

Luminescent Gold(I)-Thallium(I) Arrays through N-Bidentate Building Blocks

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Z. Naturforsch. **59b**, 1379 – 1386 (2004); received August 6, 2004

Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Heteropolynuclear gold(I)-thallium(I) complexes of the type $[\text{TlL}_n][\text{Au}(\text{C}_6\text{F}_5)_2]$ ($\text{L} = \text{py}$ (**2**), 2,2'-bipy (**3**), 1,10-phen (**4**) or 4,4'-bipy and THF (**5**); $n = 1, 2$) have been obtained from reactions of the corresponding N-donor ligands with the precursor $\{\text{Tl}[\text{Au}(\text{C}_6\text{F}_5)_2]_n\}$ (**1**). The crystal structures of complexes **3**–**5** have been determined by X-ray diffraction showing one- (**3**, **4**) or three-dimensional (**5**) arrays. All complexes are photoluminescent in the solid state at RT and at 77 K. The strong visible emissions of complexes **2**–**5** are displayed over a wide range of wavelengths (460–620 nm) depending on the environment of the thallium(I) centres and on the nature of the N-donor ligand.

Key words: Gold, Thallium, N-Donor Ligands, Luminescence

Introduction

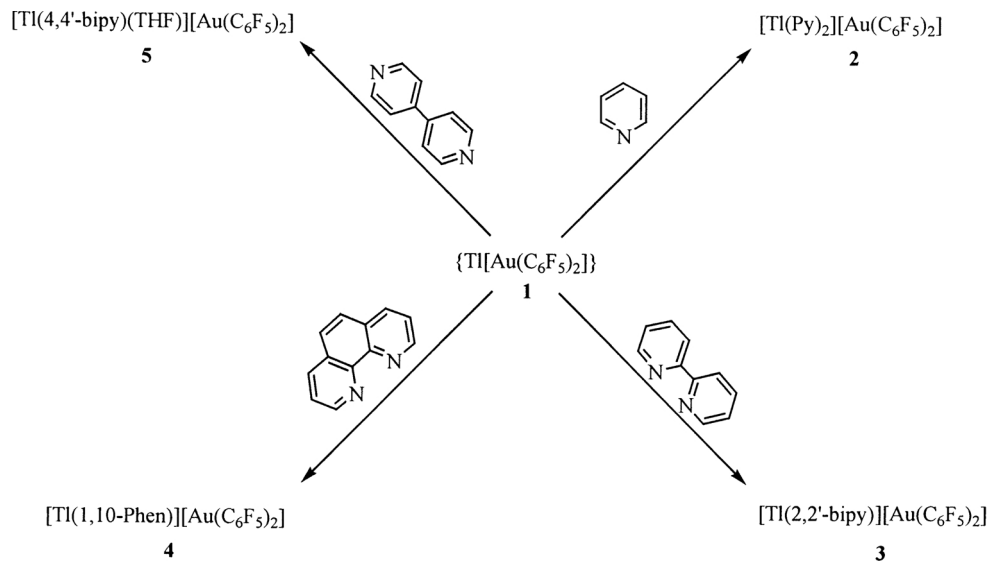
Heterometallic Au(I)-M compounds in which closed-shell intermetallic interactions are observed represent an important class of materials from both the theoretical and experimental point of view [1]. Compounds with $\text{M} = \text{Tl(I)}$ are built up by acid-base stacking between $[\text{AuR}_2]^-$ ($\text{R} = \text{C}_6\text{F}_5$ or C_6Cl_5) Lewis base units and Tl^+ Lewis acids salts, and display not only a rich structural variety but also very interesting photophysical properties [2]. Thus, $\text{Au(I)} \cdots \text{Tl(I)}$ interactions lead to a new class of supramolecular units, whereby many different types of arrangements, such as loosely bound butterfly clusters [3], 1D linear [4] or zig-zag polymeric chains [2a] or 2D- and 3D-arrays [5] can be achieved. The thallium(I) ions are very flexible as regards their coordination geometry; distorted tetrahedral and distorted trigonal bipyramidal are the preferred geometries, taking into account the presence of a stereochemically active lone pair occupying a coordination site [2a].

Since their discovery at the end of the nineteenth century [6], bipyridine ligands have been used exten-

sively in the complexation of metal ions. Whereas the 2,2'-bipyridine ligand has been widely used as a metal chelating ligand [7], 4,4'-bipyridine can in principle be used as bridge to interconnect metal centres in a well-defined structural arrangement. Other N-donor ligands such as 1,10-phenanthroline [8] and pyridine also have a well documented history in coordination chemistry.

