

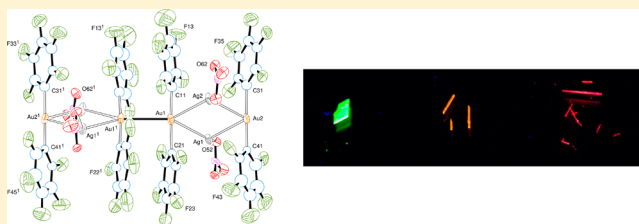
# Synthesis, Structure, and Luminescent Behavior of Anionic Oligomeric and Polymeric $\text{Ag}_2\text{Au}_2$ Clusters

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## Supporting Information

**ABSTRACT:** Mixtures of silver salts  $\text{AgX}$  ( $\text{X} = \text{NO}_3$ ,  $\text{CF}_3\text{CO}_2$ ,  $\text{CF}_3\text{SO}_3$ ) with  $\text{M}[\text{Au}(\text{C}_6\text{F}_5)_2]$  ( $\text{M} = \text{NBu}_4$ ,  $\text{PPh}_4$ ) gave respectively the ionic mixed-metal clusters  $[\text{M}_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2\text{X}_2\}]_n$  (**1**,  $\text{X} = \text{NO}_3$ ; **a**,  $\text{M} = \text{NBu}_4$ ; **b**,  $\text{M} = \text{PPh}_4$ ) and  $[\text{M}\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2\text{X}\}]_n$  (**2a,b**,  $\text{X} = \text{CF}_3\text{CO}_2$ ; **3a,b**,  $\text{X} = \text{CF}_3\text{SO}_3$ ). The degree of aggregation  $n$  of these cluster compounds depends strongly on the method of isolation (solvent evaporation or precipitation); for example, recrystallization of **1a** gave a crystalline salt of the tetraanion  $[(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2\text{X}_2]_4^{4-}$  as well as the polymer  $[(\text{NBu}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{NO}_3)_2\}]_n$ . The aurophilic  $\text{Au}\cdots\text{Au}$  interactions strongly influence the photoemission wavelength. The anion  $\text{X}$  has remarkably little effect on the luminescence color but strongly influences the conformation of the polyanionic chains, leading to a variety of solid-state structures, from well-defined dimers (**1a'**) to linear (**1b**) and curved (**1a'**, **2a**) polymeric chain aggregates.



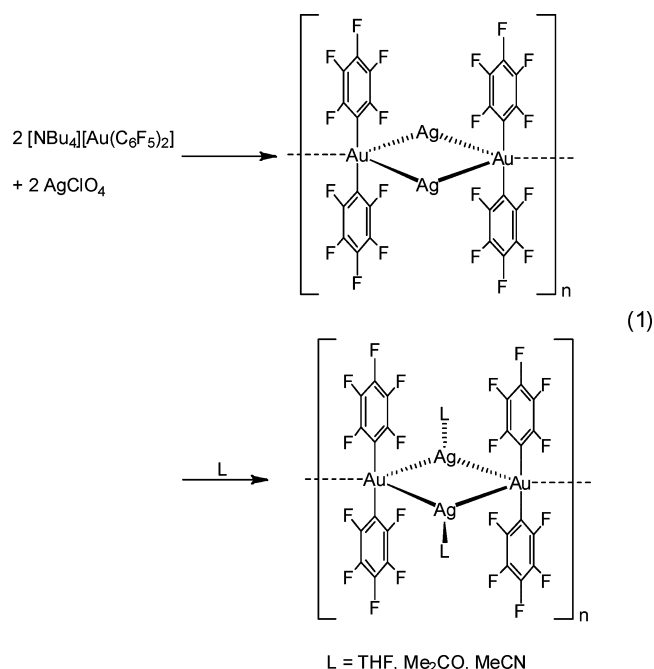
## INTRODUCTION

Heterometallic gold(I) complexes incorporating both aurophilic and metallophilic contacts have given rise to a distinct field of photoluminescent materials with possible uses in sensor and materials applications.<sup>1,2</sup> Of particular interest are complexes based on the tetrametallic  $\text{Ag}_2\text{Au}_2$  clusters,<sup>3</sup> which assemble into polymer chains in which the  $\text{Au}_2\text{Ag}_2$  cores are connected through gold–gold interactions.<sup>4</sup> The first examples of such compounds were prepared over 30 years ago by Usón and co-workers,<sup>5</sup> though their interesting photoluminescent and vapochromic properties were reported much more recently.<sup>6,7</sup> These materials are synthesized by reacting salts of the  $[\text{Au}(\text{C}_6\text{F}_5)_2]^-$  anion with silver perchlorate in dichloromethane (eq 1) and form poorly soluble one-dimensional chains. The silver sites are Lewis acidic and capable of binding donor ligands, including solvent molecules, if the solid powders are exposed to solvent vapor,<sup>6</sup> a process that is reflected in changes in the photoluminescence of these compounds.

We became interested in these types of luminescent compounds as part of a search for materials that might bind to proteins, as a means of attaching fluorescent tags to functional groups, and report here on the tendency of such complexes to bind simple anions to give polyanionic assemblies with varying degrees of aurophilic interactions.

## RESULTS AND DISCUSSION

Attempts to repeat the Usón synthesis but using silver nitrate instead of silver perchlorate gave, surprisingly, products that were readily soluble in dichloromethane and did not form precipitates on mixing of the precursors. The IR spectra showed evidence for the presence of nitrate (vide infra) and suggested that ionic compounds had been formed instead of neutral



coordination polymers. It also became apparent that attempts at isolating these products gave compounds that differed in appearance and luminescence properties, depending on the method used: evaporation of the solvent followed by washing with light petroleum gave materials that emitted orange-red light, while careful precipitation by dropwise addition of light

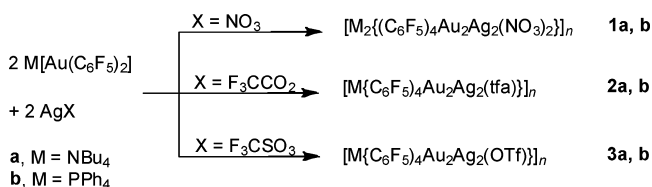
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petroleum followed by filtration afforded a powder with shorter wavelength emissions. Analogous behavior was seen when silver trifluoroacetate (tfa) or silver triflate (OTf) was used instead of  $\text{AgNO}_3$  (Scheme 1). Changing the counteranion from  $\text{NBu}_4^+$

Scheme 1



to  $\text{PPh}_4^+$  in order to improve product crystallinity showed that the cation also influenced the emission wavelengths. The phenomenological appearance of these products is collected in Table 1.

Table 1. Fluorescence Color of Compound Clusters **1a,b**–**3a,b** Obtained by Different Isolation Methods

compd	color of fluorescence after isolation by	
	evaporation	precipitation
$[(\text{NBu}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{NO}_3)_2\}]$ ( <b>1a</b> )	orange	green
$[(\text{PPh}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{NO}_3)_2\}]$ ( <b>1b</b> )	red	orange
$[\text{NBu}_4\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{tfa})\}]$ ( <b>2a</b> )	red	orange-yellow
$[\text{PPh}_4\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{tfa})\}]$ ( <b>2b</b> )	red-orange	orange-yellow
$[\text{NBu}_4\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{OTf})\}]$ ( <b>3a</b> )	orange	green
$[\text{PPh}_4\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{OTf})\}]$ ( <b>3b</b> )	red-orange	orange

Compounds **1**–**3** are stable to air and moisture, both in solution and as solids. The  $^{19}\text{F}$  NMR spectra showed the expected signals for the pentafluorophenyl groups bound to gold(I) centers. The IR spectra of these complexes displayed

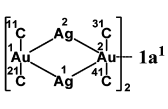
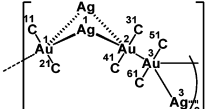
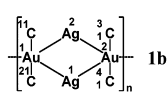
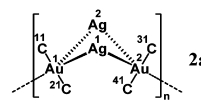
bands for the  $\text{C}_6\text{F}_5$  ligands at 1499–1505, 953–964, and 781–788  $\text{cm}^{-1}$ , corresponding to the  $\nu(\text{C}-\text{F})$  and  $\nu(\text{Au}-\text{C})$  modes. In addition, absorptions for coordinated anions were observed, at 1296–1298 and 826–831  $\text{cm}^{-1}$  ( $\text{NO}_3$ , **1a,b**), at 1661, 1193–1195, 1136–1140, 835–837, and 780–781  $\text{cm}^{-1}$  ( $\text{CF}_3\text{CO}_2$ , **2a,b**) and at 1155–1140  $\text{cm}^{-1}$  (OTf, **3a,b**).

