

Optical Properties in Heteronuclear Gold(I)/Silver(I) Complexes of Aliphatic Mixed-Donor Macrocycles Featuring Metallophilic Interactions

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The reaction of the polymeric heterometallic compound [{Au- $(C_6CI_5)_2$ }Ag]_n with the macrocyclic ligands 1-aza-4,7,10-trithiacy-clododecane (L₁), 1,7-diaza-4,11-dithiacyclododecane (L₂), 1-aza-4,10-dithia-7-oxacyclododecane (L₃) in tetrahydrofuran (THF) and 1:1 reaction molar ratio affords the new Au(I)/Ag(I) complexes [{Au(C_6CI_5)_2}Ag(L_1)] (1), [{Au(C_6CI_5)_2}Ag(L_2)] (2),

Introduction

Recently, stimuli-responsive luminescent materials have attracted a great attention because of their potential use in various applications such as photo-electronic, sensing and recording devices.^[1,2] Solid materials that exhibit a switchable luminescence in response to an external mechanical stimulus (shearing, grinding or rubbing) represent a particularly attractive class of photo-functional materials.^[3–10] It is generally recognized that in the absence of a chemical transformation, switching of the luminescence emission behaviour in solid mechanochromic materials is somehow associated to crystalline structural changes in the molecular arrangement motifs and intermolecular interactions in response to the mechanical stimulation.

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 $[{Au(C_6Cl_5)_2}{Ag(L_3)}]$ (3) and $[{Au(C_6Cl_5)_2}{Ag(L_3)}]_2$ (4) that have been structurally characterized. Despite 1–3 show the same nature of binuclear complexes, only 3 changes its luminescence properties upon grinding as a consequence of partial amorphization.

In this respect, the luminescence properties of many heteronuclear gold(I) complexes are currently considered of great interest because they are closely related to their structural features, in particular, to the intermolecular interaction patterns in the crystal lattice based on aurophilic, Au(I)...Au(I), and/or metallophilic Au(I)...M interactions [M = transition and post-transition closed-shell metal ions such as Ag(I) and TI(I)].^[4–11] In fact, solid-state phase transitions in these complexes, in response to external stimuli (grinding, but also heating, pressure and interaction with a solvent), which can involve the alteration of the metallophilic interactions and/or molecular arrangements, are generally associated to luminescence emission changes.^[4–15]

Recently, we have considered macrocyclic ligands of different ring size and nature/number of donor atoms to support Au(I)···M(I) (M=Ag, TI) metallophillic interactions in the formation of heteronuclear complexes starting from organometallic gold(I) polymeric complexes [{Au(C₆X₅)₂}M]_n (M=Ag(I), TI(I); X = CI, F) in low polar solvents (toluene, tetrahydrofuran (THF)).^[16-24] The results achieved so far clearly proved a great versatility and potentiality of these ligands, in particular, thioether crowns and mixed thia-aza macrocycles also featuring aromatic moieties, in determining unusual structural archetypes, metal ion dispositions and intermolecular Au(I)···M(I) interaction patterns in the isolated Au(I)/Ag(I) and Au(I)/TI(I) heteronuclear complexes. However, no external mechanical stimuli-responsive materials were obtained using heteronuclear gold(I) complexes with this type of ligands.

Intrigued by the possibility of using macrocyclic ligands in the preparation of heteronuclear gold(I) complexes featuring mechanocromic properties, we report herein the results achieved upon exploring the reactivity of the heterometallic compound $[{Au(C_6Cl_5)_2}Ag]_n$ with the mixed-donor macrocyclic ligands L_1 - L_3 (Scheme 1) in a 1:1 molar ratio in THF.





Scheme 1. Ligands considered in this work.

Results and Discussion

Synthesis and Characterization

The reaction between the polymeric starting organometallic gold(I) compound $[{Au(C_6Cl_5)_2}Ag]_n$ and L_1-L_3 in a 1:1 molar ratio in THF afforded in good yields the complexes 1–4 (Scheme 2) as whitish solids after precipitation from the reaction mixture by the addition of *n*-hexane. In the case of L_3 , on changing the reaction conditions, in particular, the temperature and reaction time (see Scheme 2 and Experimental Section), two different structural isomers were isolated, which feature the same L_3 /Ag stoichiometric ratio but different metallophillic interactions and, consequently, photophysical properties (see below).

Complexes 3 and 4 are soluble in O-donor solvents such as THF and acetone, partially soluble in dichloromethane and acetonitrile, insoluble in *n*-hexane and diethyl ether. Complexes 1 and 2 are nearly insoluble in all solvent tested but THF and acetone, in which a solubility sufficient enough to perform NMR measurements was observed. The elemental analyses and spectroscopic data of 1-4 are in agreement with the formulation as reported in Scheme 2 (see Experimental section).