With respect to photophysical properties, it has been shown that this type of polymeric organometallic Au(I)-Tl(I) compounds can be considered as a new class of luminescent materials in which the excitation has, in general, an $[\text{AuR}_2]^- \rightarrow \text{Tl}^+$ charge-transfer character, whereby the Tl(I) centres act as fluorophores. The differing ligand environments around Au(I) (e.g. using different perhalophenyl ligands) and Tl(I) centres influence the emissive properties of these complexes, as do the neutral donor ligands bonded to the latter [2a].

In this paper we report the synthesis, structural characterization and photophysical properties of the new polymeric organometallic Au-Tl complexes obtained in the reaction between $\{\text{Tl}[\text{Au}(\text{C}_6\text{F}_5)_2]_n\}$ (**1**) [2b] and



Scheme 1.

two equivalents of pyridine (**2**) or one equivalent of 2,2'-bipyridine (**3**), 1,10-phenanthroline (**4**) or 4,4'-bipyridine (**5**), respectively.

Results and Discussion

Synthesis and characterization: Complex $[\text{Tl}(\text{Py})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$ (**2**) (Py = pyridine) was prepared by addition of two equivalents of pyridine to a solution of one equivalent of $\{\text{Tl}[\text{Au}(\text{C}_6\text{F}_5)_2]\}_n$ (**1**) in THF. The complex is isolated as a yellow solid that is soluble in donor solvents as acetone and THF, partially soluble in dichloromethane and insoluble in diethyl ether and *n*-hexane. The elemental analyses and other physical and spectroscopic properties are in accordance with the proposed stoichiometry. Dissociative equilibria in solution involving the ionic counterparts of complex (**2**) are indicated by the conductivity measurements, consistent with an ionic formulation as 1:1 electrolyte, or by the ^{19}F NMR measurements of **2**, which display free $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$ units. These equilibria also affect the neutral ligands (pyridine) attached to Tl(I) in the solid state, since the ^1H NMR spectrum in d_6 -acetone displays the signals corresponding to the free ligands at 7.38 (m), 7.78 (t) and 8.60 (m) ppm, respectively. The IR spectrum of complex **2** shows, among others, absorptions arising from C_6F_5 groups bonded to gold(I) at 783, 957 and 1507 cm^{-1} [9]; the Tl(I)-N stretching mode corresponding to the coordination of the pyridine ligand to thallium(I) appears as a weak absorption at 372 cm^{-1} [5].

In contrast, the reactions of one equivalent of complex $\{\text{Tl}[\text{Au}(\text{C}_6\text{F}_5)_2]\}_n$ (**1**) in THF with one equivalent of the chelating ligands 2,2'-bipyridine (2,2'-bipy) or 1,10-phenanthroline (1,10-phen) give rise to complexes $[\text{Tl}(2,2'\text{-bipy})][\text{Au}(\text{C}_6\text{F}_5)_2]$ (**3**) and $[\text{Tl}(1,10\text{-phen})][\text{Au}(\text{C}_6\text{F}_5)_2]$ (**4**) as light yellow and yellow solids, respectively. These complexes are soluble in acetone and THF, partially soluble in dichloromethane and insoluble in diethyl ether and *n*-hexane. The elemental analysis and physical and spectroscopic properties are in agreement with the proposed formulas. As in the case of complex **2**, complexes **3** and **4** also dissociate into ionic counterparts as observed in the molar conductivity measurements in acetone (**2** and **3** behave as 1:1 electrolytes) and in their ^{19}F NMR spectra, which resemble the pattern of the starting material for the synthesis of complex **1**, $\text{NBu}_4[\text{Au}(\text{C}_6\text{F}_5)_2]$. Their ^1H NMR spectra in d_6 -acetone display the signals corresponding to the ligand 2,2'-bipyridine in **3** at 8.77 (d), 8.43 (d), 8.04 (dd) and 7.57 (dd) ppm or 1,10-phenanthroline in **4** at 9.23 (dd), 8.70 (dd), 8.11 (m) and 8.02 (dd) ppm. Their IR spectra display the bands arising from C_6F_5 ligands bonded to gold(I) at 780, 951 and 1505 cm^{-1} (**3**) and 787, 957 and 1504 cm^{-1} (**4**) and the Tl(I)-N stretching modes corresponding to the coordination of the ligands to thallium(I) that appear at 373 and 372 cm^{-1} for complexes **3** and **4**, respectively.

The crystal structures of **3** and **4** were determined by X-ray diffraction from single crystals obtained by slow diffusion of hexane into a solution of the com-

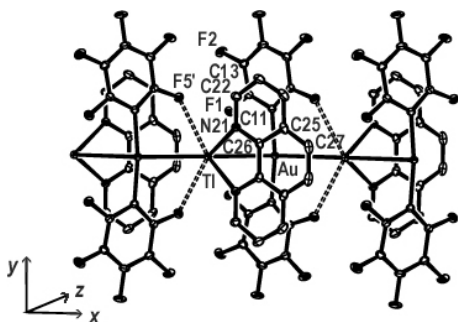


Fig. 1. Part of the polymetallic chain of complex **3** (30% probability level) with the labelling scheme for the atom positions. Hydrogen atoms have been omitted for clarity.