The formation of the anion-containing clusters is always favored over that of their neutral counterparts  $[\text{Ag}_2\text{Au}_2(\text{C}_6\text{F}_5)_4]_n$ . This can be shown by treating  $[\text{Ag}_2\text{Au}_2(\text{C}_6\text{F}_5)_4]_n$  with 1 equiv of  $[\text{NBu}_4]\text{X}$  ( $\text{X} = \text{NO}_3$ , tfa, OTf) to give the ionic clusters in quantitative yields. The weakly coordinating nature of the anions was evident by the behavior of dichloromethane solutions of **1a,b**–**3a,b**, which show color changes when acetone or THF was added before vacuum evaporation to give yellow or green powders, respectively. Solvent molecules displace the anions to form  $[\text{Ag}_2\text{Au}_2(\text{C}_6\text{F}_5)_4](\text{solvent})_2]_n$  (solvent = acetone, THF) both in solution and by exposing the solids to solvent vapor. The reactions of **1a**–**3a** with methanol also led to anion displacement, as the orange solids isolated fluoresce green under UV excitation. This reaction was found to be reversible: vacuum evaporation, redissolution in dichloromethane, and precipitation by light petroleum gave the parent ionic clusters in quantitative yields.

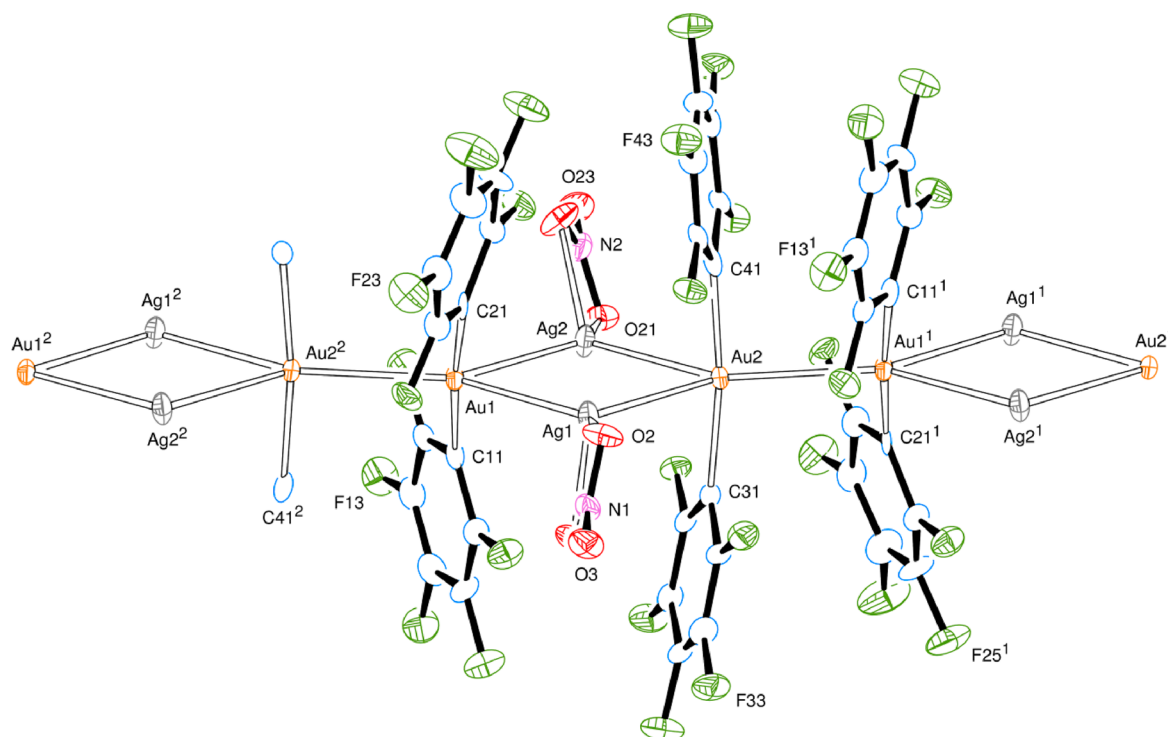
**Structural Analysis.** Slow diffusion of light petroleum to dichloromethane solutions containing the complexes cooled to  $-30^\circ\text{C}$  produced single crystals of **1a,b** and **2a** which were stable to air for days without degradation. The details of the molecular parameters of the  $[(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2]$  units in these crystals are collected in Table 2 for comparison.

The compound  $[(\text{PPh}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2(\text{AgNO}_3)_2\}]_n$  (**1b**) was isolated solely as red needles and proved to have the most straightforward structure. X-ray diffraction studies revealed that the compound consists of linear chains based on a planar  $[\text{Au}_2\text{Ag}_2]$  core, with two  $\text{C}_6\text{F}_5$  groups linearly bound to each

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Clusters **1a**<sup>1</sup>, **1a**<sup>2</sup>, **1b**, and **2a**

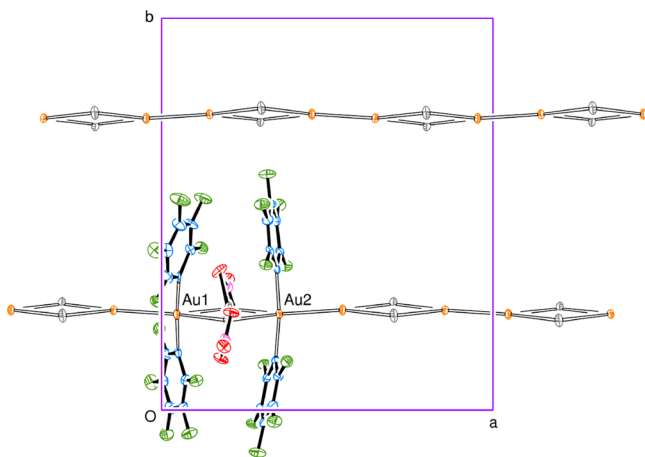
Monomeric Unit:				
				
Au–Au	3.039(3)	2.910(2), 2.901(3)	2.8171(6)	2.8997(12), 2.9319(12)
Au(1)–Ag(1)	2.773(4)	2.833(3)	2.7097(7)	2.8023(13)
Au(1)–Ag(2)	2.770(3)	2.797(3)	2.7045(7)	2.8409(13)
Au(2)–Ag(1)	2.750(3)	2.799(3)	2.7161(7)	2.8282(12)
Au(2)–Ag(2)	2.746(4)	2.773(3)	2.7262(7)	2.7921(13)
Au(3)–Ag(3)	–	2.804(3)	–	–
Au(3)–Ag(3 <sup>1</sup> )	–	2.824(3)	–	–
Au(1)–C(11)	1.96(3)	2.101(14)	2.074(6)	2.066(13)
Au(1)–C(21)	2.06(2)	2.099(2), 2.100(2) <sup>a</sup>	2.048(7)	2.074(15)
Au(2)–C(31)	2.07(2)	2.083(16)	2.062(6)	2.083(15)
Au(2)–C(41)	1.95(2)	2.112(14)	2.046(6)	2.070(17)
Ag(1)–Au(1)–Ag(2)	67.10(10)	62.47(8)	66.36(2)	61.46(3)
Ag(1)–Au(2)–Ag(2)	67.74(10)	63.21(8)	65.98(2)	61.73(3)
Au(1)–Ag(1)–Au(2)	112.49(11)	99.57(9)	113.91(3)	98.18(4)
Au(1)–Ag(2)–Au(2)	112.67(11)	101.10(9)	113.75(3)	98.12(4)
Ag(3)–Au(3)–Ag(3 <sup>1</sup> )	–	62.24(10)	–	–
Au(3)–Ag(3)–Au(3 <sup>1</sup> )	–	100.84(9)	–	–

<sup>a</sup>Dimensions in each of two disordered conformations.



