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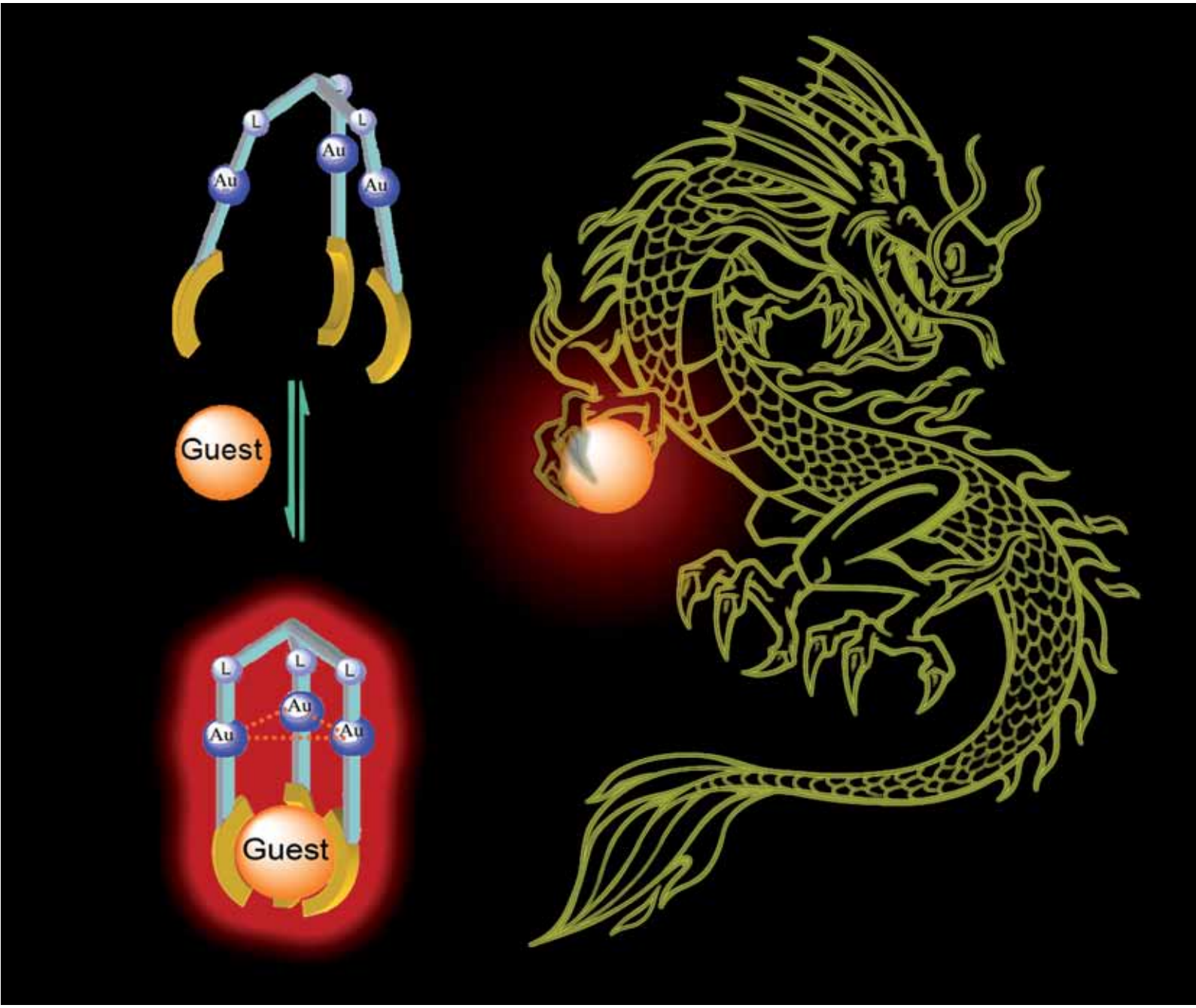

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Selective ion probe for Mg^{2+} based on Au(I)···Au(I) interactions in a tripodal alkynylgold(I) complex with oligoether pendants†

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A simple but novel tripodal alkynylgold(I) complex with oligoether pendants has been synthesized and demonstrated to be a selective ion probe for Mg^{2+} based on Au(I)···Au(I) interactions.