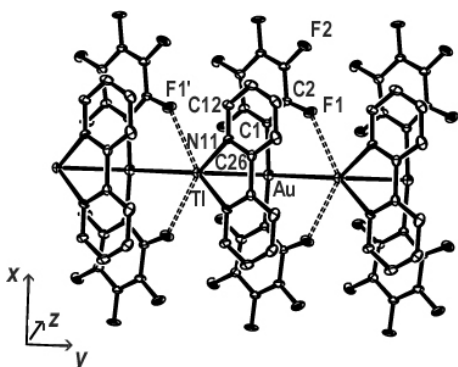


Fig. 2. Part of the polymetallic chain of complex **4** (30% probability level) with the labelling scheme for the atom positions. Hydrogen atoms have been omitted for clarity.

plex in acetone or tetrahydrofuran, respectively. In both structures, the gold and thallium atoms lie in mirror planes. Both display topologically equivalent polymeric chains of alternating gold(I) and thallium(I) centres linked *via* unsupported Au \cdots Tl interactions that run parallel to the crystallographic *x* (**3**) or *y* (**4**) axis (Figs 1 and 2) of 3.0825(4) and 3.1397(4) Å (**3**) or 3.0120(6) and 3.4899(6) Å (**4**), the last of which is somewhat longer than those previously observed in other polynuclear Au/Tl systems with unsupported metal-metal interactions (2.9078(3)–3.3205(3) Å) [2, 4, 5, 10]. Disregarding the Au \cdots Tl contacts, the coordination at gold is linear, with typical Au–C bond lengths of 2.064(3) in **3** or 2.069(8) Å in **4**. The thallium(I) centres bind the nitrogen atoms of a chelating 1,10-phen (**3**) or 2,2'-bipy (**4**) ligand with N–Tl–N angles of 62.03(9) or 60.7(3)°, respectively. The Tl–N distances of 2.676(2) (**3**) or 2.686(8) Å (**4**) compare well with those observed in other related polymeric systems containing 4,4'-bipy bridging ligands [2d, 5], but are about 0.15 Å shorter than the Tl–N bond distance found in

[AuTl(C₆Cl₅)₂(bipy)_{0.5}]_n (2.839(8) Å) [2d]. Finally, there are also Tl \cdots F contacts of 2.8984(16) in **3** or 2.8749(61) Å in **4** within the polymeric chain that may contribute to the stabilization of the structure (Figs 1 and 2). It should be noted that the compounds, despite their close similarity, are not isostructural in the stricter sense because the space groups are different.

Using the 4,4'-bipy ligand and following the same synthetic strategy, we previously reported the synthesis and characterization of complex [Tl(4,4'-bipy)]₂[Au(C₆F₅)₂]₂, in which tetranuclear moieties displaying an unusual Tl–Au–Au–Tl arrangement were observed [5]. We have now performed the reaction of one equivalent of complex {Tl[Au(C₆F₅)₂]}_n (**1**) in THF with one equivalent of the ligand 4,4'-bipyridine, changing some experimental conditions such as evaporation of THF to 2 ml instead of dryness and precipitation with *n*-hexane, thereby obtaining the complex [Tl(4,4'-bipy)(THF)][Au(C₆F₅)₂] (**5**). The complex is isolated as a colourless solid that is soluble in donor solvents as acetone and THF, partially soluble in dichloromethane and insoluble in diethyl ether and *n*-hexane. Its elemental analysis and other physical and spectroscopic properties are in accordance with the proposed stoichiometry. The molar conductivity measurement of complex **5** in acetone and the ¹⁹F NMR spectra of this complex also show the same trend of dissociation into ionic counterparts. ¹H NMR experiments in *d*₆-acetone show the chemical shifts corresponding to the 4,4'-bipy ligand at 7.75 (m) and 8.71 (m) ppm and to THF molecules at 3.60 (m) and 1.77 (m) ppm, respectively. The IR bands assigned to C₆F₅ ligands bonded to gold(I) appear at 785, 955 and 1510 cm^{−1}. The band arising from the Tl(I)–N stretching appears at 371 cm^{−1}.

