13}C NMR (75 MHz, DMSO-*d*$_6$): δ 13.8, 21.9, 25.7, 29.0, 30.5, 44.5, 111.2, 119.1, 122.3, 122.8, 128.1, 129.4, 135.8, 136.1, 142.0, 156.5 ppm. ESI-HRMS: m/z 715.2489 $[M+H]^+$ (calcd for $[C_{32}H_{38}ClHgN_4]^+$: 715.2480). Anal. calcd (%) for $C_{32}H_{37}N_4ClHg\cdot 0.5(H_2O)$: C 53.09, H 5.30, N 7.74. Found C 53.15, H 5.20, N 7.51.

Synthesis of compound [Au(L^1)Cl]$_2$[HgCl$_4$]. A mixture of Hg[L^1]Cl (73.0 mg, 0.10 mmol, 1.0 eq.), HAuCl$_4$ (34.7 mg, 0.10 mmol, 1.0 eq.) and NaHCO$_3$ (8.4 mg, 0.10 mmol, 1.0 eq.) in ethanol (14 ml) was stirred in the absence of light at room temperature overnight. The white precipitate was collected and washed with Et$_2$O. [Au(L^1)Cl]$_2$[HgCl$_4$] was obtained as a white solid (77.3 mg, 0.073 mmol, 73%). Single crystals of [Au(L^1)Cl]$_2$[HgCl$_4$]·CH$_3$CN suitable for X-ray diffraction measurements were grown by slow evaporation of acetonitrile. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.84 (t, J = 6.8 Hz, 6 H, 2×CH_3), 1.21–1.34 (m, 8 H, 4×CH_2), 1.40–1.49 (m, 4 H, 2×CH_2), 1.91 (t, J = 7.8 Hz, 4 H, 2×CH_2), 4.88 (t, J = 7.1 Hz, 4 H, 2×NCH_2), 7.57–7.64 (m, 4 H, CH_{Ar}), 7.90 (t, J = 7.9 Hz, 1 H, CH_{Ar}), 8.06 (dd, J = 6.6, 2.8 Hz, 2 H, CH_{Ar}), 8.13 (d, J = 8.0 Hz, 2 H, CH_{Ar}), 8.64 (dd, J = 6.5, 3.1 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, CD$_3$CN): δ 14.2, 23.1, 26.9, 30.4, 32.0, 46.9, 113.2, 117.1, 118.8, 126.7, 127.8, 128.9, 130.6, 134.1, 138.8 ppm. ESI-HRMS: m/z 709.2361 [M]$^+$ (calcd for [C$_{32}$H$_{37}$N$_4$AuCl]$^+$: 709.2368). Anal. calcd (%) for C$_{32}$H$_{37}$N$_4$AuCl$_5$Hg: C 36.53, H 3.55, N 5.33. Found C 36.66, H 3.57, N 5.19.

Synthesis of compound [Au(L^1)Cl][AuCl$_4$]. A mixture of Hg[L^1]Cl (353 mg, 0.49 mmol, 1.0 eq.), HAuCl$_4$ (335.6 mg, 0.98 mmol, 2.0 eq.) and NaHCO$_3$ (41.5 mg, 0.49 mmol, 1.0 eq.) in ethanol (60 ml) was stirred in the absence of light at room temperature overnight. The yellow precipitate was collected and washed with Et$_2$O. [Au(L^1)Cl][AuCl$_4$] was obtained as a yellow solid (437 mg, 0.42 mmol, 84%). Single crystals suitable for X-ray diffraction were grown by slow diffusion of diethyl ether vapor into an acetonitrile solution of the compound. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.84 (t, J = 6.9 Hz, 6 H, 2×CH_3), 1.22–1.32 (m, 8 H, 4×CH_2), 1.39–1.49 (m, 4 H, 2×CH_2), 1.87–1.96 (m, 4 H, 2×CH_2), 4.89 (t, J = 7.2 Hz, 4 H, 2×NCH_2), 7.58–7.65 (m, 4 H, CH_{Ar}), 7.90 (t, J = 7.9 Hz, 1 H, CH_{Ar}), 8.08 (dd, J = 6.4, 3.1 Hz, 2 H, CH_{Ar}), 8.13 (d, J = 8.0 Hz, 2 H, CH_{Ar}), 8.65–8.71 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, DMSO-d_6):

