Self-assembly of a neutral luminescent Au_{12} cluster with D_2 symmetry†

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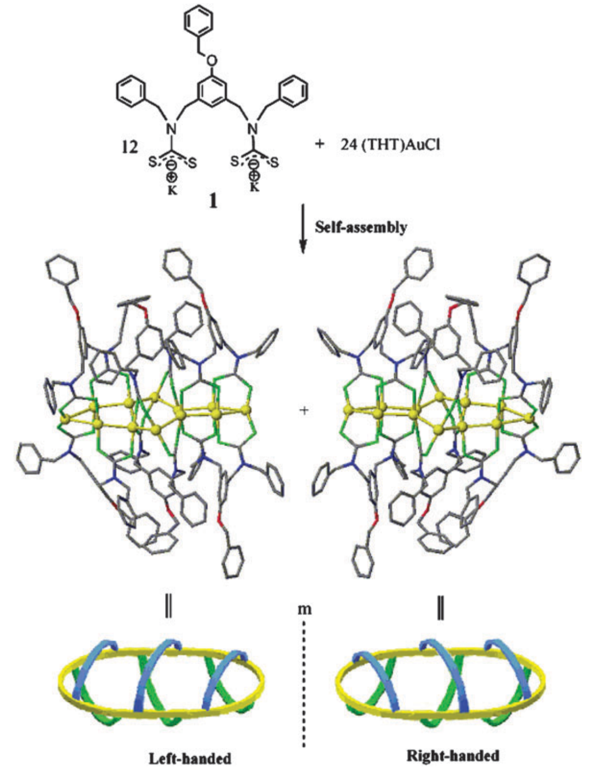
The preparation and characterization of luminescent neutral Au_{12} shuttle-like complexes is reported which shows a cyclic framework consisting of twelve gold(I) ions arranged in a closed ring *via* non-covalent Au(I)···Au(I) interactions to give a chiral D_2 symmetrical structure.

Au(I)···Au(I) bonding interaction has gained a lot of attention for the self-assembly of a large variety of supramolecular gold(I) compounds with novel structural and intriguing spectroscopic properties.[1,2] We recently reported the use of a bridging bicarbodithiolate ligand for the formation of a positively charged chiral $\mathbf{Au_{16}}$ macrocycle *via* a stepwise self-assembly process,[3] which represents a nice example of self-assembly of chiral supramolecular aggregates from achiral molecular subunits.[4,5] In this communication, we present the self-assembly and photophysical properties of a neutral gold(I) cluster, with a cyclic framework consisting of twelve gold(I) ions arranged in a closed ring *via* non-covalent Au(I)···Au(I) interactions to give a chiral D_2 symmetrical structure.

As shown in Scheme 1, addition of (THT)AuCl (THT = tetrahydrothiophene) in dichloromethane to a solution of 0.5 mol equiv. of **1** in ethanol at room temperature results in the formation of a yellow precipitate. Evaporation of the reaction mixture followed by flash chromatography of the residue with chloroform as the eluent gives the title product as a yellow solid in 90% yield.[6] The ^{1}H NMR spectrum of the product reveals proton resonances of the methylene groups in the ligands in the δ 2.29 to 6.15 ppm region, which is in contrast to the free amine ligand where only one multiplet at δ 4.13–4.10 ppm is found. Correlation signals from the ^{1}H–^{1}H COSY spectrum reveal six pairs of doublets with the largest difference in chemical shift of 3.41 ppm, indicating that there are six chemical-environmentally different methylene groups, in which the twelve protons are rigidly located. Both findings suggest a highly asymmetric structure of the product. The identity of the product has also been confirmed by MALDI-TOF-MS with *m*/*z* 5801, corresponding to the [$Au_{12}L_6$] peak (L stands for the anion of the bicarbodithiolate ligand **1**; see Fig. S3 for details†).



Scheme 1 Schematic drawing of the self-assembly process to the $\mathbf{Au_{12}}$ cluster. The color figures show the crystal structure of the $\mathbf{Au_{12}}$ clusters (top) and their intramolecular bridging topologies (bottom). All the H atoms and solvent molecules were omitted for clarity. Color scheme: Au(I) yellow, S green, O red, N blue, C gray. The yellow ring represents the $\mathbf{Au_{12}}$ macrocycle; the blue and green arch-bridges represent the bridging ligands.