Single crystals of **5** suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into a solution of the complex in THF. Its crystal structure consists of alternating [Au(C₆F₅)₂][−] and [Tl(4,4'-bipy)_{2/2}(THF)]⁺ units linked *via* unsupported Au \cdots Tl interactions that give rise to a polymeric chain similar to those in **3** and **4** running parallel to the *x* axis (Fig. 3). The Au–Tl distances of 3.2155(3) and 3.4800(3) Å are longer than those found in other polynuclear Au/Tl systems with unsupported metal-metal interactions (2.9078(3)–3.3205(3) Å) [2, 4, 5, 10]. The gold(I) atoms are linearly coordinated to two pentafluorophenyl groups (Au–C = 2.040(6) and 2.043(6) Å), whereby the additional Au \cdots Tl contacts complete a square-planar en-

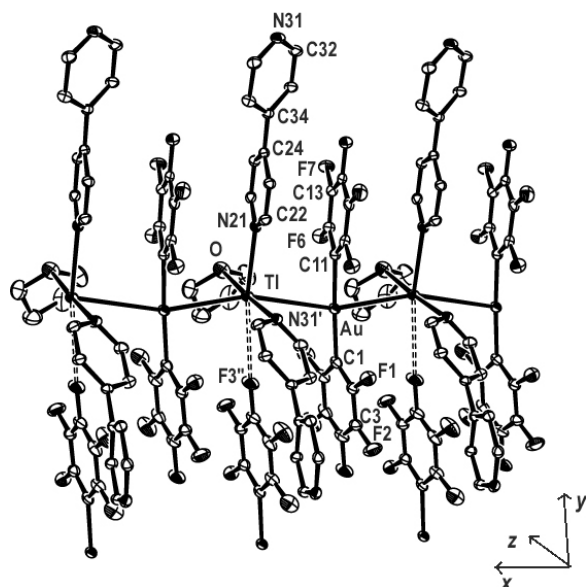


Fig. 3. Part of the polymetallic chain of complex **5** (30% probability level) with the labelling scheme for the atom positions. Hydrogen atoms have been omitted for clarity.

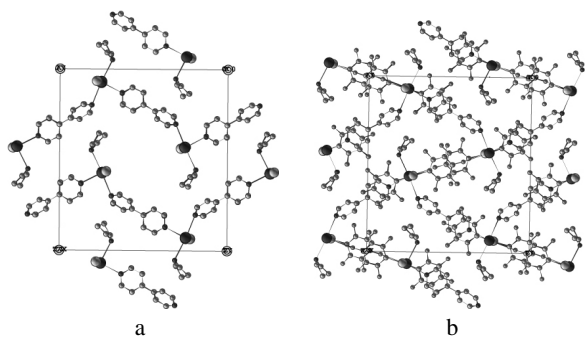


Fig. 4. View of the polymeric structure of **5** perpendicular to the *x* axis. Hydrogen atoms have been omitted for clarity. a) 2D-network without considering the Tl...F interactions. C₆F₅ groups omitted. b) 3D-network considering the Tl...F interactions. C₆F₅ groups included.

environment for Au^I (C-Au-C = 177.2(2) and Tl-Au-Tl = 163.24(1)°). The bidentate ligands in **5** act as bridges between Tl^I centres of adjacent chains resulting in a 2D-network (Fig. 4a), in contrast to the chelating ligands and 1D-polymers of **3** and **4**. A further interesting feature of this structure is the unusual distorted octahedral environment of the thallium(I) centres (Fig. 3), which bind two nitrogen atoms, one of each 4,4'-bipy ligand, the oxygen of a THF molecule and interact with two gold(I) centres and a fluorine atom of a C₆F₅ group of an adjacent layer. Considering this Tl...F contacts of 3.289(4) Å the structure can

be described as a three-dimensional polymer, as shown in Fig. 4b. The Tl-N(21) bond distance of 2.678(5) Å compares well with those described for **3** and **4** and is also similar to those found in other related polymeric systems containing 4,4'-bipy bridging ligands [2d, 5], while the Tl-N(31)#2 distance (2.847(5) Å) is comparable to that in [AuTl(C₆Cl₅)₂(bipy)_{0.5}]_n (2.839(8) Å) [2d]. The tetrahydrofuran molecule in **5** is more weakly coordinated to thallium (Tl-O = 2.810(6) Å) than in the related Au/Tl complexes {[AuTl(C₆Cl₅)₂] · 0.5THF}_n, [AuTl-(C₆Cl₅)₂(THF)₂]_n or {[Tl(bipy)][Tl(bipy)_{0.5}(THF)]-[Au(C₆Cl₅)₂]₂ · THF}_n, with Tl-O distances ranging from 2.626(8) to 2.697(6) Å [2c, 2d]; more comparable are the distances found in [Au(C₆Cl₅)₂][Tl(OPPh₃)]-[Tl(OPPh₃)(THF)] (2.766(5) Å) [2a], {[Tl(bipy)][Tl-(bipy)_{0.5}(THF)][Au(C₆Cl₅)₂]₂]_n (2.781(7) Å) [5], [Tl-(tp)(OSO₂CF₃)(THF) · (THF)] (tp = tetraphenylporphyrinato) (2.778(7) Å) [11], or {[Tl(Me)₂(THF)-(O₂C₆H(Me)(^tBu))]₂]_n (2.862(3) Å) [12].

