Photoluminescent two-dimensional gold(I) polymers bearing a macrocyclic tetraaza cavity

Biing-Chiau Tzeng, Kung-Kai Cheung and Chi-Ming Che*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

Several novel two-dimensional gold(I) polymers with the repeating $(AuX)_4L$ [L = 1,4,8,11-tetra(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane, X=Cl, Br, I] units held together by weak metal···metal interactions are prepared; the structure of $[(AuCl)_4L]$ characterized by X-ray crystal analysis shows the closest intermolecular gold(I)···gold(I) separation to be 3.104(1) Å; these polymers show interesting multistate photoluminescence in the solid state.

The design of new supramolecules having desirable photochemical and structural properties has been receiving considerable attention.[1] An intriguing approach to this area is to take the advantage of 'aurophilicity',[2] whereby appropriate gold(I) building blocks are held together *via* self-asembly reactions to form cluster-like and/or polymeric structures.[3] Herein is described a novel example illustrating the usefulness of this approach in the fabrication of photoluminescent two-dimensional polymers with the building block carrying a tetraazamacrocycle. The combined photoluminescence of the gold(I) building blocks and the cation and anion binding affinity of the polyazamacrocycle should make these kinds of gold(I) polymers have potent applications in host–guest photochemistry.

The ligand 1,4,8,11-tetra(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane (L) was prepared by the literature method.[4] A mixture of AuCl (0.41 mmol, reduced by 2,2'-thiodiethanol from $KAuCl_4$ in MeOH) and L (0.1 mmol) in CH_2Cl_2–MeOH (1 : 4, 50 ml) was stirred for 30 min at room temp. A white solid was obtained and recrystallized from CH_2Cl_2 to give $[(AuCl)_4L]$ **1**.† The reaction of $[(AuCl)_4L]$ (0.1 mmol) with NaBr (0.41 mmol) in CH_2Cl_2–MeOH (1 : 4, 50 ml) for 24 h at room temp. gave $[(AuBr)_4L]$ **2**, isolated as a white solid. A similar reaction with NaI gave $[(AuI)_4L]$ **3**.†

One-dimensional gold(I) polymers are known. These include the $(AuCl)_2L'$ {L' = 1,2-bis(diphenylphosphino)ethane, 1,1-bis-[(diphenylphosphino)methyl]ethene or 1,3-bis(diphenylphosphino)propane},[5] which are held by weak gold(I)···gold(I) interactions. However, two-dimensional gold(I) polymers are much rarer. Fig. 1 shows a perspective view of $[(AuCl)_4L]$.† An extended two-dimensional structure of the complex is shown in Fig. 2. The structure is reminiscent of the 'crowned' arborols reported by Shinkai and co-workers.[6] In each of the $(AuCl)_4L$ units, the four bent Ph_2P–Au–Cl appendages are pointing away from each other, so that the four Au–Cl bonds are well separated to allow intermolecular gold(I)···gold(I) bonding interactions to occur. This results in a novel two-dimensional polymer with repeating $(AuCl)_4L$ units and with an ordered array of tetraazamacrocycles. The closest intermolecular gold(I)···gold(I) separation is 3.104(1) Å, which is shorter than those of 3.189–3.316 Å in $(AuCl)_2L'$ {L' = 1,2-bis(diphenylphosphino)ethane,[5a] 3.189 Å; 1,1-bis[(diphenylphosphino)methyl]ethene,[5b] 3.293 Å or 1,3-bis(diphenylphosphino)propane,[5c] 3.316 Å}. An inversion centre is at the centre of the N_4 ring, and the P–Au–Cl axis is nearly linear [174.4(1)°]. Although only the structure of **1** has been characterized by X-ray crystal analysis, we propose that **2** and **3** may have similar structures to that of **1**. Following the suggestions of Pyykkö[7] and Balch[8] and