In particular, IR spectra of 1–4 show, among others, the absorption bands arising from the C_6CI_5 groups at about 836 and 615 cm⁻¹, while molar conductivity measurements in acetone solutions agree with a dissociative process of 1–4 into $[Au(C_6CI_5)_2]^-$ and $[Ag(L)]^+$ ions, showing values at about 100 Ω^{-1} cm²mol⁻¹, corresponding to uni-valent electrolytes.

The MALDI(-) mass spectra of **1–4** display a peak at m/z = 1497 due to the unit [{Au(C₆X₅)₂}Ag]⁻ and a peak at m/z = 695 corresponding to [{Au(C₆X₅)₂}]⁻. In the MALDI(+) mass spectra peaks due to the fragment [Ag(L)]⁺ appear at m/z = 331 (L₁), 312 (L₂) and 313 (L₃) having isotopic distributions in agreement

$$[\operatorname{Au}(\operatorname{C}_{6}\operatorname{Cl}_{5})_{2}\operatorname{Ag}]_{n} \left\{ \begin{array}{c} \mathbf{L}_{1} \xrightarrow{1:1} [\{\operatorname{Au}(\operatorname{C}_{6}\operatorname{Cl}_{5})_{2}\}\{\operatorname{Ag}(\mathbf{L}_{1})\}](1) \\ \mathbf{L}_{2} \xrightarrow{1:1} [\{\operatorname{Au}(\operatorname{C}_{6}\operatorname{Cl}_{5})_{2}\}\{\operatorname{Ag}(\mathbf{L}_{2})\}](2) \\ \mathbf{L}_{3} \xrightarrow{1:1} [\{\operatorname{Au}(\operatorname{C}_{6}\operatorname{Cl}_{5})_{2}\}\{\operatorname{Ag}(\mathbf{L}_{2})\}](2) \\ \mathbf{L}_{3} \xrightarrow{1:1} [\{\operatorname{Au}(\operatorname{C}_{6}\operatorname{Cl}_{5})_{2}\}\{\operatorname{Ag}(\mathbf{L}_{3})\}](3) \\ \mathbf{L}_{3} \xrightarrow{1:1} [\{\operatorname{Au}(\operatorname{C}_{6}\operatorname{Cl}_{5})_{2}\}\{\operatorname{Ag}(\mathbf{L}_{3})\}]_{2}(4) \\ 24, r.t. \end{array} \right.$$

Scheme 2. Synthesis of complexes 1-4.

with calculated ones. The ¹H-NMR spectra of the complexes recorded for solubility reasons in $[D_8]$ THF (1, 2) and $[D_6]$ DMF (3, 4) show proton resonances in the aliphatic region (see Experimental Section) very similar to those observed for the free macrocyclic ligands, in agreement with a small effect exerted by the coordination of silver(l).

Crystal Structures

Single crystals suitable for X-Ray diffraction analysis were grown for 1–4 by slow diffusion of *n*-hexane into a saturated solution of the complexes in THF (1, 2, 4) or toluene (3). Complex 4 presented structural disorder, which was modelled as described in the Experimental Section. Unfortunately, the crystals of 1–3 were of low quality and presented severe structural disorder in the neutral ligand bonded to silver, which afforded high residual electron density peaks. Nonetheless, a rough description of their crystal structures can be done, and the disposition of ligands and metals, as well as the absence of aurophilic interactions, can be definitively confirmed.

The X-Ray crystal structures of 1-3 consist of binuclear complexes featuring a $[Ag(L)]^+$ cation and a $[Au(C_6Cl_5)_2]^-$ anion connected by an unsupported Au(I)---Aq(I) metallophillic interaction [Au1-Ag1 = 2.79 (1) or 2.81 Å (2-3)] (see Figure 1). In all three complexes the silver(I) metal centre participates in a weak Ag-C interaction with the ipso carbon atom of one of the perchlorophenyl rings bonded to the gold(I) atom [Ag1- C_{inso} = 2.53 (1), 2.67 (2), 2.69 Å (3)]. A lengthening of the Au(I)-Ag(I) and Ag-Cipso distances is overall observed on going from 1 to 3, which can be attributed to the different donor properties of the involved macrocyclic ligands, which become "harder" on passing from the NS₃ donor set in L_1 to the N₂S₂ and NS₂O donor-sets in L_2 and L_3 , respectively. To date, in the literature only two examples of binuclear Au(I)/Ag(I) complexes displaying an unsupported Au(I)---Ag(I) contact and a Ag-C_{ipso}, interaction as observed in 1-3 are reported; both feature macrocyclic ligands coordinated to the silver(I) centre but different donor atoms: $[{Au(C_6Cl_5)_2}Ag([14]aneS_4)]$ (Au-Ag = 2.8200(6) Å, Ag-



Figure 1. Molecular structures of complexes 1 (left), 2 (middle) and 3 (right) with the labelling scheme adopted for the atom positions. For 2 and 3 only one component of the disorder model is shown. Hydrogen atoms are omitted for clarity. Due to the low quality of the crystals, all the structures are drawn in a ball and stick model. In the case of complex 3, the disorder present in the molecule prevented the anisotropization of the system.