Design of chemosensors for the selective detection of biologically important cations such as Na^+, K^+, Mg^{2+} and Ca^{2+} is a topic of considerable interest.[1–3] Macrocyclic receptors are the widely used cation-binding sites in these systems,[2] while chromophore-linked pseudomacrocycle- or podand-based chemosensors are relatively less well explored.[3] Signal transduction is another critical issue in the design of cation-specific chemosensors. In the majority of the chemosensors reported so far, the signaling of the binding event is achieved by photoinduced electron transfer,[4] photoinduced charge-transfer,[5] or chromophore (excimer) interaction.[6]

Recently, there has been a growing interest in the study of polynuclear gold(I) complexes, in particular with regard to the phenomenon of aurophilicity associated with these complexes, which results from weak Au···Au interactions.[7–9] Gold(I) phosphine/alkynyl compounds are of particular interest owing to their stability, ease of preparation, and intriguing photophysical properties, such as optical nonlinearity[10] and photoluminescence.[8d–g,9] We have initiated a programme to explore the utilization of the switching on and off of Au···Au interactions in optical signal transduction for chemosensing. A series of dinuclear gold(I) crown ether-containing complexes which can act as luminescence ion probes for metal ions have been reported by us previously.[8h–j] These complexes demonstrated a novel concept of the utilization of the on/off switching of Au···Au interactions for metal ion sensing.

As an extension of our previous efforts in this interesting area, we aimed at increasing the extent of Au···Au interactions upon the binding of suitable metal ions, and herein we report the design and synthesis of a simple but novel trinuclear alkynylgold(I) complex **1** with three oligoether pendants. With such a design, it is believed that once a metal ion of appropriate size and charge density is encapsulated in between the three intramolecular oligoether pendant units in **1** during the binding process, the three rigid and linear arylalkynylgold(I) units (initially far apart in solution) connected by the tridentate 1,1,1-tris(diphenylphosphinomethyl)ethane ligand (Triphos) would be forced into close proximity, and as a result would lead to the turning on of Au···Au interactions. Indeed, this receptor complex has been demonstrated to serve as a selective Mg^{2+} luminescent probe based on the switching on and off of the Au···Au interactions. Two oligoether-free analogues **2** and **3** have been designed for control experiments (Chart 1). All three complexes were synthesized by the reaction of Triphos with 3 equivalents of the respective polymer $[Au(C{\equiv}CR)]_\infty$. The identities of **1–3** were confirmed by ^{1}H NMR, ^{31}P NMR, FAB-MS and satisfactory elemental analysis, and the structure of **3** was also established by X-ray structure determination.‡

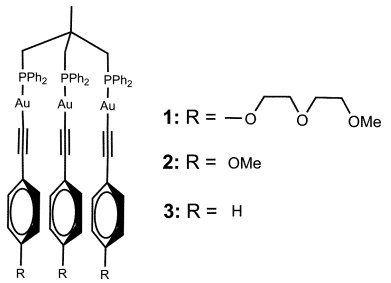

Chart 1 Structures of complexes **1–3**.

The X-ray structure of complex **3** shown in Fig. 1 features a trinuclear gold(I) complex, with each phosphorus atom coordinated to one alkynylgold(I) unit. A separation of 3.02 Å between Au(1) and Au(2) was observed, suggesting the presence of an intramolecular Au(I)···Au(I) interaction, while Au(3) was further away from the other two gold atoms.

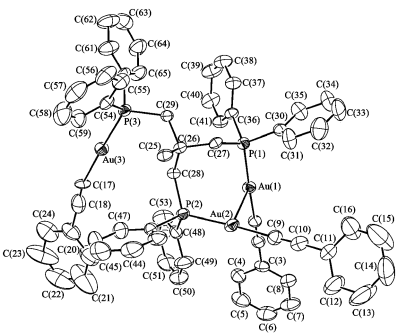

Fig. 1 Perspective drawing of complex **3** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

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† Electronic supplementary information (ESI) available: Characterization of the ligand and complexes **1–3**, crystallographic and structure determination data for complex **3**, excitation spectra for the binding of **1** and Mg^{2+}, and UV-vis binding study of complexes **2** and **3** for Mg^{2+} and **1** for Ca^{2+}. CCDC 719572. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b902690h