δ 13.8, 21.9, 25.4, 29.4, 30.8, 45.2, 112.8, 115.7, 125.5, 126.6, 128.2, 128.9, 132.9, 137.3, 158.1 ppm. ESI-HRMS: m/z 709.2365 $[M]^+$ (calcd for $[C_{32}H_{37}N_4AuCl]^+$: 709.2368). Anal. calcd (%) for $C_{32}H_{37}N_4Au_2Cl_5{\cdot}H_2O$: C 36.09, H 3.69, N 5.26. Found C 35.93, H 3.37, N 5.26.

Synthesis of complex $[Au(L^1)(C{\equiv}C\text{-}C_6H_4\text{-}CH_3)]^+$. To a solution of *p*-tolylacetylene (0.05 ml, 0.39 mmol, 2.0 eq.) in dry THF (20 ml) was added *n*-butyllithium (2.5 M in hexane, 0.19 ml, 0.46 mmol, 2.3 eq.) under nitrogen in a dropwise manner at -78°C. The resulting mixture was stirred for 5 minutes at -78 °C and transferred subsequently to a suspension of $[Au(L^1)Cl][AuCl_4]$ (202.1 mg, 0.19 mmol, 1.0 eq.) in THF (20 ml). The reaction mixture was stirred for 3 h at room temperature in the dark, and then the mixture was quenched by addition of a saturated aqueous ammonium chloride solution (0.7 ml). The crude product, which was obtained after solvent removal, was washed with dichloromethane and diethyl ether, followed by extraction with acetonitrile. The acetonitrile fraction was concentrated and placed in a flask with diethyl ether overnight. A white solid precipitated from the mixture. $[Au(L^1)(C{\equiv}CC_6H_4\text{-}CH_3)]^+$ was obtained by drying the filtrate *in vacuo* (9.2 mg, 0.008 mmol, 4.2 %). ESI-HRMS: m/z 789.3226 $[M]^+$ (calcd for $[C_{41}H_{44}N_4Au]^+$: 789.3226).

Synthesis of compound $[L^2H_2][AuBr_2][AuBr_4]$. To a stirred solution of $L^2H_2Br_2$ (64.2 mg, 0.132 mmol) in acetonitrile (1.0 ml) was added an aqueous solution (7.0 ml) of $K[AuCl_4]$ (50.0 mg, 0.132 mmol). The resulting suspension was stirred at reflux under N_2 and in the absence of light for 1 day. The solvent was evaporated until the product precipitated as a red solid. Single crystals, suitable for X-ray diffraction studies were grown by slow diffusion of diethyl ether vapor into an acetone solution of the compound (25.3 mg, 0.02 mmol, 16 %). When refluxing the same reaction mixture for 3 days the same product is obtained. ^{1}H NMR (300 MHz, CD_3CN): δ 1.02 (t, *J* = 7.3 Hz, 6 H, 2×CH_3), 1.26-1.36 (m, 8 H, CH_2), 4.32 (t, *J* = 7.3, 4 H,

$NC\mathit{H}_2$), 7.69 (t, *J* = 2.0 Hz, 2 H, $C\mathit{H}_{Ar}$), 7.92 (d, *J* = 8.1 Hz, 2 H, $C\mathit{H}_{Ar}$), 8.24 (t, *J* = 2.0 Hz, 2 H, $C\mathit{H}_{Ar}$), 8.45 (t, *J* = 8.1 Hz, 1 H, $C\mathit{H}_{Ar}$), 9.49 (s, 2 H, $C\mathit{H}_{Ar}$) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ 12.4, 18.8, 31.0, 50.1, 114.6, 119.4, 123.6, 144.6. FD-MS: m/z 592.1 $[M+AuCl_2]^+$, 638.0 $[M+AuClBr]^+$, 664.0 $[M+AuCl_4]^+$, 682.0 $[M+AuBr_2]^+$. Anal. calcd (%) for $C_{19}H_{27}N_5Au_2Br_6$: C 19.12, H 2.28, N 5.87. Found C 19.23, H 2.28, N 5.83.

