

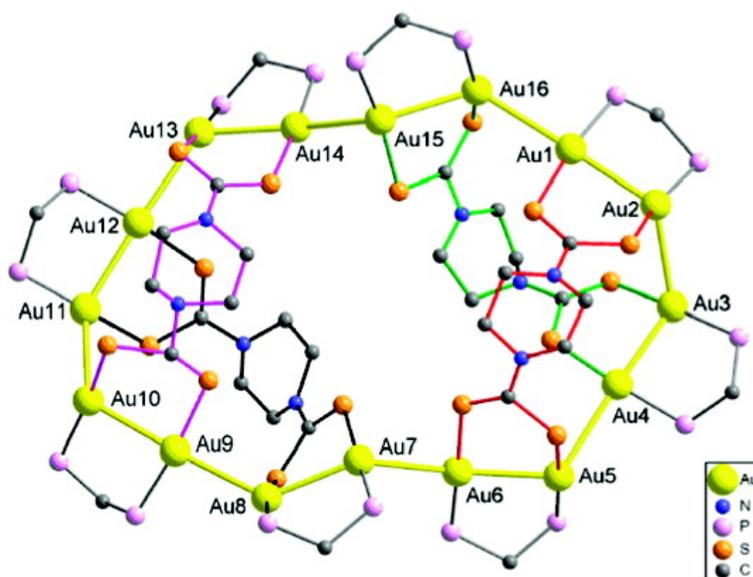
Communication

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A Chiral Luminescent Au₁₆ Ring Self-Assembled from Achiral Components

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Supramolecular chirality is a topic of growing interest in the light of its importance in biology and advanced materials.¹ Currently, considerable attention has been paid to the construction of chiral supramolecular aggregates through noncovalent self-assembly approaches from achiral molecular subunits.^{2,3} In this communication, we present the self-assembly, supramolecular chirality, and photophysical property of a novel chiral gold(I) ring, with a cyclic framework consisting of 16 gold(I) atoms arranged in a closed macrocycle via noncovalent Au(I)⋯Au(I) interactions. Although Au(I)⋯Au(I) interactions, which have similar strengths as hydrogen bonds, have emerged as unique structural motifs in the design of novel aggregates with unusual properties,⁴ chiral assemblies based on Au(I)⋯Au(I) interactions from achiral subunits have rarely been reported.^{3c,d} The present chiral Au₁₆ ring also represents the biggest one ever reported in the number of Au(I) centers among the family of Au(I) rings.^{3c,4–6} This unusual aggregate also provided a nice example of homochiral and aurophilicity-directed self-assembly.

Treatment of [Au₂(dppm)Cl₂]⁷ (dppm = bis(diphenylphosphino)methane) with 0.5 molar equiv of K₂(pipzdtc) (pipzdtc = piperazine-1,4-dicarbodithiolate) in anhydrous MeOH at room temperature gave a clear light yellow solution. Addition of an excess of NH₄PF₆ to the solution, followed by recrystallization from MeCN/MeOH/Et₂O, afforded yellow prisms of the chiral macrocyclic tetramer [(dppm)₂Au₄(pipzdtc)]₄(PF₆)₈, **1**₄, in 70% yield (Figure 1a). **1**₄ was found to exist as its monomer **1** in dilute solutions, as revealed by ¹H NMR and ESI–MS studies.

Figure 1b shows the perspective view of the cation of **1**₄, with each monomer constructed by two {(dppm)Au₂} units linked by a bridging pipzdtc²⁻ ligand with an average intramolecular Au(I)⋯Au(I) separation of 2.90 Å. Alternatively, the tetramer can be viewed as making up of two halves, namely, a dimer-to-dimer coupling. The two monomers, [(dppm)Au(15)Au(16)-pipzdtc-Au(3)Au(4)(dppm)] and [(dppm)Au(1)Au(2)-pipzdtc-Au(5)-Au(6)(dppm)], spanned each other in space and are linked together by three intermolecular Au(I)⋯Au(I) interactions (Au(16)⋯Au(1), Au(2)⋯Au(3), and Au(4)⋯Au(5)), affording a chiral dimer, although the monomer itself is achiral. Similarly, the other two monomers formed another dimer. The two dimers with the same chirality were further coupled by two intermolecular Au(I)⋯Au(I) interactions (Au(6)⋯Au(7) and Au(14)⋯Au(15)) to form a closed chiral macrocycle with a framework of 16 Au(I) centers, directly linked via short Au⋯Au contacts, with a perimeter of up to 4.822 nm. The