Photophysical properties: The five reported complexes display a very intense luminescence both at room temperature and at 77 K in the solid state.

The photophysical properties of complex **1** are similar to those of another linear chain reported by us in a previous paper [4]. Thus, it shows a single emission at room temperature in the solid state at 486 nm (exc 395 nm), which is shifted to 504 nm (exc 390 nm) when the measurement is carried out at 77 K, both independent of the excitation wavelengths. The product is not luminescent in solution, presumably because the metal-metal interactions are lost on dissolution; thus a reasonable assignment of the emission is from an excited state formed as a consequence of the interactions between the metals. Previous theoretical Time Dependent-DFT calculations performed in our group on several Au(I)-Tl(I) systems similar to the ones reported here indicate that the most important contribution to the excited state is formed in a charge transfer transition from the electron rich gold centre to the acid thallium atom that acts as fluorophore [2a]. Nevertheless, as far as the theoretical absorption spectra predicted in the calculations have other important transitions, the existence of a contribution to the excited state formed in metal-centered transitions cannot be neglected, though both Au(I) and Tl(I) ions usually have a significant contribution to the higher energy occupied orbitals and to the lower energy virtual ones. The observed thermochromism also agrees with the charge transfer assignment since the thermal contrac-

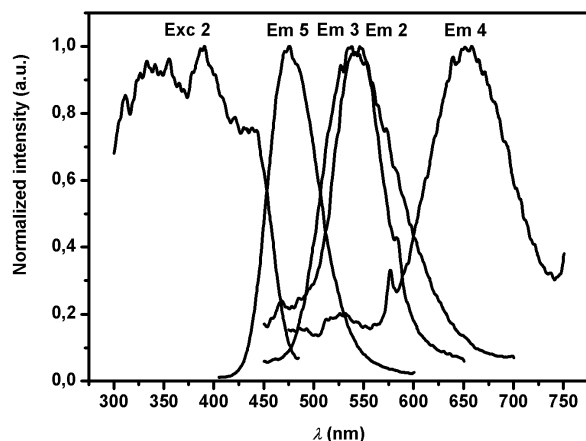


Fig. 5. Normalized excitation spectra of complex **2** (λ_{max} 356 nm) in solid state at 77 K and emission spectra of complexes **5** (λ_{max} exc 380 nm, λ_{max} em 475 nm), **2** (λ_{max} exc 356 nm, λ_{max} em 548 nm), **3** (λ_{max} exc 365 nm, λ_{max} em 537 nm) and **4** (λ_{max} exc 385 nm, em 655 nm) in solid state at 77 K.

tion in the network that occurs when the temperature is lowered reduces the metal-metal distances and, hence, the band gap energy, shifting the emissions to higher wavelengths.

In contrast, when other ligands are bonded to the metallic centres of the chain, as is the case for complexes **2**, **3**, **4** and **5**, the assignment of the excited states that lead to the emissions is not easy and includes various possibilities, such as ligand or metal centred transitions, ligand to metal, metal to ligand or ligand to ligand charge transfer transitions. Thus, each complex **2–5** displays a strong visible emission with a very complicated excitation profile. Nevertheless, the emissions are also independent of the excitation wavelengths. The emission peaks occur (from high to low energy) at 460 nm (max. exc. 375 nm) (**5**), 501 nm (max. exc. 351 nm) (**2**), 531 nm (max. exc. 373 nm) (**3**) and 602 nm (max. exc. 434 nm) (**4**) (see Fig. 5). Taking these data into account, an excited state originating from a ligand centred or ligand to ligand charge transfer seems less probable, since the emissions in those cases should appear at much higher energies [13]. As occurred for complex **1**, these emissions are shifted to 475 nm, 548 nm, 537 nm, 655 nm, respectively, when the temperature is lowered to 77 K (Fig. 5), indicating that the interatomic distances influence the excited states also in these cases. In the same way, when the measurements are carried out in solution, the original colors of the complexes as well as the optical properties disappear, but are recovered when the solvents

are evaporated. These processes can be repeated several times without apparent degradation of the samples. In spite of that this fact may favour the assumption of a charge-transfer transition between the metallic centres as the origin of the luminescence, an emission quench due to the solvent cannot be neglected.

