Cluster Compounds

Supramolecular Assembly of Luminescent Gold(I) Alkynylcalix[4]crown-6 Complexes with Planar η^2,η^2-Coordinated Gold(I) Centers**

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During the last decade, supramolecular architecture in gold(I) chemistry has attracted growing attention owing to the aurophilic nature of gold and the rich luminescence properties that many gold(I) complexes exhibit.[1,2] The majority of the work in this area has been focused on systems that involve phosphines as stabilizing ancillary ligands as well as carbon-, nitrogen-, and sulfur-donor ligands.[1b,3] Examples without phosphine ligands are limited.[1d–f,2d,4] Gold(I) alkynyl systems without phosphine ligands are usually polymeric or oligomeric in nature and their intractability usually prevents them from further study and development.[5] Molecular complexes of this type are extremely scarce. Examples include the mononuclear homoleptic dialkynylaurate(I), $[RC{\equiv}C{-}Au{-}C{\equiv}CR]^-$, and the novel molecular gold(I) alkynyl complex in the form of two catenated hexanuclear rings recently reported by Mingos et al.[6] As an extension of our recent interests on d^{10} metal–alkynyl complexes,[2d,7–11] we believed that soluble polynuclear gold(I) alkynyls with interesting bonding and luminescence properties could be prepared through specially designed alkynyl ligands. Calixarenes, apart from their well-known ability as ion receptors, are one of the most important building blocks in supramolecular chemistry owing to their unique molecular structures, simple one-pot preparations, possible modifications on the lower and upper rims, and their "tunable" molecular shapes and conformations.[12–14] Alkynylcalixarenes in predefined conformations and preorganized geometries may serve as versatile ligands for the construction of novel luminescent gold(I) alkynyl supramolecular assemblies. Herein, we report the synthesis, structural characterization, and photophysical properties of a series of novel tetranuclear gold(I)–alkynylcalix[4]crown-6 assemblies.

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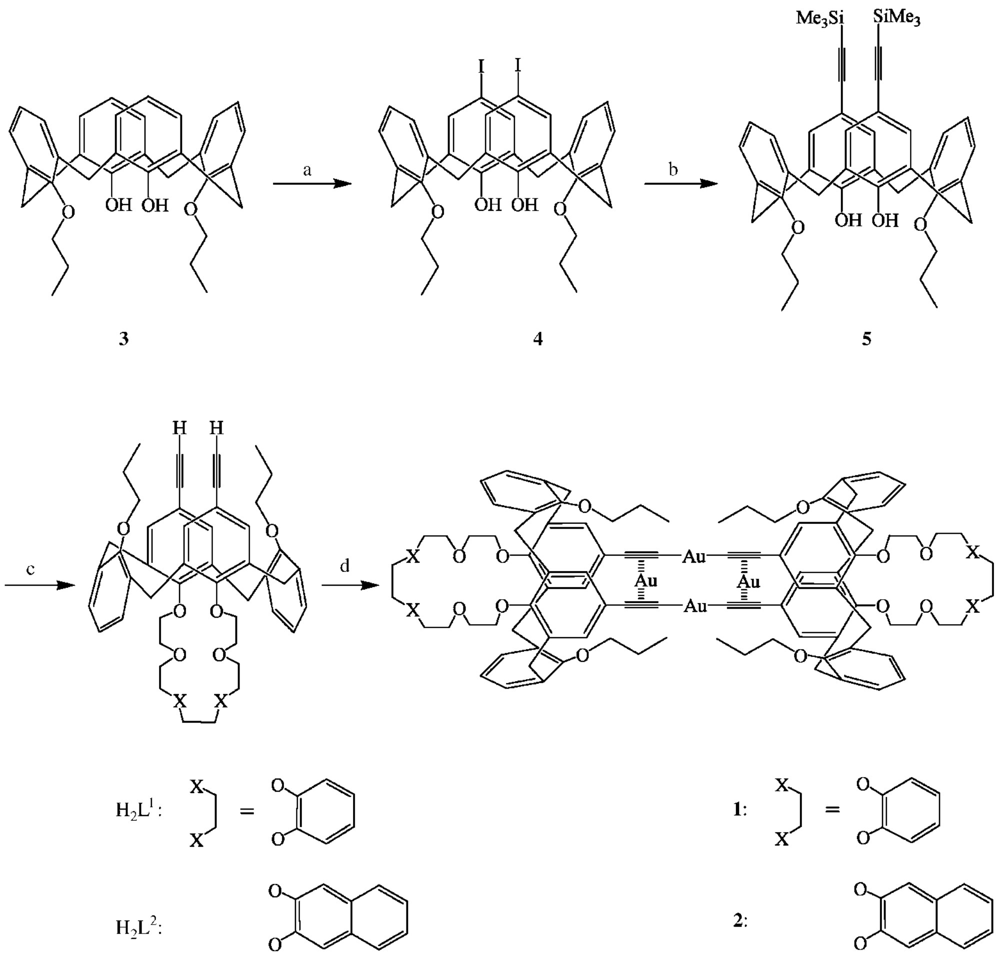