The solid-state structure was established by X-ray crystallography.‡ Slow diffusion of *n*-hexane vapour into a chloroform solution of the product gave a yellow cubic crystal, which reveals its identity to be a novel cluster comprising twelve coplanar gold atoms (with a mean deviation of 0.225 Å from the plane) and six bridging ligands. The cartoon representation in Scheme 1 shows that the kernel structure of the $\mathbf{Au_{12}}$

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† Electronic supplementary information (ESI) available: Experimental details, X-ray method, photophysical measurements and instrumentation, ^{1}H NMR, ^{1}H–^{1}H COSY, MALDI-TOF-MS and crystal data and details of the structure determination for Au_{12}. CCDC reference number 681314. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808646j

cluster bears a cocoon appearance. Three ligands above the $\mathbf{Au_{12}}$ plane and three below are arranged in the same helical direction along the "semi-major axis" (line connecting Au1 to Au7), with an average "helical angle" of 53.1° (defined by the angles between the vector from the two N centers within each ligand and the vector from Au1 to Au7) and an average "helical pitch" of 5.568 Å (defined by the distances between the bottom C centers of the bridging benzyl rings). According to the chirality definition of the helical structures,[7] we defined one of the enantiomers to be left-handed and the other to be right-handed. It can be predicted that a time-averaged structure of this molecule in solution bears a D_2 symmetry with three local orthogonal C_2 rotation axes. Thus each asymmetric unit contains one fourth of the whole molecule, which can account for the six kinds of chemical environments for all the twenty four methylene groups in the NMR experiments. Unfortunately, the product crystallized in a racemic manner in the solid state (space group $P\bar{1}$), so that each unit cell stacks two different helical enantiomers with a crystallographic symmetrical center of inversion at the centroid.

Fig. 1 shows the backbone of the twelve Au(I) centers and their "undulating" or "sewing" coordination modes. The coplanar twelve gold(I) centers act as an analogy to a planar shuttle with a dimension of 14.699 Å in length (Au1···Au7) and 8.185 Å in width (Au4···Au10). Similar to the related dithiocarbamate-bridged compounds,[8] each of the two neighboring Au(I) centers here is attached by one carbodithiolate group alternating above and below the cluster plane, resulting in a strengthened Au(I)···Au(I) interaction with Au(I)···Au(I) bond lengths varying from 2.902 Å to 3.143 Å, which are significantly shorter than the sum of the van der Waals radii for gold (3.32 Å).[9] It is worth noting that the bond lengths between Au1···Au12 (3.103 Å) and Au7···Au8 (3.143 Å) are relatively longer than the average (2.970 Å). This may be caused by the strong distortion of the bridging ligands due to the shorter spans at either end of the shuttle, which can be inferred from the apparently smaller bond angles of S2–Au1–S13 (153.037°) and S8–Au7–S19 (152.318°), as opposed to an average S–Au–S bond angle of 168.426°.

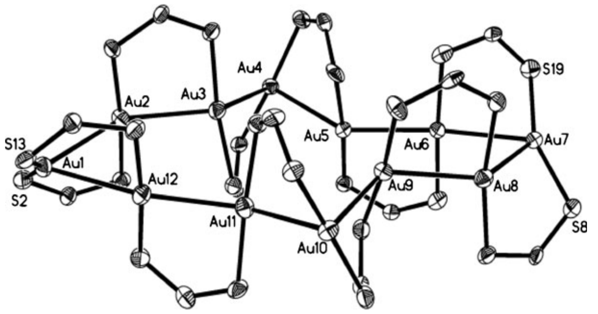

Fig. 1 Crystal structure of the twelve Au(I) centers and their "undulating" or "sewing" coordination modes to the carbodithiolate groups. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Au1–Au2 2.9809(4), Au2–Au3 2.9023(5), Au3–Au4 2.9481(4), Au4–Au5 2.9303(4), Au5–Au6 2.9036(4), Au6–Au7 2.9655(4), Au7–Au8 3.1428(4), Au8–Au9 2.9532(5), Au9–Au10 2.9861(4), Au10–Au11 2.9173(4), Au11–Au12 2.9108(4), Au1–Au12 3.1029(5); S2–Au1–S13 153.037°, S8–Au7–S19 152.318°.