Our conclusion is that the orbitals formed as a consequence of the metal-metal interactions are the main contributors to the excited states that lead to the emissions. Nevertheless, the participation of the ligands seems to be also important since the emission energies appear at different wavelengths. In this regard, previous studies of gold-thallium systems carried out in our group indicate that, of the factors that can influence the excited states, perhaps the most important is the environment around the interacting centres [2a], similarly to the results of Che for gold complexes [14]. In the case of complexes **3** and **4**, both are structurally similar and the thallium atoms display strongly distorted trigonal-bipyramidal environments. The similarity is not only structural but also with respect to the donor characteristics of the ligands bonded at the thallium centres. Therefore, keeping these factors fixed for the two complexes, the longer distances found in complex **3** should shift the emission to lower wavelengths compared to **4**, as is observed experimentally. This comparison cannot be extended to the structurally characterized complex **5**, which displays a distorted octahedral environment and different ligands, but it seems likely, as in complex **2**, that the influence of the ligands in the excited state that give rise to the emissions take place only when the gold and thallium centres preserve an interaction and, consequently, this condition is likely to be the main factor in determining the luminescence of this type of complexes.

Experimental Section

Instrumentation

Infrared spectra were recorded in the 4000–200 cm^{-1} range on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer, using Nujol mulls between polyethylene sheets. C,H,N analysis were carried out with a C.E. Instrument EA-1110 CHNS-O microanalyser. Mass spectra were recorded on a HP-5989B Mass Spectrometer API-Electrospray with interface 59987A. ^1H , ^{19}F NMR spectra were recorded on a Bruker ARX 300 in $(\text{CD}_3)_2\text{CO}$ solutions. Chemical shifts are quoted relative to SiMe_4 (^1H external), CFCl_3 (^{19}F external). Corrected excitation and emission spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer.

Compound	3	4	5
Chemical formula	C ₂₄ H ₈ AuF ₁₀ N ₂ Tl	C ₂₂ H ₈ AuF ₁₀ N ₂ Tl	C ₂₆ H ₁₆ AuF ₁₀ N ₂ OTl
Crystal color	yellow	colourless	colourless
Crystal size [mm]	0.2 × 0.15 × 0.06	0.2 × 0.2 × 0.1	0.2 × 0.15 × 0.1
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	<i>Pnma</i>	<i>Pmn</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	11.7075(16)	23.3524(7)	6.6241(1)
<i>b</i> [Å]	22.868(3)	5.6413(1)	19.1457(3)
<i>c</i> [Å]	8.1220(11)	7.9593(2)	20.9045(4)
β [°]	90	90	98.931(5)
<i>U</i> [Å ³]	2174.4(5)	1048.54(1)	2619.03(8)
<i>Z</i>	4	2	4
<i>D_c</i> [g cm ⁻³]	2.797	2.824	2.444
<i>F</i> (000)	1664	808	1776
<i>T</i> [°K]	143(2)	173(2)	173(2)
2 θ_{\max} [°]	60	68	56
μ (Mo- <i>Kα</i>)[mm ⁻¹]	14.245	14.766	11.836
No. of reflections measured	40888	7027	25500
No. of unique reflections	3264	2217	6247
<i>R</i> _{int}	0.0419	0.0580	0.0531
<i>R</i> ^a (<i>I</i> > 2 σ (<i>I</i>))	0.0167	0.0391	0.0384
<i>wR</i> ^b (<i>F</i> ² , all refl.)	0.0388	0.0923	0.0995
Absolute structure parameter		0.51 (4)	
No. of parameters	175	166	370
No. of restraints	51	68	149
<i>S</i> ^c	1.048	1.053	1.056
Max. residual electron density [e·Å ⁻³]	0.901	2.211	1.243

Table 1. Details of data collection and structure refinement for complexes **3**, **4** and **5**.

^a $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, ^b $wR(F^2) = [\Sigma \{w(F_o^2 - F_c^2)^2\} / \Sigma \{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program, ^c $S = [\Sigma \{w(F_o^2 - F_c^2)^2\} / (n - p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

Table 2. Selected bond lengths [Å] and angles [deg] for complex **3**.

Tl-Au	3.0825(4)	Tl-Au ^{#1}	3.1397(4)
Au-C(11)	2.064(3)	Tl-N(21)	2.676(2)
Tl-F(5) ^{#1}	2.8984(16)		
C(11)-Au-C(11) ^{#2}	171.86(14)	Tl-Au-Tl ^{#3}	140.520(8)
C(11)-Au-Tl	87.14(7)	C(11)-Au-Tl ^{#3}	94.05(7)
Au-Tl-Au ^{#1}	176.077(5)	N(21)-Tl-N(21) ^{#2}	62.03(9)
N(21)-Tl-Au	80.22(5)	N(21)-Tl-Au ^{#1}	103.12(5)
N(21) ^{#2} -Tl-Au ^{#1}	103.12(5)		

Symmetry transformations used to generate equivalent atoms: ^{#1} *x* - 1/2, *y*, -*z* + 1/2; ^{#2} *x*, -*y* + 1/2, *z*; ^{#3} *x* + 1/2, *y*, -*z* + 1/2.