 $\begin{array}{lll} C_{\it ipso} = 2.900(6) & \mbox{\AA}, & [14] ane S_4 = 1,4,8,11-tetrathiacyclotetradecane)^{[18]} & \mbox{and} & [\{Au(C_6Cl_5)_2\}Ag(TACN)] & (Au-Ag = 2.6915(4) & \mbox{\AA}, & Ag-C_{\it ipso} = 2.398(4) & \mbox{\AA}, & TACN = 1,4,7-triazacyclononane).^{[25]} & \mbox{A similar binuclear structure has also been ascertained for the complex } [\{Au(C_6F_5)_2\}Ag(L_2)]^{[21]} & \mbox{that}, with respect to $\mathbf{2}$, features a bis(pentafluorophenyl)aurate(I) unit. \end{array}$

The Au–Ag and Ag-C_{ipso} distances observed in **1–3** containing N/S and N/S/O mixed-donor macrocyclic ligands (L₁-L₃) are somehow intermediate to those observed in [{Au(C₆Cl₅)₂}Ag([14] aneS₄)] and [{Au(C₆Cl₅)₂}Ag(TACN)] featuring S- and N-donor atoms, respectively.^[18,25]

The Ag–N and Ag–S bond lengths in complexes 1–3 lie within the ranges 2.35-2.45 and 2.57-2.66 Å, respectively, and are similar to those observed in related silver(I) complexes with L_1 and L_3 derivatives.^[26] In 3, the conformation adopted by L_3 upon coordination to the silver(I) centre does not allow the coordination of the oxygen donor atom and, therefore, the ligand imposes a tri-coordination to the metal ion rather than a tetra-coordination as observed for L_1 and L_2 in 1 and 2, respectively.

The gold(I) centres of the $[Au(C_6CI_5)_2]^-$ units are almost linearly coordinated to the two pentachlorophenyl groups, and the perchloroaryl rings are coplanar in 1 and 2, while lie on perpendicular planes in the case of 3 (Figure 1).

Complex 4 crystallizes in the space group $P\overline{1}$ of the triclinic system, and its X-Ray crystal structure reveals the formation of a tetranuclear complex featuring an almost linear L₃-Ag–Au-Au–Ag-L₃ arrangement of ligands and metals (see Figure 2 and Tables S1 and S2 in SI) thanks to a Au(I)---Au(I) interaction of 3.3852(4) Å, which lies on a crystallographic inversion centre. The same arrangement is observed in the crystal structures of
$$\begin{split} & [\{Au(C_6F_5)_2\}Ag([9]aneS_3)_2]_2 & ([9]aneS_3=1,4,7-trithiacyclononane, \\ & Au(I)-Au(I)=3.3702(3) \ \text{Å}),^{[18]} \ \text{E/Z-}[\{Au(C_6CI_5)_2\}Ag([9]aneS_3)_2]_2 & (Au-(I)-Au(I)=3.4136(1) \ \text{Å for the E-isomer and $3.0397(3) $ \text{Å for the Z-isomer},^{[19]} and $ [\{Au(C_6F_5)_2\}\{Ag(L_1)\}]_2 & (Au(I)-Au(I)=3.2633(4) \ \text{Å}).^{[21]} \end{split}$$

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The silver atom in the asymmetric unit of **4** was found to be disordered over two sites (60:40), so two different Au(I)-Ag(I) distances in the [{Au(C₆Cl₅)₂}{Ag(L₃)}] moieties have to be considered, 2.790(4) and 2.662(6) Å. These distances are significantly shorter than that observed in **3** despite the absence of Ag-C_{ipso} interactions in **4** [Ag-C = 3.094(5) and 3.026(7) Å], which is one of the main structural differences between **3** and **4**. Interestingly, the Au(I)-Ag(I) distance of 2.662(6) Å observed in **4** is the shortest so far observed in heteronuclear Au(I)/Ag(I) complexes, if clusters are not considered.

The absence of Ag-C_{ipso} contact in **4** makes the Au–C bond distances within the linear $[Au(C_6CI_5)_2]^-$ fragment of the asymmetric unit nearly identical [2.041(5) and 2.046(5) Å], while in **3** the Au–C distances are quite different [2.01 and 2.15 Å]. As in **3**, the oxygen atom in L₃ is not coordinated to silver(I) in **4** [Ag–O > 2.93 Å], and the Ag–N [2.426(6) and 2.57(2) Å] and Ag–S bond lengths [from 2.530(7) to 2.627(4) Å] compare well with those observed in **1–3** and in related silver(I) complexes with L₁ and L₃ derivatives.^[26]

The coplanar disposition of the perchlorophenyl rings in **4** allows the aurophilic interaction that leads to the formation of the Au_2Ag_2 moiety, which is avoided in **3** due to the nearly orthogonal disposition of the aryl groups observed in this case.