Scheme 1. Synthetic route to complexes **1** and **2**: a) ICl, CH_2Cl_2; b) $HC{\equiv}CSiMe_3$, Et_3N, $[Pd(PPh_3)_2Cl_2]$, CuI, THF; c) $Ar\{(OCH_2CH_2)_2OTs\}_2$, Cs_2CO_3, MeCN; d) Et_3N, Au(tht)Cl, CH_2Cl_2. Ar = C_6H_4 or $C_{10}H_6$; tht = tetrahydrothiophene.

The syntheses of the alkynylcalix[4]crown-6 ligands and their tetranuclear gold(I) alkynylcalix[4]crown-6 complexes **1** and **2** are summarized in Scheme 1. Iodination of the dipropoxylcalixarene **3** gave the diiodocalixarene **4**,[10,15] which upon treatment with $HC{\equiv}CSiMe_3$ under Sonogashira cross-coupling reaction conditions[16] gave the bis(trimethylsilylethynyl)-substituted calixarene **5**. Subsequent reaction of **5** with the appropriate benzo- or naphtho-substituted pentaethylene glycol di-*p*-toluenesulfonate and Cs_2CO_3 to introduce the polyether linkages at the lower rim and to remove the trimethylsilyl (TMS) groups gave H_2L^1 and H_2L^2, both in 1,3-alternate conformations, in moderate yields. Reaction of Au(tht)Cl (tht = tetrahydrothiophene) with H_2L^1 and H_2L^2 in the presence of Et_3N in CH_2Cl_2 afforded the respective desired complexes $Au_4(L^1)_2$ (**1**) and $Au_4(L^2)_2$ (**2**) as pale yellow crystals after subsequent recrystallization from dichloromethane–*n*-hexane and chloroform–*n*-hexane, respectively. The complexes **1** and **2** were characterized by elemental analysis, ^{1}H NMR and IR spectroscopy, and positive-ion FAB mass spectrometry. The crystal structure of **1** was also determined by X-ray crystallography.

The perspective drawing of **1** is depicted in Figure 1. It shows a double-cage structure, with the four gold(I) centers arranged in a rhomboidal array and capped by the two diethynylcalixcrown ligands on the two ends. Two of the gold(I) centers are each σ coordinated to two alkynyl units, whereas the other two Au centers are each π coordinated to two alkynyl units in a η^2,η^2 bonding fashion. The bridging gold atoms Au(2) and Au(2*) are two-coordinated with C–Au–C angles of 179.0(4)°: an almost ideal linear geometry. The C≡C bond lengths of 1.204(11) and 1.215(11) Å are comparatively longer than for typical terminal gold(I) alkynyl complexes,[11,17] in line with a weakening of the C≡C bond as a result of π coordination to Au(1) and Au(1*). The Au–C bond lengths for Au(1) and Au(1*) are in the range of 2.150(9)–2.359(8) Å. The torsion angle between the two C≡C units of each calixcrown is 1.5(10)°, which indicates that the two ethynyl groups are nearly parallel and are preorganized for π coordination to Au(1) and Au(1*) through an unusual planar η^2,η^2 coordination mode, which is the first of its kind for Au^I despite reported examples for other d^{10} metal centers.[9,18,19] The two gold atoms Au(1) and Au(1*), sand-