**Figure 1.** Solid-state structure of a section of the polymeric anion of **1b**·CH<sub>2</sub>Cl<sub>2</sub> with a partial atomic numbering scheme. Ellipsoids are drawn at the 50% probability level. For bond lengths and angles of the [(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Au<sub>2</sub>Ag<sub>2</sub>] core see Table 2. Selected bond lengths (Å) and angles (deg) of NO<sub>3</sub><sup>−</sup> ligation: Ag(1)–O(1) = 2.448(5), Ag(1)–O(2) = 2.342(5), Ag(2)–O(21) = 2.351(5), Ag(2)–O(22) = 2.433(5); O(1)–Ag(1)–O(2) = 53.46(16), O(21)–Ag(2)–O(22) = 53.37(17).

gold center in an approximately perpendicular manner with respect to the [Au<sub>2</sub>Ag<sub>2</sub>] plane (the Au(1)–C vectors are tilted ca. 25° and the Au(2)–C vectors ca. 15° from the normal to the Au<sub>2</sub>Ag<sub>2</sub> mean plane) (Figures 1 and 2). There is one NO<sub>3</sub><sup>−</sup>



**Figure 2.** Polymeric ribbon structure of the Au<sub>2</sub>Ag<sub>2</sub> skeleton in **1b**·CH<sub>2</sub>Cl<sub>2</sub>; one complete {(Au(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)<sub>2</sub>(AgNO<sub>3</sub>)<sub>2</sub>} anion unit is included. Ellipsoids are drawn at the 50% probability level.

anion coordinated to each silver cation, in an asymmetric  $\kappa^2$ -fashion. Each tetrametallic cluster unit is therefore dianionic and is stabilized by two closely associated [PPh<sub>4</sub>]<sup>+</sup> counter-cations. The Ag<sub>2</sub>Au<sub>2</sub> moieties form a polyanionic chain along the *x* axis (Figure 2), held together by unsupported Au...Au interactions of 2.8171(6) Å, which, in spite of the accumulation of negative charges on the chain,<sup>8</sup> are slightly shorter than those found in the tetrahydrothiophene (2.889(2) Å), THF

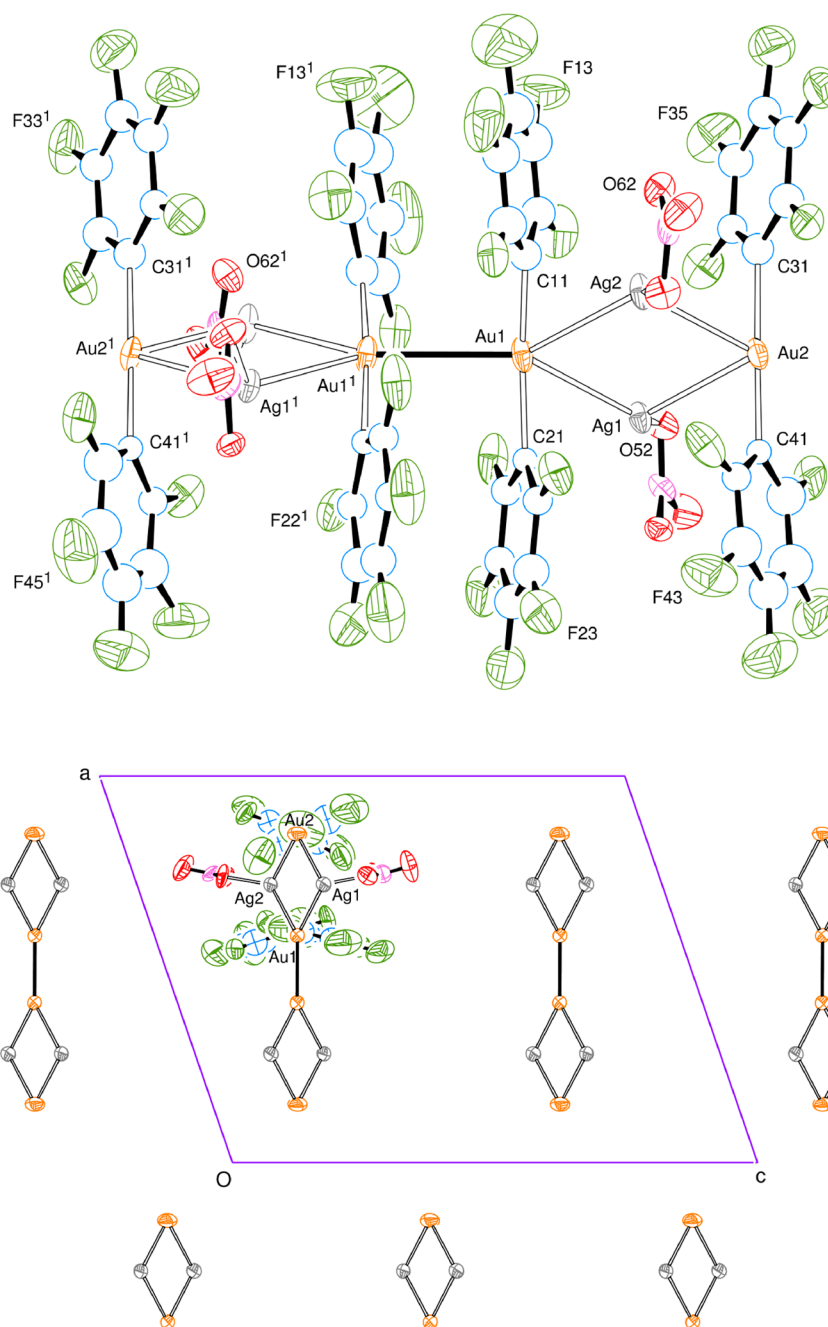
(2.8738(9)–2.8989(12) Å), and MeCN (2.9481(3) Å) adducts of the neutral Au<sub>2</sub>Ag<sub>2</sub> cluster.<sup>5a,7f</sup> The planes of neighboring [Au<sub>2</sub>Ag<sub>2</sub>] clusters are all parallel.

Crystallization of [(NBu<sub>4</sub>)<sub>2</sub>{(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Au<sub>2</sub>(AgNO<sub>3</sub>)<sub>2</sub>}]<sub>*n*</sub> (**1a**) afforded two distinct crystal forms: yellow plates which on UV irradiation emitted green light and needle-shaped crystals which luminesced orange (Figure 3). Both the yellow plates (**1a**<sup>1</sup>) and the orange needles (**1a**<sup>2</sup>) were analyzed by X-ray diffraction methods. Due to the severe disorder in the [NBu<sub>4</sub>]<sup>+</sup> cations, the data of both compounds are not of high quality, although the anionic portion in each was well-behaved.

Crystals of **1a**<sup>1</sup> showed two different unit cells and diffraction data of poor quality. Nonetheless, it was possible to establish that, in both samples, the structure of the anionic moiety is based on planar tetrametallic clusters, with one nitrate anion bonded to each silver ion. We report here the results from the analysis of the better data set measured. In contrast to the case for **1b**, compound **1a**<sup>1</sup> does not form polymer chains but consists of two [(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Au<sub>2</sub>(AgNO<sub>3</sub>)<sub>2</sub>]<sup>2−</sup> moieties related by a 2-fold symmetry axis which passes through the midpoint of an Au–Au bond; this bond (3.039(3) Å, Figure 4) is significantly longer than the aurophilic bonds in **1b**. The linear [Au(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] moieties are not perpendicular to the plane of the [Au<sub>2</sub>Ag<sub>2</sub>] core but are tilted away from the normal to this plane (ca. 57° at Au(1) and 42° at Au(2)). The nitrate anions in this case appear to be bonded through only one O atom, supported by a much weaker attraction of silver with a second oxygen of the nitrate. The two [Au<sub>2</sub>Ag<sub>2</sub>] planes in **1a**<sup>1</sup> are rotated about the Au–Au bond so that their normals are ca. 76° apart. These dimer units are arranged within the crystal lattice so that the axes of all the Au(2)···Au(1)···Au(1')···Au(2') units run parallel and are normal to the *bc* plane.