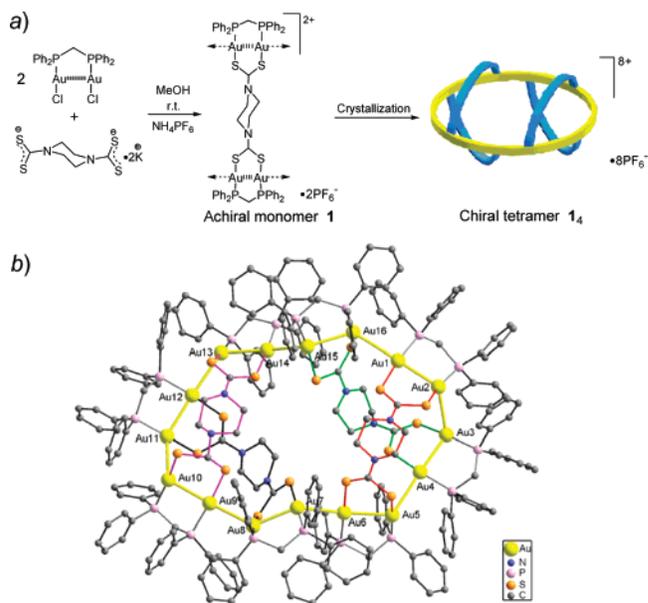


Figure 1. (a) Synthetic route for gold(I) tetramer **1**₄. The yellow ring represents the [(dppm)Au₂]₈¹⁶⁺ ring, and the blue arch-bridges represent the pipzdtc²⁻ ligands. (b) Perspective view showing the crystal structure of the cation of **1**₄. The eight PF₆⁻ anions located outside the cyclic cation and all the H atoms were omitted for clarity.

average intermolecular Au(I)⋯Au(I) separation in the ring is 3.12 Å, about 0.22 Å longer than the intramolecular ones. Both are significantly shorter than the sum of van der Waals radii for gold (3.32 Å),⁸ showing that Au(I)⋯Au(I) interactions exist in the molecule.

The chirality of the crystals of **1**₄ is further confirmed by solid-state CD spectroscopy (Figure 2a). Measurements of the crystals obtained from an MeCN/MeOH (1:1 v/v) mixture in a series of tubes showed that about 70% of the crystals in a single tube crystallized in a single chiral form, confirming that predominant chiral crystallization occurred in a given tube. However, the preference for a particular chirality varies from tube to tube, giving a statistical distribution of roughly 1:1, suggesting that the predominant chirality is essentially governed by chance, similar to the findings of some helical coordination polymers.⁹

The electronic absorption spectrum of **1** in MeCN at 293 K is dominated by a high-energy absorption band at 278 nm ($\epsilon_{\text{abs}} = 63\,550\text{ M}^{-1}\text{ cm}^{-1}$) that is attributed to an admixture of ¹(dσ* → pσ) transition typical of [Au₂(P∧P)]²⁺¹⁰ and the intraligand transition of the dppm and/or pipzdtc ligand(s). An additional low-energy absorption shoulder occurs at ca. 370 nm that becomes more obvious with increasing concentration. Figure 2b shows the UV–

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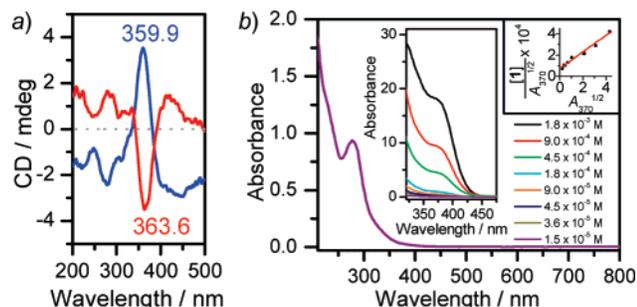