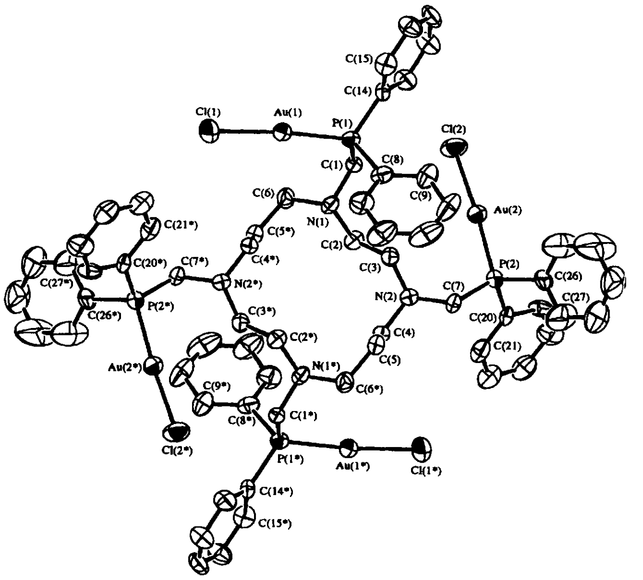

Fig. 1 A perspective view of $[(AuCl)_4L]$ **1** (bond lengths in Å, angles in °): Au(1)–Cl(1) 2.305(4), Au(2)–Cl(2) 2.301(4), Au(1)–P(1) 2.237(3), Au(2)–P(2) 2.235(4), Cl(1)–Au(1)–P(1) 173.1(1), Cl(2)–Au(2)–P(2) 175.7(1), Au(1)–P1–C(1) 111.8(4), Au(1)–P(1)–C(8) 112.0(5), Au(1)–P(1)–C(14) 117.2(4), Au(2)–P(2)–C(7) 114.5(4), Au(2)–P(2)–C(20) 112.0(5), Au(2)–P(2)–C(26) 114.4(5)

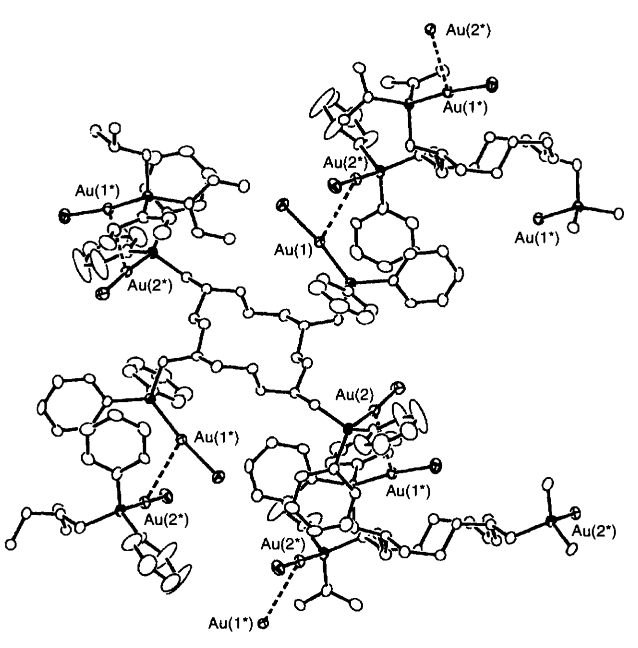

Fig. 2 An extended two-dimensional structure of $[(AuCl)_4L]$ **1** with Au(1)···Au(2) distance of 3.104(1) Å

coworkers, we anticipate that the gold(I)···gold(I) bonding interaction between the Au–X units would increase in the order Cl < Br < I. This may explain the low solubility of **2** and **3** in common organic solvents.

These gold(I) polymers show interesting photoluminescence. Fig. 3 shows the solid-state emission spectra of **1–3** measured at 77 K. At room temperature **1** is non-emissive, whereas **2** and **3** show low-energy emissions with maxima at 570 and 650 nm, respectively. Upon cooling to 77 K, **1** shows an emission with a maximum at 470 nm and possibly a very weak and broad emission at *ca.* 600 nm. For **2** and **3**, dual emissions are observed at low temperature (**2**, 530 and 600 nm; **3**, 530 and 700 nm). The high-energy emissions are most likely due to metal-to-ligand charge transfer (MLCT, Au ⟶ P) and/or intraligand transition (IL). The low-energy emission of **2** is blue-shifted relative to that of **3** (700 nm at 77 K). Similar emissions have been reported on the AuX(tpa) (X = Cl, Br, I; tpa = 1,3,5-triaza-7-phosphaadamantane) system,[9] which have been assigned to metal-centred (MC) transitions. In this case, the low-energy emissions could come from metal-centred 5d/6s ⟶ 6p mixed with ligand-to-metal charge transfer (LMCT, X ⟶ Au) transitions, which could be modified by gold(I)···gold(I) interactions. If the structure of **3** is similar to that of **1**, it is reasonable to expect the red shift in the low-energy emission from **1–3**, since the interaction between the Au–I units should be stronger than that between the Au–Cl ones.