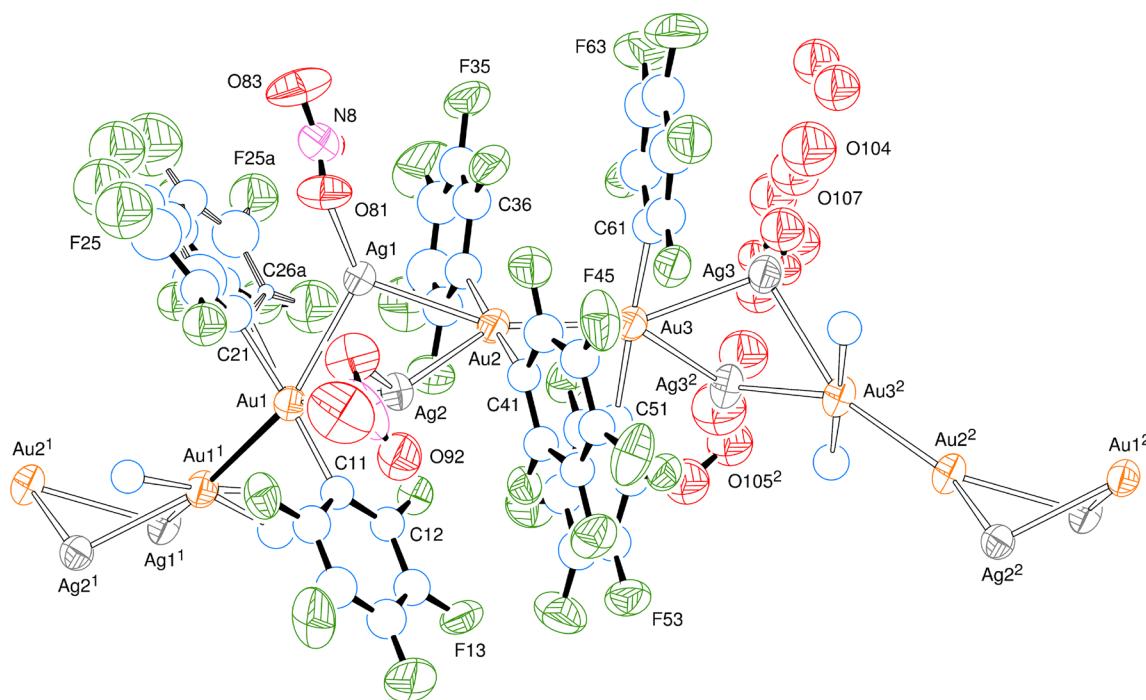


**Figure 3.** Photographs of the crystals obtained of **1a**<sup>1</sup> (left), **1a**<sup>2</sup> (center), and **1b** (right), showing crystal morphology and photoemissions on exposure to UV light.



**Figure 4.** (top) Anionic component of  $[\text{NBu}_4]_4[\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{NO}_3)_2\}_2]$  (**1a**<sup>1</sup>) at 20% ellipsoid probability, showing a partial atomic labeling scheme. (bottom) Arrangements of  $(\text{Au}_2\text{Ag}_2)_2$  dimer units (with one complete  $\{(\text{Au}(\text{C}_6\text{F}_5)_2)_2(\text{AgNO}_3)_2\}$  moiety) in the unit cell. Bond lengths and angles of the  $[(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2]$  core are given in Table 2. Selected bond lengths (Å) and angles (deg) in relation to the  $\text{NO}_3^-$  ligands:  $\text{Ag}(1)–\text{O}(51) = 2.65(2)$ ,  $\text{Ag}(1)–\text{O}(52) = 2.32(2)$ ,  $\text{Ag}(2)–\text{O}(61) = 2.30(2)$ ,  $\text{Ag}(2)–\text{O}(62) = 2.57(3)$ ;  $\text{O}(51)–\text{Ag}(1)–\text{O}(52) = 52.1(9)$ ,  $\text{O}(61)–\text{Ag}(2)–\text{O}(62) = 51.4(10)$ .

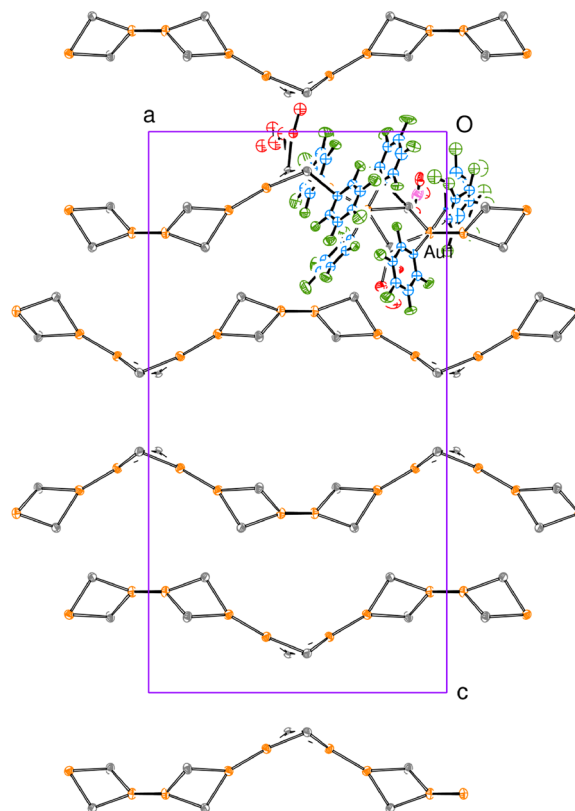




**Figure 5.** Asymmetric unit (and adjoining  $\text{Au}_2\text{Ag}_2$  units) of the polymeric anionic component in compound  $1\text{a}^2$  with a 2-fold rotational symmetry axis observed through the midpoint of the  $\text{Ag}(3)\text{--Ag}(3^2)$  vector. Ellipsoids are drawn at the 20% probability level. A partial atomic numbering scheme is shown. For bond lengths and angles of the  $[(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2]$  moiety, see Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in relation to the resolved  $\text{NO}_3^-$  ligands:  $\text{Ag}(1)\text{--O}(81) = 2.29(2)$ ,  $\text{Ag}(1)\text{--O}(82) = 2.72(3)$ ,  $\text{Ag}(2)\text{--O}(91) = 2.29(2)$ ,  $\text{Ag}(2)\text{--O}(92) = 2.54(3)$ ;  $\text{O}(81)\text{--Ag}(1)\text{--O}(82) = 49.9(9)$ ,  $\text{O}(91)\text{--Ag}(2)\text{--O}(92) = 52.8(9)$ .

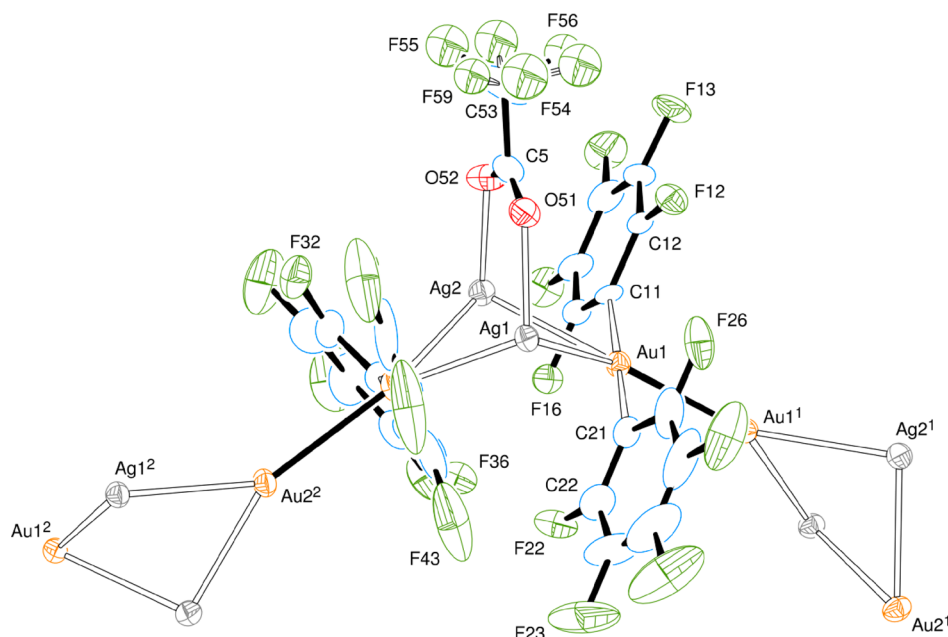
The second type of crystals obtained from this recrystallization,  $1\text{a}^2$ , also posed disorder problems, but the polymeric structure of the anionic moiety of this compound was unequivocally identified. The compound forms a polyanionic  $[(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2]_n$  ribbon, generally well-defined except for disorder in one  $\text{C}_6\text{F}_5$  ligand (resolved) and in one of the Ag ligands (assumed to be nitrate but not resolved); the elemental analysis was in agreement with the presence of one nitrate per silver atom. A unique unit consists of half of a  $[\text{Au}_2\text{Ag}_2]_3$  polymer moiety,  $([\text{NBu}_4]_{\sim 2.5}[\text{Au}_3\text{Ag}_3(\text{C}_6\text{F}_5)_6(\text{NO}_3)_2\text{X}])$ , where X is probably a nitrate ligand (Figures 5 and 6). The cluster forms polymeric corkscrew chains in which the  $[\text{Au}_2\text{Ag}_2]$  units are linked through  $\text{Au}\cdots\text{Au}$  bonds. The main difference to the previously discussed structures is that here the  $\text{Au}_2\text{Ag}_2$  clusters are butterfly-shaped. Currently there is no obvious explanation why the clusters adopt this arrangement, as no additional coordination to silver is observed to perturb the expected planar structure. In the asymmetric  $[(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2]$  unit, the silver atoms  $\text{Ag}(1)$  and  $\text{Ag}(2)$  are coordinated to the nitrate ions by a single O atom, supported by a weak interaction to a second nitrate oxygen. A 2-fold symmetry axis passes through the midpoint of the  $\text{Ag}\cdots\text{Ag}$  vector in the second  $[\text{Au}_2\text{Ag}_2]$  moiety, with each  $\text{Ag}(3)$  atom coordinated to an unresolved array of “O” atoms at a distance of approximately 2.55  $\text{\AA}$ , which might be parts of disordered and unresolved nitrate ions. The Au atoms all show the normal linear coordination of  $\text{C}_6\text{F}_5$  ligands. Again, the  $[\text{NBu}_4]^+$  cations are highly disordered, with only partial occupancy of the cations observed.