General comments

NBu₄[Au(C₆F₅)₂] was prepared according to literature procedures [15]. TIPF₆ was purchased from Alfa Aesar; 2,2'-bipyridine, 4,4'-bipyridine and 1,10-phenanthroline were purchased from Aldrich and used as received.

Preparation of the complexes [Tl(Py)₂][Au(C₆F₅)₂] (2) (Py = pyridine) [Tl(2,2'-bipy)][Au(C₆F₅)₂] (3) (2,2'-bipy = 2,2'-bipyridine) and [Tl(1,10-phen)][Au(C₆F₅)₂] (4) (1,10-phen = 1,10-phenanthroline)

To a solution of {Tl[Au(C₆F₅)₂]}_{*n*} (**1**) (0.090 g, 0.12 mmol) in 20 ml of THF was added pyridine (19.7 μl, 0.24 mmol), 2,2'-bipyridine (0.019 g, 0.12 mmol) or 1,10-phenanthroline (0.024 g, 0.12 mmol). The solution was

Table 3. Selected bond lengths [Å] and angles [deg] for complex **4**.

Au-C(1)	2.069(8)	Tl-N(11)	2.686(8)
Au-Tl	3.0120(6)	Au-Tl#2	3.4899(6)
Tl-F1 ^{#3}	2.875(6)		
C(1)-Au-C(1) ^{#1}	173.2(4)	C(1)-Au-Tl	87.9(2)
C(1)-Au-Tl ^{#2}	93.4(2)	Tl-Au-Tl ^{#2}	120.19(2)
N(11) ^{#1} -Tl-N(11)	60.7(3)	N(11)-Tl-Au	83.10(18)
N(11)-Tl-Au ^{#3}	143.02(14)	Au-Tl-Au ^{#3}	120.19(2)

Symmetry transformations used to generate equivalent atoms: ^{#1} -*x*, *y*, *z*; ^{#2} *x*, *y* - 1, *z*; ^{#3} *x*, *y* + 1, *z*.

Table 4. Selected bond lengths [Å] and angles [deg] for complex **5**.

Au-C(1)	2.040(6)	Au-C(11)	2.043(6)
Au-Tl	3.2155(3)	Au-Tl ^{#1}	3.4800(3)
Tl-N(21)	2.678(5)	Tl-O	2.810(6)
Tl-N(31) ^{#2}	2.847(5)	Tl-F(3) ^{#3}	3.289(4)
C(1)-Au-C(11)	177.2(2)	C(1)-Au-Tl	92.35(15)
C(11)-Au-Tl	85.37(15)	C(1)-Au-Tl ^{#1}	104.37(15)
C(11)-Au-Tl ^{#1}	77.96(15)	Tl-Au-Tl ^{#1}	163.237(12)
N(21)-Tl-O	91.59(17)	N(21)-Tl-N(31) ^{#2}	84.84(16)
O-Tl-N(31) ^{#2}	176.43(17)	N(21)-Tl-Au	97.32(10)
O-Tl-Au	92.16(13)	N(31) ^{#2} -Tl-Au	88.31(11)
N(21)-Tl-F(3) ^{#3}	170.20(15)	O-Tl-F(3) ^{#3}	96.25(18)
N(31) ^{#2} -Tl-F(3) ^{#3}	87.31(16)	Au-Tl-F(3) ^{#3}	88.29(8)
N(21)-Tl-Au ^{#4}	98.86(10)	O-Tl-Au ^{#4}	91.75(13)
N(31) ^{#2} -Tl-Au ^{#4}	88.79(11)	Au-Tl-Au ^{#4}	163.237(12)
F(3) ^{#3} -Tl-Au ^{#4}	75.08(8)		

Symmetry transformations used to generate equivalent atoms: ^{#1} *x* + 1, *y*, *z*; ^{#2} -*x*, *y* + 1/2, -*z* + 1/2; ^{#3} -*x*, -*y* + 2, -*z*; ^{#4} *x* - 1, *y*, *z*.