This tetranuclear arrangement in **4** is further stabilized by π -contacts of 3.661 Å (centroid-centroid distance) between the aromatic rings of the two facing bis(pentachlorophenyl)aurate(l) units.

Photophysical Properties

The absorption spectra of **1–4** see Figure 3 and Table 1 were recorded in THF solution $(2.5 \times 10^{-5} \text{ M})$. The similarity of the spectra of **1–4** with those recorded for the precursors [{Au-



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Figure 3. Absorption spectra of complexes 1–4 and the gold(I) precursors $[{Au(C_6Cl_5)_2}Ag]_n$ and $NBu_4[Au(C_6Cl_5)_2]$.



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Table 1. Photophysical properties of complexes 1–4.								
	Uv-Vis in THF $\lambda(nm)/\epsilon(mol^{-1} cm^{-1})$	Solid state (RT) λem(nm)/ λex(nm)	Solid state (77 K) λem(nm)/ λex(nm)	τ(ns)	Φ(%)			
1	241/30400 297/13200	463/362	472/363	$2082\pm\!11$	7.5			
2	241/34400 288/12000	461/369	461/369	1492 ± 78	5.2			
3	242/36000	442/323	458/351	$892\!\pm\!21$	7.0			
4	247/36000 297/14450	501/405	496/360	$1020\!\pm\!13$	5.8			

 $(\mathsf{C}_6\mathsf{Cl}_5)_2\mathsf{Ag}]_n$ and $\mathsf{NBu}_4[\mathsf{Au}(\mathsf{C}_6\mathsf{Cl}_5)_2]$ allows to tentatively assign the observed bands at about 240 and 290 nm to $\pi{\rightarrow}\pi^*$ and Au ${\rightarrow}\pi^*$ transitions involving the pentachlorophenyl rings. For the high energy absorptions, the contribution of $\pi{\rightarrow}\sigma^*$ transitions involving the N/S/O-mixed-donor macrocyclic ligands cannot be ruled out since these ligands show an absorption at 234 nm of less intensity at concentrations similar to that used for 1–4.

While complexes 1–3 display a strong blue luminescence in solid state between 442 and 472 nm, complex 4 shows an emission at about 500 nm, both at room temperature (RT) and at 77 K (liquid nitrogen temperature, see Figure 4 and Table 1). No emission is observed in solution probably due to the dissociation in into $[Au(C_6CI_5)_2]^-$ and $[Ag(L)]^+$ ions as suggested the conductivity measurements and mass spectra.

Complexes 1–3 show a decrease in the emission wavelength both at RT (from 463 to 442 nm) and at 77 K (from 472 to 458 nm) that one is tempted to relate with the increase of the Au(I)-Ag(I) distances (from 2.79 in 1 to 2.81 Å in 2 and 3) and, consequently in the Ag- C_{ipso} distances (from 2.53 in 1 to 2.67 in 2 and 2,69 Å in 3); nevertheless, as can be observed, the energy emissions in 1 and 2 are similar.

The very close Au–Ag distances for the three complexes and the distinct emissive behaviour is likely to indicate that the

Au(I)---Ag(I) interaction is not exclusively the responsible for the optical behaviour, and that the ligands have influence in the emissive states.

As compared to 1–3, a slight shift to higher values is observed for the emission wavelength of 4 (Table 1, Figure 4) probably due to the aurophillic interaction, which causes a lower degree of compressibility in the system.

The red-shift at lower temperatures of the emission bands in the cases of 1 and 3 is commonly due to a contraction of the crystal system, which causes a decrease in the energy difference between the frontier orbitals. In the case of 2, the temperature variation does not influence the emission energy of the compound (rigidochromism), probably because the symmetry of the ligand L₂ and the interaction with the metal centre strongly influences the structural rigidity of the system (a similar behaviour has been observed in [{Au(C₆Cl₅)₂}Ag(TACN)].^[25] The blue-shift in the case of 4 has also been observed for the compound [{Au(C₆F₅)₂}Ag([9]aneS₃)₂].^[18]

Only in the case of **3** an interesting strong change in the luminescence emission (from blue to green) is observed when the crystalline compound is ground in a mortar. As shown in Figure 5, the broad band at 442 nm (black line) corresponding to the crystalline species disappears completely upon grinding and a narrower emission band appears at 517 nm (red line) for the ground compound with an overall red-shift displacement of 75 nm for the emission band.

Powder X-Ray diffraction spectra on compound **3** show identical patterns before and after grinding, which allows to rule out a phase change process at the base of luminescence emission changes observed upon grinding. However, the appreciable widening of the peaks in the spectrum recorded after mechanical stimulus (Figure 6) is consistent with a crystallite size reduction and partial amorphization of the compound. This crystal-to-amorphous conversion in mechano-



Figure 4. Excitation and emission spectra of complexes 1 (a), 2 (b), 3 (c), 4 (d) in the solid state at RT and at 77 K.