The two crystal forms of  $1\text{a}$  illustrate that the degree of association of the  $[(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2]$  clusters dictates the photoemission wavelength, with multiple aurophilic interactions resulting in a red shift.



**Figure 6.**  $[\text{Au}_2\text{Ag}_2]$  polymer ribbons of  $1\text{a}^2$ , with the asymmetric unit of the anionic polymer.

The trifluoroacetate-containing cluster  $[(\text{NBu}_4)\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{tfa})\}]_n$  ( $2\text{a}$ ) forms block-shaped crystals

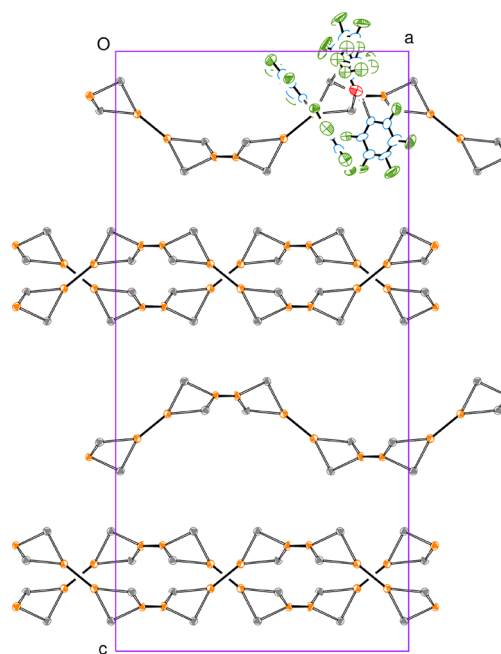


**Figure 7.** View of one anionic block (and adjoining  $\text{Ag}_2\text{Au}_2$  units) in  $[\text{NBu}_4\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{tfa})\}]_n$  (**2a**), showing a partial atomic numbering scheme. Ellipsoids are drawn at the 30% probability level. Bond lengths and angles of the  $[(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2]$  moiety are given in Table 2. Bond lengths ( $\text{\AA}$ ) in relation to the tfa ligand:  $\text{Ag}(1)\text{--O}(51) = 2.301(12)$ ,  $\text{Ag}(2)\text{--O}(52) = 2.267(12)$ .

which fluoresce red under UV excitation. X-ray crystallography shows that this compound contains a single trifluoroacetate ligand which bridges the two silver centers in the cluster. This forces the  $[\text{Au}_2\text{Ag}_2]$  framework to adopt a butterfly configuration (Figure 7). Auophilic interactions result in a polymeric structure where the chains form a corkscrew-type lattice along the crystallographic  $a$  axis, with the planes of the  $[\text{AuAg}_2]$  moieties of neighboring units rotated ca.  $49^\circ$  about  $\text{Au}(1)\text{--Au}(1')$  and ca.  $97^\circ$  about the  $\text{Au}(2)\text{--Au}(2')$  bond (Figure 8). Unfortunately, crystals of the  $[\text{PPh}_4]^+$  analogue **2b** were unsuitable for X-ray diffraction.

A number of  $\text{AuAg}_x$  mixed metal trifluoroacetate complexes are known, for example  $[\text{AuR}_2\text{Ag}_4(\text{tfa})_5]^{2-}$ ,  $[\{\text{AuR}(\text{THT})\}_2\text{Ag}_2(\text{tfa})_2]_n$  ( $\text{R} = \text{C}_6\text{F}_3\text{Cl}_2$ ),  $[\text{AuAg}_4(\text{mes})(\text{THT})(\text{tfa})_4]_n$  and  $[\text{AuAg}_4(\text{C}_6\text{F}_5)(\text{CH}_2\text{PPh}_3)(\text{tfa})_3]_n$  which contain doubly acetate bridged  $\text{Ag}\text{--Ag}$  moieties,<sup>9–12</sup> whereas the  $\text{Ag}_2$  unit in **2a** is singly bridged. There is a wide variation in  $\text{Ag}\text{--O}$  distances, although most are longer than those in  $\text{Ag}_2(\text{tfa})_2$  ( $2.151(3)\text{--}2.367(3)\text{ \AA}$ );<sup>10</sup> the  $\text{Ag}\text{--O}$  distances in **2a** (ca.  $2.3\text{ \AA}$ ) fall within the expected range. While this work was in progress, the synthesis of a more closely related compound with a  $\text{Au}_2\text{Ag}_2$  core was reported,  $[\text{NBu}_4]_2[\text{Au}_2\text{Ag}_2(2\text{-C}_6\text{F}_4\text{I})_4(\text{tfa})_2]$ .<sup>13</sup> In contrast to complexes **1a,b** and **2a,b** discussed here, this compound is a monomeric anion without auophilic interactions, and since the *o*-iodo-substituted aryl ligands are designed to coordinate to the silver ions, the trifluoroacetate is monodentate, with long  $\text{Ag}\text{--O}$  distances of  $2.524(6)\text{--}2.645(11)\text{ \AA}$ .

The trifluoromethanesulfonate-containing compounds **3a,b** were obtained similarly. Crystallization of **3a** gave a mixture of green needles and orange-red blocks, very similar to the observations for compound **1a**. Unfortunately, crystals of the triflate compounds showed unexpectedly poor thermal stability at room temperature and deteriorated within 1 h, leaving a metallic deposit when redissolved. Attempts at structure determination were unsuccessful, and the monomeric or dimeric nature of the green form of **3a** could not be



**Figure 8.** View of the polymer skeleton (and the anionic unit) of **2a** showing the chain conformation.

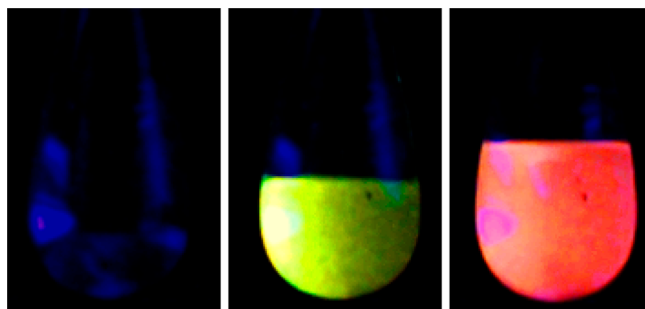
ascertained. However, the  $^{19}\text{F}$  NMR spectrum indicated a ratio of perfluorophenyl groups to triflate anions of approximately 4.5:1, which leads us to conclude that the triflates have a structure similar to that of the trifluoroacetate **2a**, with one  $\text{O}_3\text{SCF}_3^-$  anion bridging two silver cations.