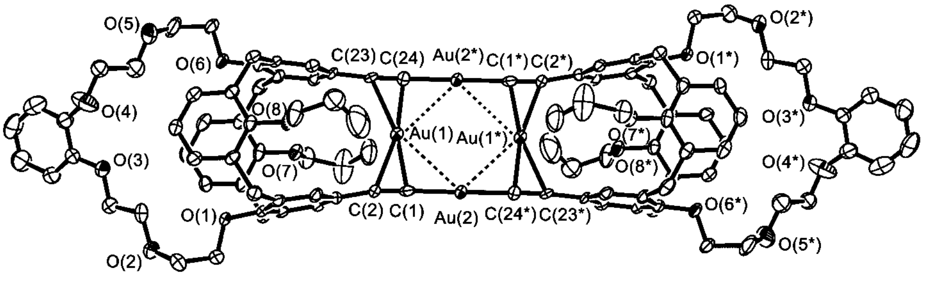

Figure 1. Perspective drawing of **1** with atomic numbering; thermal ellipsoids are shown at the 30% probability level.

wiched through π interactions between the alkynyl units, are also located on the same plane as the two C≡C–Au–C≡C bridging units to form a rhomboidal array with an inversion center at the center of the Au_4 unit. The Au···Au distances between adjacent gold atoms are 3.1344(8) and 3.2048(8) Å, indicative of the presence of significant Au–Au interactions.

Table 1: Photophysical data for **1** and **2**.

Complex	Absorption[a] λ_{abs} [nm] (ε_{max} [M^{-1} cm^{-1}])	Emission medium (T [K])	λ_{em} [nm] (τ_o [µs])[d]	Φ_{lum}[f]
1	278 (48820), 314 (40900), 344 (83260)	$CHCl_3$ (298)	588 (7.1)	0.22
		solid (298)	592 (0.8, 4.0)[e]	
		solid (77)	591 (1.1, 5.3)[e]	
		glass(77)[b]	586 (8.0)	
2	278 (48840), 312 (37950), 326 (40680), 344 (69550)	$CHCl_3$ (298)	587 (6.9)	0.21
		solid (298)	611 (0.4, 4.8)[e]	
		solid (77)	616 (0.9, 5.7)[e]	
		glass (77)[c]	587 (7.7)	

[a] In $CHCl_3$ at 298 K. [b] In $CHCl_3$–MeOH–EtOH (2:1:3 v/v). [c] In $CHCl_3$–MeOH–EtOH (4:1:2 v/v). [d] Emission lifetimes recorded with ±10% uncertainty. [e] Biexponential decay. [f] Luminescence quantum yield, measured at room temperature by using quinine sulfate in H_2SO_4 (1.0 N) as reference.

To have a better understanding of the factors that govern the structures of these tetranuclear gold(I) complexes, attempts have been made to synthesize a related tetranuclear gold(I) complex with 5,17-diethynyl-25,27-dipropoxycalix[4]crown-6 (H_2L^3, also in 1,3-alternate conformation) under similar conditions. Upon treatment of a solution of H_2L^3 in CH_2Cl_2 with Au(tht)Cl in the presence of Et_3N, the reaction mixture turned dark immediately, indicative of decomposition. The stability of **1** and **2** is believed to be associated with the crown ether unit. The presence of benzo- and naphtho- groups in the crown ether unit increases the rigidity of the calixcrown. Furthermore, the close proximity of the two ethynyl groups in the calixcrown ligand promotes the encapsulation of the two gold atoms through π coordination, with protection provided by the propoxy chains of the calixcrown ligands. All these factors would account for the much better stability of **1** and **2** relative to “$Au_4(L^3)_2$”.