Figure 5. Emission spectra of compound **3** at RT before (black line) and after (red line) grinding of the compound. Images show the luminescence change upon application of the mechanical stimulus.





Figure 6. X-Ray powder diffraction patterns: simulated PXRD spectrum from the single crystal data of 3 (black); compound 3 before (red) and after (blue) grinding.

chromic complexes has been found in several metals as Ag(I), Cu(I), Al(III), Ir(III), etc. and described several years ago.^[27] In addition, we^[28] and others have previously reported such mechanochromic behaviour for many gold based complexes, including perhalophenyl derivatives as it is in our case.^[29-33]

In order to support the observed changes of the PXRD profile of **3** after grinding, we have represented the corresponding Williamson-Hall plots (see Figure S1 in SI). From the analysis of the ungrounded sample of **3**, the crystallite size is around 410 nm and the microstrain is 5.9×10^{-3} . The Williamson-Hall plot of the grounded sample of **3** provides a clearly smaller crystallite size of ca. 75 nm and a slight increase in the microstrain of 6.4×10^{-3} . From these data, we can assume that the grinding process clearly reduces the crystallite size and slightly affects to the crystal microstrain.

Interestingly, although with similar structures, compounds 1 and 2 do not show mechanochromic properties as 3. For them, a widening of the emission band was observed upon grinding without changes in the wavelength of the emission maximum (Figure S2 in SI).

Considering the X-Ray structures on single crystal of 1-3, the greatest difference among them in addition to Au(I)-Ag(I) and Aq-Cinso distances, resides in the relative position of the perchlorophenyl rings, being coplanar in 1 and 2, and located on perpendicular planes in 3. Probably, the emission shift observed for 3 upon grinding could be due to a modification of the relative orientation of the π systems. Although we do not have experimental evidences for this (the IR data show that the orientation of the rings do not affect the IR bands of the ligands, since all appear at very similar wavenumbers), DFT calculations (see below) clearly show that the photophysical properties of the compounds considered are largely affected in the solid state by the relative orientation of the perchloroaromatic rings. Indeed, the subtle change in the relative orientation of the perhalophenyl ligands in models 1a and 3a gives rise to completely different electronic excitations of ³IL and ³MLCT nature, respectively, what would support a large emission shift if this molecular change of the π systems would occur upon grinding of compound 3. Therefore, we cannot prove that the modification of the orientation of the aromatic rings is the cause of the emission shifts, although this possibility cannot be ruled out.

Computational Studies

Single-point DFT calculations on simplified models were performed to explain the origin of the observed optical properties of the complexes on the basis of their solid state structures. We chose model systems **3a** and **4a** (see Figure S3, SI), representing complexes [$\{Au(C_6Cl_5)_2\}\{Ag(L_3)\}\}$] (**3**) and [$\{Au(C_6Cl_5)_2\}\{Ag(L_3)\}\}$] (**4**), respectively. Both complexes bear the same ligand bonded to Ag(I) centres (L₃), but display different nuclearities and arrangements. Thus, model **3a** displays a binuclear heterometallic arrangement built up through the heterometallic Au(I)--Ag(I) interaction between the corresponding counterionic fragments, whereas model **4a** consists of the link of two binuclear Au(I)-Ag(I) units by an additional Au(I)--Au-(I) in C_i symmetry, leading to a tetranuclear model system.

Initially, a population analysis (see SI, Tables S3 and S5) was considered to investigate the contribution of each atom to the Molecular Orbitals (Mos) involved in the most intense TD-DFT excitations (see below), for models 3a and 4a. In the case of model 3a, the highest occupied molecular orbital (HOMO) displays a pentachlorophenyl ligand-based character (90% contribution) while the lowest empty molecular orbital (LUMO) is mainly localized on the other perchlorophenyl ligand (68%), with some contribution from the Au(I) (8%) and Ag(I) (17%) metal centres. HOMO-1 display a large metal-based character (Au(I) 29% and Ag(I) 24%) with additional ligand contributions; HOMO-2 shows a pentachlorophenyl character (82%) with some Au(I) contribution (14%) and, finally, HOMO-4 displays a mixed pentachlorophenyl (48%) and metal-based character (Au(I) 13% and Ag(I) 24%). LUMO+1 to LUMO+4 are pentachlorophenvl based, whereas LUMO + 5 is located at the $[Aq(L_3)]^+$ moiety (L 71% and Aq(I) 27%). In the case of model 4a, the HOMO displays a metal-based character (Au(I) 42% and Ag(I) 20%) with some contribution from L_3 (18%) and C_6Cl_5 ligands. The LUMO is located on the pentachlorophenyl ligands (48%) and on the metals (Au(I) 24% and Ag(I) 16%). HOMO-2 to HOMO-4 are mainly perchlorophenyl ligand-based, with a minor contribution from Au(I) to HOMO-2 and HOMO-3. Similarly, LUMO+1 and LUMO+2 are mostly percholorphenyl ligand-based, with a minor contribution from Au(I). The MO diagram for models 3a and 4a is also depicted in Figure 7, including the MOs involved in the computed electronic excitations (see below). The obtained HOMO-LUMO gap computed energies agree well with the excitation and emission red-shift observed for complex 4. This tendency agrees with the formation of aurophilic interactions in 4, which produces a rise in energy of the corresponding antibonding HOMO and decrease of the bonding LUMO, both Au(I)--Au(I) based orbitals.