Table 2 shows the bond lengths and angles for selected atoms in the  $[(\text{C}_6\text{F}_5)_2\text{Au}_2\text{Ag}_2]_n$  backbone of the clusters **1a**<sup>1</sup>, **1a**<sup>2</sup>, **1b**, and **2a**. The main features of interest are the different auophilic bond lengths observed in the clusters: the planar polymer **1b** has far shorter  $\text{Au}\cdots\text{Au}$  distances than the dimer **1a**<sup>1</sup>. The consequence of a shorter  $\text{Au}\cdots\text{Au}$  bond is the

lengthening of the bonds to the  $C_6F_5$  rings, as **1a**<sup>1</sup> has Au–C bonds  $\sim 0.05$  Å shorter than those of **1b**. The butterfly clusters **1a**<sup>2</sup> and **2a** have aurophilic bond lengths between these two extremes, possibly as a consequence of the small changes in both the Au–Ag bonds and the Ag–Au–Ag angles observed in these complexes altering the frontier orbital shape of the gold centers.

**Trends in Photoemission.** As pointed out above, when isolated by vacuum evaporation, all of the complexes emit in the orange to red region of the spectrum (566–620 nm), indicative of the powders consisting mainly of polymeric chains. Slow precipitation from dichloromethane solutions of **1a** and **3a** with light petroleum gave green luminescent powders, in agreement with the formation of a dimer cluster system seen in **1a**<sup>1</sup>.

The compounds **1b**, **2a,b** and **3b**, when isolated by slow precipitation, showed emission colors in the yellow-orange region of the spectrum (553–582 nm) in a range narrower than that for samples prepared by evaporation. However, closer inspection showed that very freshly precipitated samples of these compounds gave yellow-green luminescence which, however, red-shifted rapidly on standing over a period of minutes (although never quite matching the hues of the evaporation products). Evidently the process of polymerization through formation of aurophilic interactions proceeds over a time scale of minutes in the solid precipitates, as illustrated in Figure 9 for **1b**. Fernández et al. noted earlier that acetone



**Figure 9.** Aggregation of **1b** precipitates as a function of time: (left) dichloromethane solution under UV illumination before petroleum addition; (center) precipitation immediately on addition of light petroleum; (right) luminescence after 5 min.

solutions of compounds of the related  $[Ag_2Au_2(C_6F_5)_4(acetone)_2]_n$  clusters deviated from the Lambert–Beer law, an indication of concentration-dependent aggregation in solution.<sup>6d</sup> We see a similar phenomenon here in freshly precipitated solids.

**Fluorescence Spectroscopy of 1–3.** When exposed to UV light, the complexes **1a,b–3a,b** luminesce in the solid state at room temperature, with only very faint emissions observed in dichloromethane solution. The results of the luminescence studies are summarized in Table 3.

The emission spectra of dichloromethane solutions (ca.  $2 \times 10^{-4}$  M) give rise to intense signals at 499–538 nm when excited within the region of 400–410 nm. The excitation spectra of the complexes show complicated profiles with poorly resolved absorbances within the region of excitation, illustrated in Figure 10 for **1a**. Secondary excitations for **2a,b** give rise to very weak emissions in the orange region of the visible spectrum. The intense emissions within the green region are most probably from dimers in solution, with the weak signals in

the orange-red region occurring from aggregation in solution. Emissions exhibit a biexponential decay, with lifetimes in dichloromethane solutions at room temperature on the nanosecond scale, which together with the short Stokes shifts suggest the emissions are associated with spin-allowed fluorescence transitions.<sup>6d</sup>

Fluorescence data for powders isolated in both the precipitated and evaporated forms are collated in Table 3. For complexes **1a** and **3a**, the slow precipitation method produced bright green glowing powders, with emission properties somewhat matching those of the solution fluorescence (Figure 10). The dimer complex **1a**<sup>1</sup> emits at  $\lambda$  532–538 nm, which is nearly identical with the emission seen for the monomeric compound  $[NBu_4]_2[Au_2Ag_2(2-C_6F_4I)_4(tfa)_2]$  ( $\lambda$  540 nm).<sup>12</sup> This would seem to suggest that the presence of no or one gold–gold interaction has little influence on the emission wavelength. The other clusters give yellow-orange emissions:  $\lambda$  553–588 nm. The poorly resolved excitation signals in the solid state closely correspond to the fluorescence spectrum in solution. On isolation by vacuum evaporation, the compounds gave broad emission signals with some fine structure in the red region of the spectrum, attributed to the formation of a mixture of aggregates. The emissions from the solution precipitates have a narrower half-width, within the green to yellow region of the spectrum, suggestive of a more homogeneous mixture.

## CONCLUSIONS

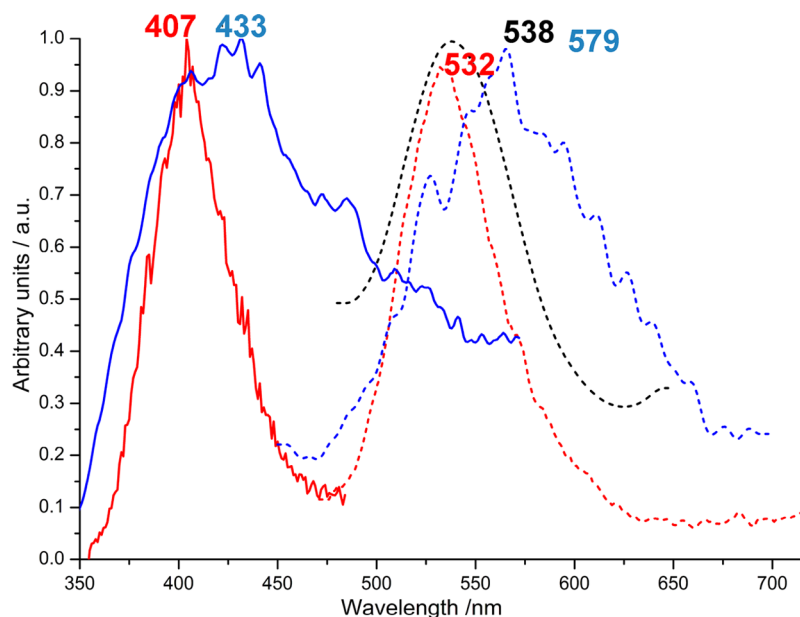
Mixtures of the diarylaurates  $M[Au(C_6F_5)_2]$  ( $M = NBu_4$ ,  $PPh_4$ ) with silver nitrate, trifluoroacetate, and triflate, i.e. salts containing anions that are slightly more strongly coordinating than perchlorate, give  $Ag_2Au_2$  tetranuclear clusters in which the anions are coordinated to the silver ions. These compounds are soluble in dichloromethane and in solution show only very weak photoluminescence in the yellow-green region of the spectrum, suggestive of monomeric or dimeric clusters. On attempted isolation, however, individual  $Ag_2Au_2$  cores aggregate by means of Au–Au interactions to give dimers or polymers, with the degree of aggregation depending strongly on the method of isolation. The aggregation has a major influence on the photoluminescence wavelength, and by monitoring the color changes of the solid precipitates this aggregation can be seen to proceed within a matter of minutes. On the other hand, the chemical nature of the coordinated anions exerts little influence on the emission energy. Anion binding proved rather variable, with  $\kappa^1$ - or  $\kappa^2$ -bonded nitrate, while trifluoroacetate prefers to bridge two silver ions. As a result, the  $Ag_2Au_2$  tetrametallic cores may be planar or bent, and the polymeric aggregates are therefore linear or curved chains which may intertwine in the crystal. The nitrate compound forms as two crystalline polymorphs, an Au–Au-bonded polymer  $[(NBu_4)_2\{(C_6F_5)_4Au_2(AgNO_3)_2\}]_n$  and a rare example of a dimeric tetraanion,  $[NBu_4]_4\{[Au_2(C_6F_5)_4(AgNO_3)_2]_2\}$ . Although the accumulation of negative charge in the polymeric chain structures might be expected to lead to Coulomb repulsion and hence weaken the aurophilic interactions, the opposite is observed, with closer Au–Au contact in the polymers than in the dimeric anion.