	298 K		77 K	
	Exc. /nm	Emiss. /nm	Exc. /nm	Emiss. /nm
[Tl(py) ₂][Au(C ₆ F ₅) ₂] (2)	351	501	356	548
[Tl(2,2'-bipy)][Au(C ₆ F ₅) ₂] (3)	373	531	365	537
[Tl(1,10-phen)][Au(C ₆ F ₅) ₂] (4)	434	602	385	655
[Tl(4,4'-bipy)(THF)][Au(C ₆ F ₅) ₂] (5)	313, 375	460	313, 380	475

Table 5. Excitation and emission spectra of complexes **2–5** in solid state.

stirred for 30 min, and the solvent was evaporated *in vacuo*. The resulting solids were washed with a portion of CH₂Cl₂ (20 ml) and filtered, yielding complexes **2** (71%), **3** (76%) and **4** (56%) as yellow solids. Complex **2**: – ¹⁹F NMR (282 MHz, 298 K, (CD₃)₂CO): δ = –114.90 (m, 4F, F_o), –163.29 (t, ³J(F_p–F_m) = 19.0 Hz, 2F, F_p), –164.36 (m, 4F, F_m). – ¹H NMR (300 MHz, 298 K, (CD₃)₂CO): δ = 7.38 (m, 2H), 7.78 (t, 1H), 8.60 (m, 2H). – MS (ES–): *m/z* (%) = 531 (100) [Au(C₆F₅)₂][–]. – C₂₂H₁₀AuTlF₁₀N₂ (893.64): calcd. C 29.57, H 1.13, N 3.13; found: C 29.11, H 1.32, N 2.86. Complex **3**: – ¹⁹F NMR (282 MHz, 298 K, (CD₃)₂CO): δ = –114.92 (m, 4F, F_o), –163.07 (t, ³J(F_p–F_m) = 19.8 Hz, 2F, F_p), –164.20 (m, 4F, F_m). – ¹H NMR (300 MHz, 298 K, (CD₃)₂CO): δ = 7.57 (dd, 2H), 8.05 (dd, 2H), 8.44 (d, 2H), 8.77 (d, 2H). – MS (ES–): *m/z* (%) = 531 (100) [Au(C₆F₅)₂][–]. – C₂₂H₈AuTlF₁₀N₂ (933.66): calcd. C 31.44, H 0.88, N 3.05; found C 31.61, H 0.72, N 2.89. Complex **4**: – ¹⁹F NMR (282 MHz, 298 K, (CD₃)₂CO): δ = –115.00 (m, 4F, F_o), –162.96 (t, ³J(F_p–F_m) = 19.9 Hz, 2F, F_p), –164.09 (m, 4F, F_m). – ¹H NMR (300 MHz, 298 K, (CD₃)₂CO): δ = 8.02 (dd, 2H), 8.11 (m, 2H), 8.69 (dd, 2H), 9.22 (dd, 2H). – MS (ES–): *m/z* (%) = 531 (100) [Au(C₆F₅)₂][–]. – C₂₄H₈AuTlF₁₀N₂ (891.62): calcd. C 31.48, H 0.88, N 3.06; found C 31.21, H 0.75, N 2.89.

Preparation of complex [Tl(4,4'-bipy)(THF)][Au(C₆F₅)₂] (**5**) (4,4'-bipy = 4,4'-bipyridine)

To a solution of {Tl[Au(C₆F₅)₂]}_n (**1**) (0.090 g, 0.12 mmol) in 20 ml of THF was added 4,4'-bipyridine (0.019 g, 0.12 mmol). The solution was stirred for 30 min, and the solvent was evaporated to *ca.* 2 ml. Addition of *n*-hexane led to complex **5** (67%) as a colourless solid. – ¹⁹F NMR (282 MHz, 298 K, (CD₃)₂CO): δ = –114.80 (m, 4F, F_o), –161.10 (t, ³J(F_p–F_m) = 19.6 Hz, 2F, F_p), –164.35

(m, 4F, F_m). – ¹H NMR (300 MHz, 298 K, (CD₃)₂CO): δ = 1.77 (m, 4H, THF), 3.60 (m, 4H, THF), 7.75 (m, 4H, 4,4'-bipy), 8.71 (m, 4H, 4,4'-bipy). – MS (ES–): *m/z* (%) = 531 (100) [Au(C₆F₅)₂][–]. – C₂₆H₁₆AuTlF₁₀N₂O (963.76): calcd. C 32.40, H 1.67, N 2.91; found C 32.17, H 1.49, N 3.03.

Crystallography

Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Bruker SMART 1000 CCD (**3**) or Nonius Kappa CCD (**4** and **5**) diffractometer equipped with corresponding low-temperature attachment. Data were collected using monochromated MoK_α radiation (λ = 0.71073 Å). Scan type ω and φ. Absorption corrections: numerical (based on multiple scans). The structures were solved by direct methods and refined on F² using the program SHELXL-97 [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Complex **4** was refined as a twin and the refined Flack parameter is 0.51(4) as expected for a racemic twin. Further details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are collected in Tables 2–4; the crystal structures of complexes **3–5** appear in Figs. 1–4. CCDC-245098–245100 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

The D.G.I. MCYT/FEDER (BQU2001-2409) project is acknowledged for financial support. M. Monge thanks the MCYT-Universidad de La Rioja for his research contract “Ramón y Cajal”. M. Montiel thanks the C.A.R. for a grant.

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