Figure 2. (a) Solid-state CD spectra of a single crystal of **1**₄ in its two enantiomeric forms measured by the Nujol mull method. (b) UV-vis spectral traces of **1** at various concentrations in MeCN solution. The insert shows the dimerization plot for a monomer–dimer equilibrium. The absorbance values have been corrected to a 1 cm path length equivalence.

vis spectral traces of **1** at various concentrations, and a plot of absorbance with concentration shows a deviation from the Beer–Lambert Law, suggesting the presence of an intermolecular aggregation process in solution. A plot of $[1]/(A_{370})^{1/2}$ versus $(A_{370})^{1/2}$ shows a straight line plot that conforms to a dimerization process involving a monomer–dimer equilibrium,¹¹ with $\epsilon_{\text{abs}}(\mathbf{1}_2)$, K , and ΔG determined to be $2600 \text{ M}^{-1} \text{ cm}^{-1}$, 6800 M^{-1} , and 22 kJ mol^{-1} , respectively. The absence of additional bands beyond 370 nm up to the highest attainable concentration of $\sim 1.8 \times 10^{-3} \text{ M}$ is suggestive of very little to no trimer or higher oligomer formation under the conditions studied.¹² Similar dimerization processes for a series of dinuclear gold(I) phosphine thiolate complexes were also reported.^{13d}

Photoexcitation of **1**₄ in the solid state produces intense green phosphorescence, and a slight blue shift from 531 to 524 nm has been observed on lowering the temperature from 293 to 77 K. **1** displays intense orange emission at ca. 605–608 nm in acetonitrile and acetone solutions at 293 K, with an excitation band centered at 324–331 nm. In ⁿPrCN glass at 77 K, the emission maximum of **1** is significantly blue-shifted to 501 nm. With reference to previous spectroscopic studies on related Au(I) phosphine thiolate systems,^{4d,13} the emission has been attributed to originate from [S → Au] ligand-to-metal charge transfer (LMCT) excited states, probably modified by the presence of weak Au⋯Au interactions. Similar blue shift has also been reported in the related gold(I) sulfido system with decreasing temperature and has been attributed to the increased rigidity of the molecular structure at low temperature, which renders a smaller geometrical distortion in the excited states and hence a smaller Stokes shift.¹⁴ The BF₄[−] and ClO₄[−] counterparts have also been prepared in a similar manner as that of **1** and have been found to exhibit very similar phosphorescence properties.

In contrast to the electronic absorption studies, concentration dependence is not significant on the phosphorescence energy of **1**. The lack of concentration dependence in the emission properties in the concentration range studied may be suggestive of an emission origin that has a ligand-to-metal–metal charge transfer (LMMCT) character localized on the intramolecular Au⋯Au interaction in the Au₂ unit or one that has a predominant ligand-centered or ligand-to-ligand charge transfer character.

On the basis of UV-vis and crystal structure studies, a speculation on the chiral assembly process for the formation of the chiral Au₁₆ ring may proceed as follows. In dilute solutions, **1** exists mainly in its monomeric form. However, upon an increase in the concentration, intermolecular aurophilic interactions become important, as revealed by the growth of the absorption shoulder at ca. 370 nm in the UV-vis spectra. Intermolecular Au(I)⋯Au(I) interactions between the two monomers serve as the driving force to induce the two achiral monomers to pair up. The configuration

and the size of the spacer in the monomer govern the dimer formed to adopt a “cross-shaped” structure, resulting in its chirality (Scheme S1).¹⁵ It is likely that, upon diffusion of diethyl ether vapor, two dimers with the same handedness would aggregate further with better packing to afford the chiral tetramer, probably induced and facilitated by the presence of Au(I)⋯Au(I) interactions. In summary, a giant Au₁₆ ring with supramolecular chirality that self-assembled from achiral Au₂ subunits based on Au(I)⋯Au(I) interactions has been described.

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Supporting Information Available: Synthetic and solid-state CD experimental procedures, X-ray crystal data and tables, luminescence data, proposed self-assembly scheme for **1**₄. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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