## EXPERIMENTAL SECTION

Unless indicated otherwise, solvents were purified by distillation under nitrogen from sodium benzophenone (diethyl ether, light petroleum bp 40–60 °C) or calcium hydride (dichloromethane). NMR solvents

Table 3. UV–Vis Absorptions and Solution and Solid-State Fluorescence Data for 1a,b–3a,b

compd	absorbance/nm ( $\epsilon/10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ )	fluorescence (in $\text{CH}_2\text{Cl}_2$ soln, $\sim 2 \times 10^{-4} \text{ mol}$ )			fluorescence (solid state)			
		$\lambda_{\text{max}}^{\text{ex}}/\text{nm}$	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$	lifetime/ns ( $\chi^2$ )	evaporates		precipitates	
					$\lambda_{\text{max}}^{\text{ex}}/\text{nm}$	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$	$\lambda_{\text{max}}^{\text{ex}}/\text{nm}$	$\lambda_{\text{max}}^{\text{em}}/\text{nm}$
1a	231 (6.7), 258 (3.6)	405	538	$\tau_1 = 56$ , $\tau_2 = 183$ (1.33)	433	579	407	532
1b	233 (7.1) 263 (2.3) 268 (2.2) 277 (1.9)	410	528	$\tau_1 = 66$ , $\tau_2 = 112$ (1.18)	429	609	418	588
2a	239 (6.4) 261 (4.1)	402	500	$\tau_1 = 41$ , $\tau_2 = 93$ (1.18) n/a	425	582	401	555
2b	233 (6.5) 261 (2.3) 269 (2.5) 276 (2.1)	402	499	$\tau_1 = 52$ , $\tau_2 = 137$ (1.39) n/a	432	599	404	553
3a	233 (6.9) 259 (4.8) 292 (6.8)	411	529	$\tau_1 = 98$ , $\tau_2 = 167$ (1.17)	430	620	398	525
3b	232 (6.9) 263 (2.3) 269 (2.5) 277 (2.8) 293 (2.9)	408	531	$\tau_1 = 125$ , $\tau_2 = 179$ (1.11)	434	566	431	584



**Figure 10.** Normalized photoluminescence of 1a: (a) emission spectrum in  $\text{CH}_2\text{Cl}_2$  ( $\sim 2 \times 10^{-4} \text{ mol}$ , black dashed line); (b) excitation (red solid line) and emission (red dashed line) spectra of the precipitate; (c) excitation (blue solid line) and emission (blue dashed line) spectra of the evaporate.

were degassed by several freeze–pump–thaw cycles and dried over activated 4 Å molecular sieves.  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$  was made as described;<sup>6a</sup> the  $\text{PPh}_4$  salt was made analogously. Elemental analysis was carried out by London Metropolitan University. NMR spectra were recorded on a Bruker Avance DPX-300 spectrometer.  $^1\text{H}$  NMR spectra (300.1 MHz) were referenced to the residual protons of the deuterated solvent used.  $^{19}\text{F}$  (282.4 MHz) and  $^{31}\text{P}$  (121.5 MHz) NMR spectra were referenced externally to  $\text{CFCl}_3$  and 85%  $\text{H}_3\text{PO}_4$ , respectively. IR spectra were recorded on a Perkin-Elmer Spectrum BX spectrometer equipped with a diamond ATR attachment. UV–visible absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrometer. Excitation and emission spectra of solutions as well as lifetime experiments were recorded in a (TCSPC) FluoroLog Horiba Jobin Yvon spectrofluorometer using quartz

cuvettes, with solid samples run on a Perkin-Elmer LS55 fluorescence spectrometer with a solids mount attachment. Time-resolved fluorescence data were collected using Horiba Jobin Yvon DataStation v2.4 software. A NanoLED of 370 nm was used as the excitation source with a repetition rate of 1 MHz and a full width at half-maximum of 1.2 ns. The collected data were analyzed using Horiba Jobin Yvon DAS6 v6.3 software.

**$[\text{PPh}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$ .** The compound was made following the procedure described for  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$ ,<sup>6a</sup> to give an off-white powder (0.54 g, 0.62 mmol, 55%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.83 (4 H, m,  $\text{PPh}_4$ ), 7.68 (8 H, m,  $\text{PPh}_4$ ), 7.54 (4 H, m,  $\text{PPh}_4$ ).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  −114.9 (4 F, d,  $J_{\text{F-F}} = 22.6 \text{ Hz}$ ,  $o\text{-C}_6\text{F}_5$ ), −162.4 (2 F, t,  $J_{\text{F-F}} = 19.8 \text{ Hz}$ ,  $p\text{-C}_6\text{F}_5$ ), −163.8 (4 F, m,  $m\text{-C}_6\text{F}_5$ ).  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  23.3 (1 P,  $\text{PPh}_4$ ).



**Synthesis of  $[(\text{NBu}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{NO}_3)_2\}]_n$  (**1a**).** To a solution of  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$  (78 mg, 0.101 mmol) in  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  (1/1, 4 mL) was added  $\text{AgNO}_3$  (17 mg, 0.1 mmol) dissolved in 1 mL of methanol. After 30 min of stirring, the yellow solution was filtered and the solvent removed in vacuo to give **1a** as an orange powder (94 mg, 0.45 mmol, 89%). Recrystallization of this product from a dichloromethane solution layered with light petroleum (1/1) at  $-30^\circ\text{C}$  gave a mixture of yellow platelets of  $[\text{NBu}_4]_4[\text{Au}_2(\text{C}_6\text{F}_5)_4(\text{AgNO}_3)_2]_2$  (**1a**<sup>1</sup>) and orange needles of  $[(\text{NBu}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2(\text{AgNO}_3)_2\}]_n$  (**1a**<sup>2</sup>).

<sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  3.14 (2H, m,  $\text{NCH}_2$ ,  $\text{NBu}_4$ ), 1.55 (2H, m,  $\text{NBu}_4$ ), 1.36 (2H, m,  $\text{NBu}_4$ ), 0.95 (3H, t,  $\text{NBu}_4$ ). <sup>19</sup>F NMR ( $\text{CDCl}_3$ ):  $\delta$  -112.1 (8F, m,  $o\text{-C}_6\text{F}_5$ ), -155.2 (4F, m,  $m\text{-C}_6\text{F}_5$ ), -161.9 (8F, m,  $p\text{-C}_6\text{F}_5$ ). IR (solid):  $\nu(\text{Au}-\text{C}_6\text{F}_5)$  1504, 964, 782;  $\nu(\text{NBu}_4)$  2968, 2943, 2877, 877;  $\nu(\text{NO}_3)$  1298, 826  $\text{cm}^{-1}$ . Anal. Found: C, 35.75; H, 3.75; N, 2.90. Calcd for  $\text{C}_{56}\text{H}_{72}\text{Ag}_2\text{Au}_2\text{F}_{20}\text{N}_4\text{O}_6$ : C, 35.63; H, 3.85; N, 2.97.

**Synthesis of  $[(\text{PPh}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{NO}_3)_2\}]_n$  (**1b**).** The procedure was the same as for the preparation of **1a**, with  $[\text{PPh}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$  employed, yielding **1b** as a red powder (89 mg, 0.43 mmol, 92%). Recrystallization of **1b** from a dichloromethane solution layered with light petroleum (1/1) at  $-30^\circ\text{C}$  gave red needles suitable for X-ray crystallographic analysis.

<sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  7.86 (4H, t,  $J_{\text{H-H}} = 7.6$  Hz,  $\text{PPh}_4$ ), 7.72 (8H, dt,  $J_{\text{H-H}} = 3.7, 7.6$  Hz,  $\text{PPh}_4$ ), 7.58 (8H, dd,  $J_{\text{H-H}} = 7.60, 12.9$  Hz,  $\text{PPh}_4$ ). <sup>19</sup>F NMR ( $\text{CDCl}_3$ ):  $\delta$  -112.5 (8F, m,  $o\text{-C}_6\text{F}_5$ ), -155.9 (4F, m,  $m\text{-C}_6\text{F}_5$ ), -162.5 (8F, m,  $p\text{-C}_6\text{F}_5$ ). <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  23.4 ( $\text{PPh}_4$ ). IR (solid):  $\nu(\text{Au}-\text{C}_6\text{F}_5)$  1500, 959, 784;  $\nu(\text{PPh}_4)$  1590, 1439, 1105, 722, 685;  $\nu(\text{NO}_3)$  1296.7, 831  $\text{cm}^{-1}$ . Anal. Found: C, 41.22; H, 1.88; N, 1.27. Calcd for  $\text{C}_{72}\text{H}_{40}\text{Ag}_2\text{Au}_2\text{F}_{20}\text{N}_2\text{O}_6\text{P}_2$ : C, 41.54; H, 1.94; N, 1.35.