The present work highlights that novel two-dimensional supramolecular hosts could be easily formed *via* self-assembly reactions of gold(I) building blocks. Since the structure of the polyazamacrocycle which has potential cation and anion binding affinity is easily tuned, it may be possible to design new luminescent polymeric systems for molecular recognition reactions and host–guest photochemistry.

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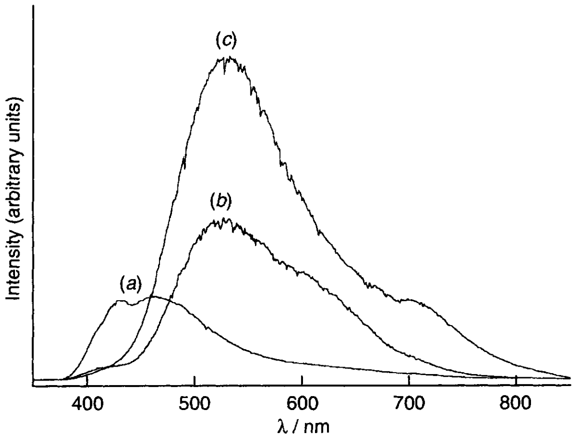

Fig. 3 The solid-state emission spectra of complexes **1–3** measured at 77 K; (*a*) **1**, (*b*) **2**, (*c*) **3**

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† Characterization for complex **1**, Anal. Calc.: C, 42.00; H, 2.80; N, 9.80. Found: C, 42.38; H, 2.44; N, 9.57%. FABMS, *m/z* 1887 $[Au(AuCl)_3L]$ (100%). A ^{31}P NMR spectrum recorded in $CDCl_3$ shows a singlet at δ 28.28. Complex **2**, Anal. Calc.: C, 35.43; H, 3.24; N, 2.67. Found: C, 36.19; H, 3.32; N, 2.45%. FABMS: *m/z* 2021 $[Au(AuBr)_3L]^+$ (45%). Complex **3**, Anal. Calc.: C, 32.52; H, 2.97; N, 2.45. Found: C, 32.39; H, 2.85; N, 2.21%. FABMS: *m/z* 2162 $[Au(AuI)_3L]^+$ (60%).

Crystal data for $[(AuCl)_4L]$ **1**: $C_{68}H_{82}Au_4Cl_4N_6O_2P_4$, $M = 2069.01$, monoclinic, space group $P2_1/n$, $a = 12.371(3)$, $b = 17.344(5)$, $c = 17.163(3)$ Å, $\beta = 102.87(2)°$, $U = 3590(1)$ Å^3, $Z = 2$, $D_c = 1.914$ g cm^{-3}, $D_m = 1.927$ g cm^{-3}, crystal dimensions 0.2 × 0.15 × 0.25 mm, μ(Mo-Kα) = 84.61 cm^{-3}, $F(000) = 1984$. Intensity data were collected on Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å) using ω–2θ scan mode with $2\theta_{max} = 45°$. The unit-cell dimensions were obtained from 25 reflections. The space group was determined from systematic absences, and the structure was solved by the direct method. 4877 unique reflections were measured and 3344 reflections with $I > 3\sigma(I)$ were used in the refinement by full-matrix least squares using the teXsan crystallographic software package (Crystal Structure Analysis Package, Molecular Structure Corporation, 1985, 1992). Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (398 variables) converged to $R = 0.039$ and $R_w = 0.043$, and the H atoms were placed at calculated positions with isotropic thermal parameters equal to 1.3 times those of the attached C atoms, but not refined. The final Fourier difference map showed residual extrema in the range of 1.76 to −1.39 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number 182/117.

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