Cite this: Chem. Commun., 2011, 47, 8778-8780

## COMMUNICATION

## Highly selective ion probe for $Al^{3+}$ based on $Au(1) \cdots Au(1)$ interactions in a bis-alkynyl calix[4]arene Au(1) isocyanide scaffold<sup>†</sup>

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*Received 6th May 2011, Accepted 21st June 2011* DOI: 10.1039/c1cc12677f

A bis-alkynyl calix[4]arene Au(1) isocyanide complex has been synthesized and demonstrated to be a selective ion probe for  $Al^{3+}$  based on Au(1)...Au(1) interactions.

The development of chemosensors for the selective binding of various biological and environmental relevant cations has gained considerable attention in recent years with their great potential applications.<sup>1,2</sup> Aluminum, a group 3 metal, is the most abundant metal on the crust of the earth and it is commonly used in daily life. However, it is toxic and environmentally harmful. For example, it is the potential culprit of Parkinson's disease<sup>3</sup> and Alzheimer's disease,<sup>4</sup> and it also inhibits plant growth on acid soils.<sup>5</sup> Therefore, it is crucial for the development of sensitive and selective Al<sup>3+</sup> sensors. Compared with other metal ions, limited examples of Al<sup>3+</sup> chemosensors have been reported so far<sup>6</sup> and most of their signal transduction is achieved by photoinduced electron transfer, photoinduced charge-transfer or Förster resonance energy transfer (FRET).

The study of polynuclear gold(I) complexes, in particular, with regard to the phenomenon of aurophilicity, has attracted increasing attention in recent years.<sup>7-10</sup> Amongst organogold(1) complexes, gold(1) isocyanides and alkynyls are usually photoluminescent, and they have been used for developing cluster compounds,<sup>11</sup> mesogenic materials,<sup>12</sup> polymorphic materials<sup>11,13</sup> and rigid-rod polymers.<sup>14</sup> Furthermore, due to the sterically undemanding property of the isocyanide and alkynyl moieties, gold(I) isocyanides and alkynyls are promising candidates for developing chemosensors.<sup>15</sup> Previous works by our group have demonstrated the novel concept of the utilization of the on-off switching of Au. Au interactions for metal ion sensing with dinuclear gold(1) complexes with bridging diphosphines and crown ether-functionalized thiolate ligands.8c,g With our recent success in the employment of calixarenes in chemosensing work<sup>15</sup> together with their unique molecular structures and ease of chemical transformations, it is envisaged that the calixarene moiety would serve as an ideal building block for the construction

of dinuclear gold(1) scaffolds that exhibit sensitive and selective chemosensing properties.

Herein we report the design, synthesis and characterization of an amide-containing calixarene bis-alkynyl-bridged Au(i) isocyanide complex **1** and show that this receptor complex is capable of serving as a selective luminescent ion probe for Al<sup>3+</sup> based on the switching on of the Au···Au interactions. The amide-free analogue **2** has been designed for the control studies (Chart 1). The gold(i) alkynyl polymers were prepared by reacting the respective alkyne with the gold(i) precursor. Both complexes were then synthesized by the reaction of 2,6-dimethylphenyl isocyanide with 0.5 equivalents of the respective gold(i) alkynyl polymer. The identities of **1** and **2** have been confirmed by <sup>1</sup>H NMR, ESI-MS and satisfactory elemental analysis.

The electronic absorption spectrum of complex **1** in CH<sub>2</sub>Cl<sub>2</sub>–MeCN (1:1 v/v, 0.1 M <sup>*n*</sup>Bu<sub>4</sub>NPF<sub>6</sub>) solution at 298 K shows intense high-energy absorption bands at *ca*. 260–280 nm, and low-energy bands at *ca*. 300–330 nm (Fig. 1). With reference to previous spectroscopic work on related alkynylgold(1) complexes, <sup>7d,8,10d</sup> the high-energy bands are tentatively assigned as the intraligand transitions of the coordinated phenylalkynyl and the aryl isocyanide units. The lower-energy absorption bands, which are absent in the free ligand, should be assigned to arise from the alkynyl-to-aryl isocyanide ligand-to-ligand charge transfer (LLCT) transition.