**Synthesis of  $[(\text{NBu}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{tfa})\}]_n$  (**2a**).** To a  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  solution (1/1, 4 mL) of  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$  (82 mg, 0.106 mmol) was added  $\text{AgO}_2\text{CCF}_3$  (20 mg, 0.100 mmol). A bright yellow solution formed immediately. After 30 min of stirring the solvent was removed under reduced pressure and the orange solid residue washed with  $\text{Et}_2\text{O}$  ( $2 \times 5$  mL) to give crude **2a** as a red solid (72 mg, 0.44 mmol, 88%). Recrystallization from a dichloromethane solution layered with light petroleum (1/1) at  $-30^\circ\text{C}$  gave **2a** as red needles.

<sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  3.17 (2H, m,  $\text{NBu}_4$ ), 1.55 (2H, m,  $\text{NBu}_4$ ), 1.35 (2H, m,  $\text{NBu}_4$ ), 0.94 (3H, t,  $\text{NBu}_4$ ). <sup>19</sup>F NMR ( $\text{CDCl}_3$ ):  $\delta$  -73.5 (3F, s,  $\text{CF}_3$ ), -111.3 (8F, m,  $o\text{-C}_6\text{F}_5$ ), -154.3 (4F, m,  $m\text{-C}_6\text{F}_5$ ), -161.4 (8F, m,  $p\text{-C}_6\text{F}_5$ ). IR (solid):  $\nu(\text{Au}-\text{C}_6\text{F}_5)$  1503, 962, 781;  $\nu(\text{NBu}_4)$  2970, 2920, 2880, 881;  $\nu(\text{tfa})$  1661, 1193, 1140, 837, 780  $\text{cm}^{-1}$ . Anal. Found: C, 31.06; H, 2.29; N, 0.97. Calcd for  $\text{C}_{42}\text{H}_{36}\text{Ag}_2\text{Au}_2\text{F}_{23}\text{NO}_2$ : C, 30.87; H, 2.22; N, 0.86.

**Synthesis of  $[(\text{PPh}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{tfa})\}]_n$  (**2b**).** This complex was made from  $[\text{PPh}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$  as described for **2a**, to give **2b** as an orange-red powder (81 mg, 0.47 mmol, 85%). Recrystallization from a dichloromethane solution layered with light petroleum (1/1) at  $-30^\circ\text{C}$  gave pure **2b** as orange-red needles, which were found to be polymorphic.

<sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  7.89 (4H, m,  $\text{PPh}_4$ ), 7.76 (8H, m,  $\text{PPh}_4$ ), 7.59 (8H, m,  $\text{PPh}_4$ ). <sup>19</sup>F NMR ( $\text{CDCl}_3$ ):  $\delta$  -74.7 ( $\text{CF}_3$ ), -110.8 (8F, m,  $o\text{-C}_6\text{F}_5$ ), -154.0 (4F, m,  $m\text{-C}_6\text{F}_5$ ), -161.2 (8F, m,  $p\text{-C}_6\text{F}_5$ ). <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  23.6 ( $\text{PPh}_4$ ). IR (solid):  $\nu(\text{Au}-\text{C}_6\text{F}_5)$  1499, 953, 781;  $\nu(\text{PPh}_4)$  1588, 1436, 1107, 721, 687;  $\nu(\text{tfa})$  1661, 1195, 1136, 835, 781  $\text{cm}^{-1}$ . Anal. Found: C, 34.88; H, 1.22. Calcd for  $\text{C}_{50}\text{H}_{26}\text{Ag}_2\text{Au}_2\text{F}_{23}\text{O}_2\text{P}$ : C, 34.69; H, 1.17.

**Synthesis of  $[(\text{NBu}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{OTf})\}]_n$  (**3a**).** To a  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  solution (1/1, 4 mL) of  $[\text{NBu}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$  (78 mg, 0.10 mmol) was added  $\text{AgOSO}_2\text{CF}_3$  (26 mg, 0.10 mmol). A deep orange solid precipitate formed over 10 min. After 30 min of stirring the solid product was filtered off and dried in vacuo to yield **3a** as a crude orange powder (138 mg, 0.08 mmol, 87%). Recrystallization from a dichloromethane solution layered with light petroleum (1/1) at  $-30^\circ\text{C}$  gave pure **3a** as a mixture of green needles and orange-red blocks. These crystals decomposed at room temperature after  $\sim 1$  h; satisfactory elemental analyses could therefore not be obtained.

<sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  3.17 (2H, m,  $\text{NBu}_4$ ), 1.58 (2H, m,  $\text{NBu}_4$ ), 1.34 (2H, m,  $\text{NBu}_4$ ), 0.93 (3H, t,  $\text{NBu}_4$ ). <sup>19</sup>F NMR ( $\text{CDCl}_3$ ):  $\delta$  -77.2

( $\text{CF}_3$ ), -109.9 (8F, m,  $o\text{-C}_6\text{F}_5$ ), -151.3 (4F, m,  $m\text{-C}_6\text{F}_5$ ), -161.0 (8F, m,  $p\text{-C}_6\text{F}_5$ ). IR (solid):  $\nu(\text{Au}-\text{C}_6\text{F}_5)$  1503, 963, 783;  $\nu(\text{NBu}_4)$  2967, 2921, 2879, 882;  $\nu(\text{OTf})$  1155  $\text{cm}^{-1}$ .

**Synthesis of  $[(\text{PPh}_4)_2\{(\text{C}_6\text{F}_5)_4\text{Au}_2\text{Ag}_2(\text{OTf})\}]_n$  (**3b**).** The compound was made as described for **3a**, using  $[\text{PPh}_4][\text{Au}(\text{C}_6\text{F}_5)_2]$ , to give crude **3b** as an orange-to-red powder (110 mg, 0.06 mmol, 88%). Purification by recrystallization from a dichloromethane solution layered with light petroleum (1/1) at  $-30^\circ\text{C}$  gave red blocks which broke down after a short period of time at room temperature; satisfactory elemental analyses could therefore not be obtained.

<sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  7.78 (4H, m,  $\text{PPh}_4$ ), 7.75 (8H, m,  $\text{PPh}_4$ ), 7.60 (8H, m,  $\text{PPh}_4$ ). <sup>19</sup>F NMR ( $\text{CDCl}_3$ ):  $\delta$  -77.8 ( $\text{CF}_3$ ), -109.8 (8F, m,  $o\text{-C}_6\text{F}_5$ ), -151.5 (4F, m,  $m\text{-C}_6\text{F}_5$ ), -160.5 (8F, m,  $p\text{-C}_6\text{F}_5$ ). <sup>31</sup>P NMR ( $\text{CDCl}_3$ ):  $\delta$  23.3 ( $\text{PPh}_4$ ). IR (solid):  $\nu(\text{Au}-\text{C}_6\text{F}_5)$  1508, 958, 788;  $\nu(\text{PPh}_4)$  1585, 1439, 1108, 724, 687;  $\nu(\text{OTf})$  1140  $\text{cm}^{-1}$ .

**Isolation of Clusters 1–3 by Precipitation.** The selected cluster was dissolved in dichloromethane (5 mL), and light petroleum (20 mL) was added dropwise, with stirring, over a 5 min period. The precipitate was filtered by cannula, washed with 5 mL of light petroleum, and dried under vacuum to give the products in quantitative yields. These compounds show luminescence within the green-to-orange region of the visible spectrum.

**X-ray Crystallography.** Crystals of **1a**<sup>1</sup> were examined at 140(1) K on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo  $K\alpha$  radiation and graphite monochromator, and crystals of **1a**<sup>2</sup>, **1b**, and **2a** were examined at 100(2) K at the EPSRC National Crystallography Service, using the instrumentation and procedures described elsewhere.<sup>14</sup> The structures were determined by direct methods in SHELXS<sup>15</sup> and refined, on  $F^2$ , in SHELXL.<sup>15</sup> Further details of the analyses may be found in the Supporting Information.

## ■ ASSOCIATED CONTENT

### Supporting Information

Text, a table, and CIF files giving crystallographic experimental details and structural data for **1a**<sup>1</sup>, **1a**<sup>2</sup>, **1b**, and **2a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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