The electronic absorption spectra (not shown) of **1** and **2** as solutions in chloroform are dominated by very intense low-energy absorption bands at 344 nm which tail off towards ≈480 nm and a comparatively less intense high-energy band at ≈275–330 nm. With reference to previous spectroscopic work on gold(I) ethynyl complexes[2d,8,10,11] and the similarities of the absorption bands of the complexes with the corresponding free ligands, the high-energy absorption bands at ≈275–330 nm are tentatively assigned to the intraligand transitions of the ethynylcalixcrown ligands. On the other hand, the low-energy absorption band, which is not observed in the free ligands, is likely to originate from metal-perturbed intraligand π→π*(C≡C) transitions probably with some mixing of metal-cluster-centered (ds/dp) states, characteristic of the polynuclear gold(I) ethynyl system.[2d,8,10,11]

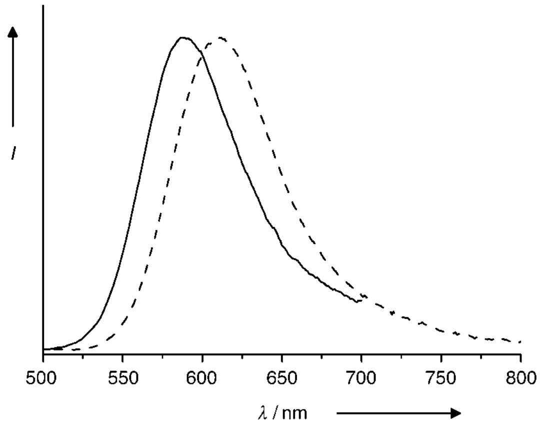

Figure 2. Normalized emission spectra of **2** as a solution in $CHCl_3$ (——, λ_{exc} = 350 nm) and in the solid state (-----, λ_{exc} = 370 nm) at room temperature.

Both **1** and **2** show rich luminescence properties (see Table 1). Upon excitation at ≈370 nm, the solid-state emission spectra of complexes **1** and **2** show low-energy emission bands at ≈590–620 nm at both 77 K and room temperature that are red-shifted with respect to the emission bands observed in solution (see Figure 2). In fact, the solid-state emissions of **1** and **2** were found to occur at a much lower energy than that for other dinuclear gold(I) calixcrown complexes, such as $[Au(PR_3)]_2L$ (R = Aryl; H_2L = 5,17-diethynyl-25,27-dimethoxycalix[4]crown-5) for which emission was observed at ≈450–480 nm.[10] Given the presence of short Au···Au distances as observed in the crystal structure of **1** and the likelihood of similarly short Au···Au distances in **2**, the relative red shift in the solid-state emission spectra is attributed to the presence of intramolecular Au···Au interactions in **1** and **2** in the solid state. Such intramolecular Au···Au interactions would give rise to a narrowing of the HOMO–LUMO energy gap, most probably as a result of dσ–dσ*, dπ–dπ*, dδ–dδ*, sσ–sσ*, and pσ–pσ* orbital splittings. It is likely that the low-energy emission is derived from states of metal-cluster-centered (ds/dp) character that are modified by Au···Au interactions and mixed with metal-perturbed intraligand π→π*(C≡C) states.

Upon excitation at ≈350 nm, the tetranuclear gold(I) calixcrown complexes **1** and **2** both gave intense emission bands at ≈587 nm at room temperature as solutions in chloroform and at 77 K as frozen matrices (glass). The luminescence quantum yields Φ_{lum} of complexes **1** and **2** in degassed chloroform are 0.22 and 0.21, respectively. Given the large Stokes shifts and the observed lifetimes, which are in the microsecond range, the emission is thought to have a triplet parentage. It is likely that the emission is derived from triplet states of a metal-cluster-centered (ds/dp) character with some mixing of metal-perturbed intraligand character.

In summary, we have demonstrated the importance and significance of strategic ligand designs on the structure and bonding of d^{10} metal complexes. The successful isolation and discovery of the planar η^2,η^2 bonding mode in the gold(I) alkynyl systems should provide an understanding of the intriguing and unique photophysical properties of this class of compounds and should form the basis for the future design and isolation of luminescent molecular materials and supramolecular assemblies.