A structured emission band centered at about 448–478 nm was observed in complex 1 (Fig. 2), with vibrational progessional spacings of about 1300 cm<sup>-1</sup>, corresponding to the C···C vibrational modes of the aromatic rings. Given the close similarity of the emission to that of other alkynylgold(i) complexes,<sup>7d,8,10d</sup> an origin of triplet states arising from a metal-pertubed intraligand



Chart 1 Structures of gold(1) isocyanide complexes 1 and 2.

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<sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures and the computational details. See DOI: 10.1039/c1cc12677f



**Fig. 1** Electronic absorption spectral traces of **1** ( $1.24 \times 10^{-5}$  M) in CH<sub>2</sub>Cl<sub>2</sub>-MeCN (1:1 v/v, 0.1 M "Bu<sub>4</sub>NPF<sub>6</sub>) upon addition of Al(ClO<sub>4</sub>)<sub>3</sub> at 298 K. Upper Inset: Plot of absorbance (**1**) at 310 nm as a function of Al<sup>3+</sup> concentration and its theoretical fit (—) for the 1:1 binding of complex **1** with Al<sup>3+</sup>. Lower Inset: Job's plot for the binding of complex **1** with Al<sup>3+</sup> showing 1:1 stoichiometry. The absorbance (**0**) at 370 nm was plotted as a function of the molar ratio  $\chi_{\rm M}$ , where  $\chi_{\rm M} = [Al^{3+}]/([1] + [Al^{3+}])$ 



**Fig. 2** Emission spectral changes of  $1 (1.24 \times 10^{-4} \text{ M})$  upon addition of various concentrations of Al(ClO<sub>4</sub>)<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>–MeCN (1:1 v/v, 0.1M "Bu<sub>4</sub>NPF<sub>6</sub>) upon excitation wavelength at 345 nm. Inset: Photograph showing the luminescence colour change upon the addition of Al<sup>3+</sup> to induce the switching on of Au···Au interactions.

transition, mixed with an alkynyl-to-aryl isocyanide LLCT character is tentatively assigned.

Upon addition of  $Al^{3+}$ , the absorption band at *ca.* 306 nm showed a drop in intensity, with a concomitant growth of a higher energy band at *ca.* 264 nm and and a new low-energy shoulder at *ca.* 350 nm (Fig. 1). Three well-defined isosbestic points at *ca.* 254, 281 and 345 nm were observed, indicative of a clean conversion of **1** to a new chemical species, probably the ion-bound adduct. A binding constant, log  $K_s$ , of  $4.6 \pm 0.04$  was obtained from a nonlinear least-squares fit according to a 1:1 binding stoichiometry (Fig. 1 upper inset). The close agreement of the experimental data to the theoretical fit is supportive of a 1:1 complexation stoichiometry. Furthermore, this 1:1 binding mode has been confirmed by the Job's method of continuous variation<sup>16</sup> (Fig. 1 lower inset).

More interestingly, the emission showed a drop in intensity of the green emission at ca. 455 nm with the concomitant formation of a new low-energy orange-red emission band at 665 nm with an isoemissive point of about 537 nm (Fig. 2). The binding process can be monitored by naked eyes (Fig. 2 inset). The new lowenergy emission band at about 665 nm presumably results from the switching on of the Au ··· Au interaction upon the binding of the Al<sup>3+</sup> ion, which gives rise to a reduced HOMO-LUMO energy gap. The excitation spectra of 1 in the absence and in the presence of Al<sup>3+</sup> ion revealed that the low-energy and the highenergy bands were derived from different excited state origin (Fig. S1 in ESI<sup>†</sup>). The 665-nm emission band is derived from an excitation band at about 375 nm, which coincides with the new absorption shoulder formed at about 350 nm in the UV-Vis spectra resulting from the switching on of the  $Au(I) \cdots Au(I)$ interaction upon Al<sup>3+</sup> ion-binding.