Synthesis of compound $[Ag_2(L^2)_2](PF_6)_2$. A mixture of Ag_2O (0.72 g, 3.12 mmol) and $L^2H_2Br_2$ (0.60 g, 1.2 mmol) in anhydrous methanol (54 ml) was stirred in the dark at room temperature under N_2 for 2 days. Then the mixture was filtered through celite. Subsequently a solution of KPF_6 in anhydrous methanol (21.5 ml) was added to the filtrate. The resulting white precipitate was collected and washed with hot methanol to afford colorless crystals of $[Ag_2(L^2)_2](PF_6)_2$ (0.40 g, 0.35 mmol, 30 %). ^1H NMR (300 MHz, CD_3CN): δ 0.67 (t, *J* = 7.3 Hz, 12 H, $4\times C\mathit{H}_3$), 1.03 (h, *J* = 7.3, 7.3 Hz, 8 H, $C\mathit{H}_2$), 1.22-1.39 (m, 4 H, $C\mathit{H}_2$), 3.79 (t, *J* = 7.6 Hz, 8 H, $NC\mathit{H}_2$), 7.36 (t, *J* = 1.8 Hz, 4 H, $C\mathit{H}_{Ar}$), 7.78 (d, *J* = 8.0 Hz, 4 H, $C\mathit{H}_{Ar}$), 7.88 (t, *J* = 1.7 Hz, 4 H, $C\mathit{H}_{Ar}$), 8.32 (t, *J* = 8.0 Hz, 2 H, $C\mathit{H}_{Ar}$) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ 12.3, 18.7, 32.4, 51.7, 113.6, 123.0, 123.1, 143.4, 148.8 ppm. ^{31}P NMR (162 MHz, acetone-d_6): δ -144.2 (septuplet for PF_6^- anion). Positive-ion ESI-MS: m/z 432.0 $[M]^{2+}$.

Synthesis of compound $[Au_2(L^2)_2](PF_6)_2$. A solution of gold(III) acetate (80.0 mg, 0.21 mmol) in 2-methoxyethanol (8.0 ml) was added to a solution of $[Ag_2(L^2)_2](PF_6)$ (112 mg, 0.09 mmol) in 2-methoxyethanol (15 ml). The mixture was stirred at 110 °C in the dark under N_2 for 12 h. After cooling to room temperature, the reaction mixture was filtered through celite and the filtrate was concentrated under reduced pressure. The residue was dissolved in hot acetone (30 ml) and filtered through celite. Slow evaporation of acetone afforded colorless crystals of $[Au_2(L^2)_2](PF_6)_2$ which were suitable for X-ray diffraction (23.2 mg, 0.017 mmol, 20 %). ^1H

NMR (300 MHz, CD_3CN): δ 0.63 (t, $J = 7.3$ Hz, 12 H, 4×CH_3), 1.00 (q, $J = 7.3$, 7.3 Hz, 8 H, CH_2), 1.23-1.35 (m, 8 H, CH_2), 3.85-3.99 (m, 8 H, NCH_2), 7.35 (d, $J = 2.1$ Hz, 4 H, CH_{Ar}), 7.80 (d, $J = 8.1$ H, 4 H, CH_{Ar}), 7.88 (d, $J = 2.1$ Hz, 4 H, CH_{Ar}), 8.32 (t, $J = 8.1$ Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ 13.5, 19.9, 33.4, 52.7, 114.9, 120.1, 124.3 ppm. ESI-MS: m/z 520.1 $[M]^{2+}$. Anal. calcd (%) for $C_{38}H_{50}N_{10}Au_2P_2F_{12}\cdot(H_2O)_2\cdot(C_3H_8O_2)$: C 34.11, H 4.33, N 9.71. Found C 33.89, H 4.44, N 9.55.