The first 20 singlet-singlet excitation energies were computed for **3a** and **4a** at the TD-DFT level of theory (see Experimental Section). Since the measured lifetime for **3** and **4** is near the microseconds range, the lowest singlet-triplet





Figure 7. Molecular Orbital diagram (energy in Hartrees) for model systems 3a and 4a and representative MOs (isovalue = 0.03) (L=LUMO; H=HOMO).

excitation at the TD-DFT level was also computed for both model systems (see SI, Tables S4 and S6).

The TD-DFT analysis of the most important single-singlet transitions calculated for model **3a** shows that they appear between 388 and 309 nm, being the most intense singlet-singlet excitations at 388, 333 and 324 nm, whereas the lowest singlet – triplet excitation appears at 443 nm (see Table S4 in SI). The intense singlet-singlet excitation at 388 nm consists of an admixture of a metal (Au and Ag) to ligand (C₆Cl₅) charge transfer transition together with an intraligand transition in the perchlorophenyl ligand. The excitation at 333 nm can be assigned to an intraligand transition in the perchlorophenyl ligand and the one at 324 nm consists of a metal (Au and Ag) to ligand (C₆Cl₅) charge transfer transition.

The lowest singlet-triplet excitation at 443 nm is mainly due to the HOMO \rightarrow LUMO+2 transition, which implies forbidden intraligand transitions ³IL within the C₆Cl₅ ligands, only slightly perturbed by the metals in the HOMO orbital. This value is slightly lower in energy than the experimental excitation spectrum that shows two maxima at 320 and 370 nm.

In the case of model **4a**, the TD-DFT analysis of the most important single-singlet transitions displays very strong low energy excitations at 483, 418 and 333, whereas the lowest singlet – triplet excitation appears at 533 nm (see Table S6 in SI). The computed excitations appear red-shifted compared to the experimental ones. This tendency is usually observed when charge transfer excitations are computed, since DFT tends to underestimate the energy of charge-transfer states. The intense singlet-singlet excitation at 483 nm consists of a charge transfer transition between the interacting metals (Ag···Au···Au···Ag) and the pentachlorophenyl ligand. The excitation at 418 nm can be assigned to a charge-transfer transition from the ligand (C₆Cl₅) to the interacting metals (Ag···Au···Ag) and the one at 333 nm consist of a metal-perturbed intraligand $(\mathsf{C}_6\mathsf{Cl}_5)$ transition.

The lowest singlet-triplet excitation at 533 nm is due to a HOMO \rightarrow LUMO transition, which implies a forbidden ³MLCT charge transfer transition between the interacting metals (Ag.-Au.-Au.-Ag) and the pentachlorophenyl ligand.

In order to explain how the conformational difference between complexes 1 and 2 with 3 (C_6Cl_5 ligand twist) affects to their optical response, we have carried out DFT and TD-DFT calculations on model system 1 a and we have compared it with model 3a. In Figure S4 (SI) we can observe several interesting features. First, the computed HOMO-LUMO gaps for these models are very similar. Taking into account that both compounds emit from the lowest triplet excited state and the similarity of the experimental emission energies, this calculated result agrees with the experimental findings. Indeed, we have also computed the lowest singlet-triplet excitation for model 1 a (Table S7), obtaining a HOMO-LUMO transition at 426 nm, very similar to the one obtained for model 3a at 443 nm. In addition, if we also have a look to the shape of the frontier Mos. we can observe that the subtle structural conformational C_6Cl_5 ring twist change from model 1a (coplanar pentachlorophenyl rings) to model 3a (perpendicular rings) produces a large impact in the energy and shape of the Mos. As we have mentioned before, in the case of model 3a, the lowest singlettriplet transition is of intraligand nature (³IL), since both HOMO and HOMO+2 are located in the twisted pentachlorophenyl ring. However, in the case of model 1a the analogous orbital located in the pentachlorophenyl ring is more stable (HOMO-3) leaving the highest occupied HOMO mainly located at the gold centre. Since the lowest singlet-triplet transition computed for model 1 a involves HOMO and LUMO, in this case the origin of



the emissive properties arises from a metal to ligand charge transfer transition (3 MLCT).