Experimental Section

$Au_4(L^1)_2$ (**1**): Au(tht)Cl (24 mg, 0.076 mmol) was added to a stirred solution of H_2L^1 (30 mg, 0.037 mmol) and Et_3N (5 mL) in CH_2Cl_2 (15 mL), and the reaction mixture was stirred under an inert atmosphere (N_2) for 30 mins. The solvent was then removed under reduced pressure, and the residue was washed with MeOH and Et_2O. Subsequent recrystallization by layering *n*-hexane onto a solution of the product in CH_2Cl_2 gave **1** as yellow crystals (22 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 1.22$ (t, 12H, $J = 7.5$ Hz; CH_3), 2.06 (m, 8H; $OCH_2CH_2CH_3$), 3.40–3.77 (m, 24H; OCH_2CH_2O), 3.98 (s, 8H; Ar-CH_2-Ar), 4.02 (s, 8H; Ar-CH_2-Ar), 4.17 (t, 8H, $J = 6.8$ Hz; $OCH_2CH_2CH_3$), 4.32 (t, 8H, $J = 7.0$ Hz; $ArOCH_2CH_2O$), 6.62 (t, 4H, $J = 7.5$ Hz; Ar H *para* to OPr), 6.99 (m, 8H; 1,2-phenylene), 7.10 (d, 8H, $J = 7.5$ Hz; Ar H *meta* to OPr), 7.31 ppm (s, 8H; Ar H *meta* to crown linkage); IR (KBr disk): $\tilde{\nu} = 2011$ cm^{-1} (w), $\nu(C\equiv C)$; FAB MS (+ mode): m/z: 2435 $[M+K]^+$; elemental analysis: calcd for $C_{104}H_{104}Au_4O_{16}\cdot CHCl_3\cdot\frac{1}{2}C_6H_{14}$: C 50.67, H 4.40; found: C 50.65, H 4.34%.

$Au_4(L^2)_2$ (**2**): As for **1** but by using H_2L^2 (30 mg, 0.035 mmol). The product was recrystallized from chloroform–*n*-hexane to give **2** as yellow crystals (28 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 1.22$ (t, 12H, $J = 7.5$ Hz; CH_3), 2.05 (m, 8H; $OCH_2CH_2CH_3$), 3.41–3.77 (m, 24H; OCH_2CH_2O), 4.00 (s, 8H; $ArCH_2Ar$), 4.04 (s, 8H; $ArCH_2Ar$), 4.25 (t, 8H, $J = 6.7$ Hz; $OCH_2CH_2CH_3$), 4.46 (t, 8H, $J = 6.5$ Hz; $ArOCH_2CH_2O$), 6.62 (t, 4H, $J = 7.5$ Hz; Ar H *para* to OPr), 7.10 (d, 8H, $J = 7.5$ Hz; Ar H *meta* to OPr), 7.22 (s, 4H; 1,2-naphthalene), 7.31 (s, 8H; Ar H *meta* to crown chain), 7.36 (q, 4H, $J = 3.1$ Hz; 1,2-naphthalene), 7.72 ppm (q, 4H, $J = 3.1$ Hz; 1,2-naphthalene); IR (KBr disk): $\tilde{\nu} = 2006$ cm^{-1} (w), $\nu(C\equiv C)$; FAB MS (+ mode): m/z: 2497 $[M+H]^+$, 2535 $[M+K]^+$; elemental analysis calcd for $C_{112}H_{108}Au_4O_{16}\cdot CHCl_3$: C 51.86, H 4.20; found: C 51.65, H 4.49%.

Crystal data for **1**: $[C_{104}H_{104}Au_4O_{16}]$; $M_r = 2397.74$, crystal dimensions $0.4 \times 0.3 \times 0.2$ mm^3, monoclinic, space group $C2/c$, $a = 36.517(7)$ Å, $b = 12.551(3)$ Å, $c = 24.041(5)$ Å, $\beta = 123.90(3)°$, $V = 9146(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.741$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 6.464$ mm^{-1}, $F(000) = 4688$, $T = 253$ K; $R_1 = 0.0383$, $wR_2 = 0.0879$ for 26699 reflections with $[I > 2\sigma(I)]$. MAR diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); collection range $2\theta_{max} = 50.80°$ with 2°-oscillation step of φ, 480-seconds exposure time and scanner distance at 120 mm. 100 images were collected.

CCDC 238889 contains 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 CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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