Synthesis of compound $[Hg_2(L^3)_2][HgI_4]_2$. A mixture of $L^3H_2I_2$ (600 mg, 0.82 mmol, 1.0 eq.) and $Hg(OAc)_2$ (260 mg, 0.82 mmol, 1.0 eq.) was dissolved in ethanol (20 ml) and heated to reflux overnight. Then the reaction mixture was cooled to room temperature. The white precipitate was collected and washed with H_2O. After drying *in vacuo* $[Hg_2(L^3)_2][HgI_4]_2$ could be obtained as a white solid (629 mg, 0.23 mmol). ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.89 (t, $J = 6.7$ Hz, 6 H, 2×CH_3), 1.12–1.43 (m, 16 H, 8×CH_2), 1.62 (s, 2 H, CH_2), 4.21 (s, 2 H, NCH_2), 7.60 (d, $J = 8.3$ Hz, 2 H, CH_{Ar}), 7.70 (t, $J = 7.8$ Hz, 2 H, CH_{Ar}), 7.80 (t, $J = 7.8$ Hz, 2 H, CH_{Ar}), 8.05 (d, $J = 8.3$ Hz, 2 H, CH_{Ar}), 8.49 (d, $J = 7.9$ Hz, 2 H, CH_{Ar}), 8.80 (t, $J = 8.0$ Hz, 1 H, CH_{Ar}) ppm. ESI-MS: m/z 808.13 $[M]^+$. Anal. calcd (%) for $C_{62}H_{76}N_{10}Hg_4I_8$: C 26.82, H 2.69, N 5.04. Found C 26.94, H 2.77, N 5.04.

Synthesis of compound $[(AuI_2Cl)_2(L^3)]$. A suspension of $[Hg_2(L^3)_2][HgI_4]_2$ (150 mg, 0.05 mmol, 2.0 eq.) and $K[AuCl_4]$ (44.9 mg, 0.12 mmol, 1.1 eq.) in CH_3CN (7 ml) was heated to reflux in the dark for 24 h. During the heating process the color of the mixture changed from yellow to deep red. Then the mixture was cooled to room temperature and a solid precipitated. $[(AuI_2Cl)_2(L^3)]$ was obtained as a red solid (39.9 mg, 0.027 mmol, 25%). Single crystals of $[(AuI_2Cl)_2(L^3)]\cdot(Et_2O)$ suitable for X-ray diffraction were grown by slow diffusion of diethyl ether vapor into a dichloromethane solution of the compound. ^{1}H NMR (300 MHz, DMSO-d_6): δ

0.92 (t, $J = 6.7$ Hz, 6 H, 2×CH_3), 1.31–1.51 (m, 12 H, 6×CH_2), 2.05 (t, $J = 7.2$ Hz, 4 H, 2×CH_2), 4.71 (t, $J = 7.1$ Hz, 4 H, 2×NCH_2), 7.52–7.68 (m, 4 H, CH_{Ar}), 8.05 (dd, $J = 8.2$, 3.6 Hz, 4 H, CH_{Ar}), 8.50 (d, $J = 7.9$ Hz, 2 H, CH_{Ar}), 8.70 (dd, $J = 8.5$, 7.4 Hz, 1 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, DMDO-d_6): δ 13.1, 21.2, 24.8, 28.5, 29.9, 40.1, 99.1, 100.9, 111.8, 112.7, 121.4, 124.6, 124.8, 131.6, 131.8, 148.5, 176.1 ppm. ESI-MS: m/z 908.2 $[\mathrm{M{-}I_4Cl}]^+$, 1000.14 $[\mathrm{M{-}I_3Cl_2}]^+$.