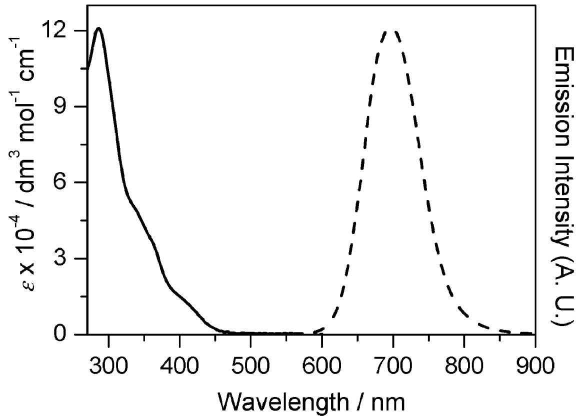

Fig. 2 Electronic absorption spectrum (—) of $\mathbf{Au_{12}}$ in CH_2Cl_2 at room temperature and emission spectrum (—) of the cluster in the solid state at 77 K upon photoexcitation at 350 nm.

A tentative explanation for the preference of a $\mathbf{Au_{12}}$ ring is suggested. On the one hand, if one focuses on the kernel structure of the twelve gold centres, it can be readily realized that somehow the ring can be regarded as a tetramer of four small open triangular golden rings brought together by strong Au(I)···Au(I) interactions. So the tendency for the gold cluster to form a triangle may have some contributions to the final structure. On the other hand, if the "arch spacer" is longer and the outer substituents are smaller, there will be a tendency to form an oligomer of linear assembly in order to reduce the steric influence exerted by the ligands.

The electronic absorption spectrum of $\mathbf{Au_{12}}$ in dichloromethane at room temperature shows low-energy shoulders at *ca.* 362 and 408 nm with extinction coefficients (ε) on the order of 10^4 dm^3 mol^{-1} cm^{-1} (Fig. 2). With reference to the previous studies on Au(I) thiolate complexes,[1c,2c,3,10,11] the shoulders are tentatively assigned as an admixture of metal-centered (ds/dp) and ligand-to-metal charge transfer transitions modified by Au(I)···Au(I) interactions. The cluster in the solid state is non-emissive at ambient temperature but displays long-lived red luminescence at 77 K (695 nm, 7.8 μs) upon photoexcitation (Fig. 2). The emission property of the macrocyclic $\mathbf{Au_{12}}$ is highly comparable to the tetranuclear gold(I) systems with strong Au(I)···Au(I) interactions, [Au(dithioacetate)]$_4$ and [Au(piperidine)Cl]$_4$.[10] Thus it is likely that the low-energy emission is derived from a triplet metal-centered (ds/dp) excited state origin that has been modified by strong Au(I)···Au(I) interactions, given the observation of short Au(I)···Au(I) distances in the crystal structure, which leads to a narrowing of the HOMO–LUMO energy gap, giving rise to a low-energy emission and a large Stokes shift. However, the possible assignment of the emission origin to a ligand-to-metal–metal charge transfer character, which commonly occurs in Au(I) thiolate complexes,[1c,2c,3,11,12] cannot be completely excluded.

In summary, the present study describes the preparation and characterization of luminescent neutral $\mathbf{Au_{12}}$ shuttle-like complexes that are formed by gold–gold interaction directed self-assembly. Further work is underway to carry out the enantioselective preparation and characterization of the two isomers. The present method may provide an alternative way for the construction of neutral golden clusters and may open up new avenues for the preparation of novel metallamacrocyclic gold(I) clusters of various sizes and shapes upon an appropriate design of the bridging ligands. Further studies along these lines are also in progress.

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Notes and references

‡ Crystal data for **Au_{12}**: the diffraction data were measured at 291 K [wavelength (λ) = 0.71073 Å]. Empirical formula $C_{186}H_{168}Au_{12}N_{12}O_6S_{24}$, $3CHCl_3$, $7H_2O$, formula weight 6284.58, triclinic, $P\bar{1}$, a = 18.3910(9) Å, b = 21.5894(11) Å, c = 28.2586(14) Å, α = 84.629(2)°, β = 82.1110(18)°, γ = 88.706(2)°, V = 11064.6(10) Å^3, Z = 2, T = 291(2) K, ρ_{calcd} = 1.886 g cm^{-3}; 119 200 reflections were measured, of which 42 914 were unique (R_{int} = 0.0386) and were used in all calculations. The absorption correction was performed using SADABS. The structures were solved by direct method and refined employing full-matrix least-squares on F^2 by using SHELXTL (Bruker, 2000) program and expanded using Fourier techniques. All non-H atoms of the complexes were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions. R_1 = 0.0487 ($I > 2\sigma(I)$) and wR_2 = 0.1069, GOF = 1.039, max/min residual density 0.736/−1.563 e Å^{-3}. CCDC 681314.

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6 See supporting information for detailed experimental section.

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