Conclusion

In summary, we have synthesized and characterized the new heteronuclear Au(I)/Ag(I) complexes 1-4 featuring metallophillic interactions and mixed-donor macrocyclic ligands coordinated to the silver(I) centre(s). Despite the very similar structure of 1-3, only 3 shows mechanochromism as it changes its luminescence emission from 442 to 517 nm upon grinding at room temperature. X-Ray powder diffraction point out a possible partial amorphization and an important crystallite size reduction of the compound upon application of the external mechanical stimulus as the main reason of the luminescence behaviour observed. The fact that in 1 and 2 the perchlorophenyl rings are coplanar, while in 3 they lie on perpendicular planes, together with the different donor properties of the macrocyclic ligands in 1-3 allow to conclude how small structural differences in this kind of gold(I) complexes can generate large variations in the observed photophysical properties.

Experimental Section

General. 1-aza-4,7,10-trithiacyclododecane (L_1) ,^[34] 1,7-diaza-4,11-dithiacyclododecane (L_2) ,^[35] 1-aza-4,10-dithia-7-oxacyclododecane (L_3) ,^[36] and $[Au(C_6Cl_5)_2Ag]_n^{[37]}$ were prepared according to the literature.

Instrumentation. Infrared spectra were recorded in the 4000-500 cm⁻¹ range on a PerkinElmer FT-IR Spectrum Two with an ATR accessory. C, H, and S analyses were carried out with a PerkinElmer 240 C microanalyzer. The conductivity measurements were made using a Jenway 4010 digital equipment in acetone solutions ($2 \times$ 10^{-5} M). Mass spectra were recorded with a Bruker Microflex MALDI-TOF using dithranol (DIT) or 11-dicyano-4-tertbutylphenyl-3methylbutadiene (DCTB) as the matrix. ¹H-NMR spectra were recorded with a Bruker Avance 400 in [D₈]THF and [D₆]DMF. Chemical shifts are quoted relative to SiMe₄ (¹H, external). Absorption spectra in solution were recorded on a Hewlett-Packard 8453 diode array UV-vis spectrophotometer. Diffuse reflectance UVvis spectra of pressed powder samples diluted with KBr were recorded on a Shimadzu (UV3600 spectrophotometer with a Harrick Praying Mantis accessory) and recalculated following the Kubelka-Munk function. Excitation and emission spectra amd quabtum yields in the solid state were recorded with a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter. Lifetime measurements were recorded with a Datastation HUB-B with a nanoLED controller and DAS6 software. The nanoLED employed for lifetime measurements was one of 370 nm with pulse lengths of 0.8-1.4 ns. The lifetime data were fitted with the Jobin-Yvon software package.

[{Au(C₆Cl₅)₂}{Ag(L₁)}] (1). L₁ (13.8 mg, 0.062 mmol) was added to a suspension of [{Au(C₆Cl₅)₂}Ag]_n (50.0 mg, 0.062 mmol) in THF. The mixture was stirred at room temperature for 2 h, and then the solvent was partially removed under reduced pressure. Finally, the addition of n-hexane led to the precipitation of product 1 as a white-grey solid, which was filtered and washed with *n*-hexane (48.0 mg, 75% yield). Elemental analysis (%) calcd. for C₂₀H₁₇AgAuCl₁₀NS₃ (1026.91): C 23.39, H 1.67, N 1.36 S 9.37. Found: C 23.12, H 1.71, N 1.39 S 9.50. ¹H-NMR (400 MHz, [D₈]THF, ppm): $\delta_{\rm H}$

2.66-2.73 (m, 4H, N-CH₂), 2.80 (m, 12H, S-CH₂). MALDI-TOF(–) m/z (%): 695 [Au(C₆Cl₅)₂]⁻ (100), 1497 [{Au(C₆Cl₅)₃}₂Ag]⁻ (42). MALDI-TOF (+) m/z (%): 331 [Ag(L₁)]⁺ (100). ATR: ν([Au(C₆Cl₅)₂]⁻) at 836 and 614 cm⁻¹. $\Lambda_{\rm M}$ (acetone): 105 Ω^{-1} cm²mol⁻¹.

[{**Au**(C₆Cl₅)₂}{**Ag**(L₂)}] (2). L₂ (12,8 mg, 0.062 mmol) was added to a suspension of [{Au(C₆Cl₅)₂}Ag]_n 50 mg, 0.062 mmol) in THF. After 2 h of stirring, the solution was concentrated under vacuum. Finally, the addition of n-hexane led to the precipitation of product **2** as a pink-white solid that was filtered and washed with *n*-hexane (47.8 mg, 76% yield). Elemental analysis (%) calcd. for C₂₀H₁₈AgAuCl₁₀N₂S₂ (1009.86): C 23.79, H 1.80, N 2.77, S 6.35. Found C 24.01, H 1.90, N 2.90, S 6.25. ¹H-NMR (400 MHz, [D₈]THF, ppm): δ_H 2.62-2.65 (m, 8H, CH₂N), 2.68-2.70 (m, 8H, CH₂S). MALDI-TOF(–) m/z (%): 695 [Au(C₆Cl₅)₂]⁻ (100). ATR: v([Au(C₆F₅)₂]⁻) at 836 and 617 cm⁻¹. $\Lambda_{\rm M}$ (acetone): 105 Ω^{-1} cm²mol⁻¹.