Synthesis of compound $[\mathrm{Au_2(L^3)_2}][\mathrm{Hg_2I_6}]$. A solution of $[(\mathrm{AuI_2Cl})_2(\mathrm{L^3})]$ (65.0 mg, 0.06 mmol, 1.0 eq.) in CH_2Cl_2 (8 ml) was added to a solution of $[\mathrm{Hg_2(L^3)_2}][\mathrm{HgI_4}]_2$ (183.3 mg, 0.07 mmol, 2.2 eq of $[\mathrm{Hg(L_3)}]^{2+}$) in CH_3CN (8 ml). Then the mixture was heated to reflux in the dark overnight. During the reaction the color of the mixture changed from red to colorless. Finally, the reaction mixture was cooled to room temperature and concentrated to a small volume (~4 ml). The greenish solid was collected and washed with CH_3CN, methanol, acetone, H_2O and CH_2Cl_2 to yield $[\mathrm{Au_2(L^3)_2}][\mathrm{Hg_2I_6}]$ as a pale green solid (49.7 mg, 0.025 mmol, 42 %). Single crystals suitable for X-ray diffraction were grown by slow evaporation of acetonitrile. ^{1}H NMR (300 MHz, DMSO-d_6): δ 0.72 – 0.79 (m, 12 H, CH_3), 1.16 (d, $J = 3.7$ Hz, 12 H, 6xCH_2), 1.21 – 1.33 (m, 12 H, 6×CH_2), 1.73 – 1.84 (m, 8 H, 4×CH_2), 4.60 (t, $J = 7.3$ Hz, 8 H, 4×NCH_2), 7.53 – 7.66 (m, 8 H, CH_{Ar}), 7.79 (d, $J = 7.9$ Hz, 4 H, CH_{Ar}), 7.99 (d, $J = 7.8$ Hz, 4 H, CH_{Ar}), 8.19 (d, $J = 7.9$ Hz, 4 H, CH_{Ar}), 8.46 (t, $J = 7.9$ Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, DMDO-d_6): δ 13.8, 21.9, 25.8, 29.7, 30.66, 48.7, 112.8, 113.2, 121.4, 125.8, 125.9, 132.4, 132.7, 148.6, 188.6 ppm. ESI-HRMS: m/z 676.2709 $[\mathrm{M}]^{2+}$ (calcd for $[\mathrm{C_{62}H_{74}N_{10}Au_2}]^{2+}$: 676.2712). Anal. calcd (%) for $\mathrm{C_{62}H_{74}Au_2N_{10}Cl_6Hg_2\cdot(HgI_2)\cdot 2(H_2O)}$: C 30.27, H 3.20, N 5.70. Found C 29.94, H 3.04, N 5.57.

The crystallographic data were collected with a Bruker APEX II diffractometer (in Bordeaux), equipped with a graphite monochromator centred on the path of MoK$_\alpha$ radiation. Single crystals were coated with Paratone N-oil and mounted on a fiber loop, followed by data collection at 120 K (except for $[Au_2(L^2)_2](PF_6)_2$ which was measured at 100 K). The program SAINT was used to integrate the data, which was thereafter corrected using SADABS.[-62] All structures were solved by direct methods and refined by a full-matrix least-squares method on F^2 using SHELXL-97.[63] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions using suitable riding models. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-97. Some parts of the hexyl chains in $[Au(L^1)Cl]_2[HgCl_4](MeCN)$, $[Au(L^1)Cl][AuCl_4]$, $[L^2H_2][AuBr_2][AuBr_4]$, $[(AuI_2Cl)_2(L^3)](Et_2O)$, and $[Au_2(L^3)_2][Hg_2I_6]$ were refined using DFIX, DANG and SIMU contraints/restrains. Parts of some of the alkyl chains were found to have further positional disorders: In $[Au(L^1)Cl]_2[HgCl_4](MeCN)$, C26 was refined on two positions (named C26A and C26B) with identical anisotropic displacement parameters. For atoms C29 to C32 and C56 to C58 we did proceed in the same manner. The relative occupancies between the two positions of each atom were refined with 1:1 ratios. In the structure of $[L^2H_2][AuBr_2][AuBr_4]$, the C2 and C3 atoms were refined on two positions (named C2A/C2B and C3A/C3B) with identical anisotropic displacement parameters. The relative occupancies between the A and B position were found to be ca. 3:1. In the structure of $[(AuI_2Cl)_2(L^3)](Et_2O)$, the C31 atom was refined on two positions (C31A/C31B) with identical anisotropic displacement parameters and relative occupancies. In the structure of $[Au_2(L^3)_2][Hg_2I_6]$, small channels occupying 4.8 % of the volume of the crystal are located along the b crystallographic axis. The highest residual electronic density in these channels was found to be 1.35e-/Å^3, which does not give clear evidence for the presence of any solvent molecules in this void space. Further details about the crystal structure refinements can be found directly in the cif files.

Associated Content

X-ray diffraction data, crystal packing figures, synthesis protocols and product characterization data for the organic ligands. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC 911958, 911959, 911960, 911961, 911962, 911963, and 911964 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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