To examine the selectivity of 1 toward various metal ions, the luminescence response upon addition of different metal ions was investigated. A drastic spectral change is shown by  $Al^{3+}$  binding (Fig. 3), indicating the high selectivity of 1 toward  $Al^{3+}$ . While  $In^{3+}$  shows a similar emission enhancement, the change is to a much lesser extent. Competition experiments of  $Al^{3+}$  binding with other metal ions have also been performed and interferences were low (Fig. S2 in ESI<sup>†</sup>). This result suggests that 1 can be used as a selective chemosensor for the detection of  $Al^{3+}$ . A detection limit of  $1.2 \times 10^{-7}$  M is found for  $Al^{3+}$ .

Due to the small size, high charge density and oxophilicity of  $Al^{3+}$ , the binding site would possibly involve the carbonyl oxygen atoms. To verify this hypothesis, the amide free-analogue **2** was synthesized and its interaction with  $Al^{3+}$  studied. The emission spectrum of **2** showed essentially no spectral changes even in the presence of a large excess of  $Al^{3+}$  salt (Fig. S3 in ESI†). This indicates that the amide carbonyl oxygen is crucial for the binding of  $Al^{3+}$ . The binding of the  $Al^{3+}$  ion to the carbonyl oxygen of the amide could also be rationalized by the fact the higher electron density located on the oxygen of amide through the delocalization of the nitrogen lone pair on the carbonyl oxygen is favourable for the binding of the electron-deficient  $Al^{3+}$ .

Computational studies have been performed by using local density functionals of the Slater type to investigate the molecular structure of complex 1 and its  $Al^{3+}$  ion-bound adduct  $(1 \cdot Al^{3+})$  (see the computational details in ESI†). The optimized structure of 1 reveals a cone conformation of the



Fig. 3 Responses of 1 ( $1.6 \times 10^{-4}$  M) in CH<sub>2</sub>Cl<sub>2</sub>–MeCN (1:1 v/v, 0.1 M "Bu<sub>4</sub>NPF<sub>6</sub>) upon addition of 3 equiv of different metal ions. Excitation was at their respective isosbestic wavelength, and the emission was monitored at 665 nm.



**Fig. 4** The optimized geometries of 1 (left) and  $1 \cdot \text{Al}^{3+}$  (right). The methyl groups on the calix[4]arene unit and hydrogen atoms except those on the amide and phenolic groups are omitted for clarity.

calix[4]arene framework with a circular intramolecular hydrogenbond arrangement (Fig. 4). In the cone structure, the two alkynyl Au(I) isocyanide units are far apart. Upon complexation of the  $Al^{3+}$  ion to 1, reorganization of the lower rim of the calix[4]arene framework took place, bringing the two gold centres into close proximity with a short Au. Au contact of 3.062 Å, supporting the presence of the Au. Au interactions in the Al<sup>3+</sup> ion-bound adduct. As depicted in Fig. 4, the aluminum(III) ion has a distorted trigonal-prismatic coordination geometry with the two ether, two phenolic and two carbonyl oxygen atoms from the two amide subunits coordinated to it. The average Al-O(ether), Al-O(phenolic) and Al-O(carbonyl) bond distances are 2.058, 1.943 and 1.891 Å, respectively. This binding mode has further been supported by <sup>1</sup>H NMR spectroscopy of **1** in the presence of  $Al^{3+}$  in d<sub>6</sub>-acetone. A downfield shift of the amide proton and neighbouring proton resonances was observed as a result of the electron-withdrawing effect of the cation-binding. Nevertheless, a slight upfield shift of the hydroxy proton resonances was found. It may be due to the removal of the intramolecular hydrogen bonding interactions between the ether oxygen and the OH groups upon Al<sup>3+</sup> ion binding (Fig. S4 in ESI<sup>†</sup>).

In conclusion, a novel calix[4]arene alkynylgold(1) isocyanide complex has been designed and synthesized, and demonstrated to show selective binding towards  $Al^{3+}$ . The unique mode of signal transduction by the switching on of  $Au \cdots Au$  interactions to give a visual luminescence change from green to orange-red color has been demonstrated.

V.W.-W.Y. acknowledges support from the University Grants Committee Areas of Excellence Scheme (AoE/P-03/08) and the Research Grants Council of Hong Kong Special Administrative Region, China (HKU 7060/09P). F.K.-W.H acknowledges the receipt of a Postgraduate Studentship administered by The University of Hong Kong. We also thank the Computer Centre at the University of Hong Kong for providing the computational resources.

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