[{**Au**(C₆Cl₅)₂}{**Ag**(L₃)}] (3). L₃ (12.1 mg, 0.062 mmol) was added to a suspension of [{Au(C₆Cl₅)₂}Ag]_n (50.0 mg, 0.062 mmol) in THF. The mixture was stirred at room temperature for 2 h, and then the solvent was partially removed under reduced pressure. Finally, the addition of n-hexane led to the precipitation of product **3** as a white solid, which was filtered and washed with n-hexane (48.0 mg, 77% yield). Elemental analysis (%) calcd. for C₂₀H₁₇AgAuCl₁₀NS₂O (1010.84): C 23.76, H 1.70, N 1.39 S 6.34. Found: C 23.12, H 1.73, N 1.44 S 6.50. ¹H-NMR (400 MHz, [D₆]DMF, ppm): $\delta_{\rm H}$ 2.75-2.92 (m, 12H, N-CH₂,S-CH₂), 3.58 (m, 4H, O-CH₂). MALDI-TOF(–) m/z (%): 695 [Au(C₆Cl₅)₂]⁻ (100), 1497 [{Au(C₆Cl₅)₂]₂Ag]⁻ (42). MALDI-TOF(+) m/z (%): 313 [Ag(L₃)]⁺ (100). ATR: ν([Au(C₆Cl₅)₂]⁻) at 836 and 614 cm⁻¹. $A_{\rm M}$ (acetone): 105 Ω⁻¹cm² mol⁻¹.

[{Au(C₆Cl₅)₂}{Ag(L₃)}]₂ (4). L₃ (12.1 mg, 0.062 mmol) was added to a suspension of [{Au(C₆Cl₅)₂}Ag]_n (50.0 mg, 0.062 mmol) in THF. The mixture was stirred under reflux for 2 h and 24 h at room temperature, then the solvent was partially removed under reduced pressure. Finally, the addition of n-hexane led to the precipitation of product **4** as a grey solid, which was filtered and washed with *n*-hexane (38.0 mg, 61% yield). Elemental analysis (%) calcd. for C₂₀H₁₇AgAuCl₁₀NS₂O (1010.84): C 23.76, H 1.70, N 1.39 S 6.34. Found: C 23.12, H 1.73, N 1.44 S 6.50. ¹H-NMR (400 MHz, [D₆]DMF, ppm): δ_H 2.73-2.90 (m, 12H, N-CH₂, S- CH₂), 3.58 (m, 4H, O-CH₂). MALDI-TOF(-) m/z (%): 695 [Au(C₆Cl₅)₂]⁻ (100), 1497 [{Au(C₆Cl₅)₂]⁻ (42). MALDI-TOF(+) m/z (%): 313 [Ag(L₃)]⁺ (100). ATR: v([Au(C₆Cl₅)₂]⁻) at 837 and 615 cm⁻¹. Λ_M (acetone): 107 Ω⁻¹ cm² mol⁻¹.

Crystallography

Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Nonius Kappa CCD (2, 4) or in a Bruker APEX-II CCD diffractometer (1, 3) equipped with an Oxford Instruments low-temperature attachment. Data were collected using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and scan types ω and ϕ . Absorption effects were treated by semiempirical corrections based on multiple scans. The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.^[38] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. 1-3 presented severe structural disorder in L_1 , L_2 or L_3 , respectively, which could not be resolved, thus affording high residual electron density peaks. 4 presented structural disorder in two different parts: the silver atom was disordered over two sites (60:40), and the oxygen and nitrogen atoms of the neutral ligand bonded to silver (L_3) were found to be disordered over two different positions (80:20). Further details of the data collection and refinement for 4 are collected in Table S2, while selected bond lengths and angles are collected in Table S1 (Supporting Information). The cif files containing the supplementary



crystallographic data for 1–3 are included as Electronic Supplementary Information.

Deposition Number 2095237 (for **4**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Computational Details

All calculations were performed using TURBOMOLE 6.4 program^[39] using the pbe functional^[40,41] and the dispersion correction DFT-D3.^[42] The def2-TZVP basis sets^[43] and the corresponding ECPs were employed for gold(I) and silver(I). The atoms N, CI, F, H, and C were treated using the SVP basis sets.^[44] All the calculations were performed on model systems built from their corresponding X-ray structures. Tables S3-S6 provide the population analysis and TD-DFT results for model systems **3a-4a**, while Table S7 provides the TD-DFT results for the model system **1a**.

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Conflict of Interest

The authors declare no conflict of interest.

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