Table 1 Photophysical data of complexes **1–3**

Complex	λ_{abs}[a]/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm (τ_0/μs)	Medium (T/K)
1	276 (6.17), 288 (7.38), 300 sh (6.76), 324 sh (1.14)	454 (1.0)	CH_2Cl_2 (298)
		550 (15.4)	Solid (298)
		545 (90.5)	Solid (77)
2	276 (5.26), 288 (6.18), 300 sh (5.58), 324 sh (0.89)	459 (1.0)	CH_2Cl_2 (298)
		641 (5.4)	Solid (298)
		665 (14.1)	Solid (77)
3	272 (6.40), 284 (6.64), 294 sh (4.20), 308 sh (1.08)	454 (1.8)	CH_2Cl_2 (298)
		573 (5.7)	Solid (298)
		571 (18.7)	Solid (77)

[a] Absorption data from dichloromethane solution.

The angle of 173.9° for P(2)–Au(2)–C(9) is close to linearity and is typical of sp hybridization for the Au(I) and the acetylenic carbon. The C≡C bond distance of 1.213 Å is also typical of gold(I) alkynyl systems.[11]

The electronic absorption spectra of **1–3** in dichloromethane show intense high-energy absorption bands at *ca.* 276–290 nm, and low-energy bands at *ca.* 300–330 nm. The photophysical data of complexes **1–3** are tabulated in Table 1. With reference to previous spectroscopic work on gold(I) complexes, such as [Au(PPh$_3$)Cl],[9a] [Au(PPh$_3$)(C≡CPh)],[9a] [Au(PPh$_3$)-(C≡CC$_6$H$_4$OMe-*p*)][8f] and [Au$_2$(dppb)(C≡CPh)$_2$],[8g] the high-energy bands were tentatively assigned to originate from intraligand (IL) transitions characteristic of arylphosphine ligands, while the low-energy bands were assigned to the π → π* intraligand transition of the alkynyl ligands. All complexes produced intense long-lived emission at *ca.* 450–460 nm in dichloromethane at room temperature. An origin tentatively assigned to states arising from σ(Au–P) → π*(C≡C) or metal-perturbed intraligand π → π*(C≡C) transition is suggested. The relatively large Stokes shift, together with the observed luminescence lifetimes in the microsecond range, are suggestive of emission of triplet parentage. In the solid state at both 298 and 77 K, upon excitation at $\lambda > 350$ nm, complexes **1–3** show emission bands at 545–665 nm that are red-shifted from those observed in solution. The lifetimes of the emissive states in the microsecond range were also suggestive of a triplet parentage. With reference to previous spectroscopic work on luminescent gold(I) phosphine alkynyl complexes,[8d–g,9] such low-energy emission in the solid state is likely to originate from triplet excited states associated with the possible presence of one weak Au···Au interaction among two of the three gold(I) centres, given the presence of one short intramolecular Au···Au contact observed in the solid-state structure of the related halo complexes [Triphos(AuX)$_3$] (X = Cl (3.091 Å),[11a] Br (3.095(8) Å, 3.122(9) Å),[11b] I (3.326 Å)[11b]) and **3**. The absence of such a red-shifted low-energy emission band in solution is likely to be due to the lack of short Au···Au contacts, and hence the absence of Au···Au interactions in the solution state given the floppy nature of the pendants on the trigold(I) complexes.

The cation-binding ability of complex **1** was studied by electronic absorption spectroscopy. Upon addition of Mg^{2+} to a solution of **1** in CH_2Cl_2–MeOH (1 : 1 v/v) containing 0.1 M ^{n}Bu$_4$NPF$_6$ as supporting electrolyte (Fig. 2), the absorption band at *ca.* 290 nm showed a drop in intensity, with the growth of a new low-energy band at *ca.* 360 nm. Two well-defined isosbestic points at *ca.* 264 and 323 nm were observed, indicative of a clean conversion of **1** to a new chemical species, probably the ion-bound adduct. The inset of Fig. 2 shows the binding isotherm, obtained by a plot of the absorbance at 360 nm as a function of pM, where pM = −log[M], from which a binding constant log K_s of 2.0 ± 0.1 for Mg^{2+} was determined. The identity of the ion-bound adduct, $[\mathbf{1}\cdot Mg^{2+}\cdot ClO_4^-]^+$ was established by the observation of an ion cluster at 1996 in the positive ESI-MS, further supporting the binding event.

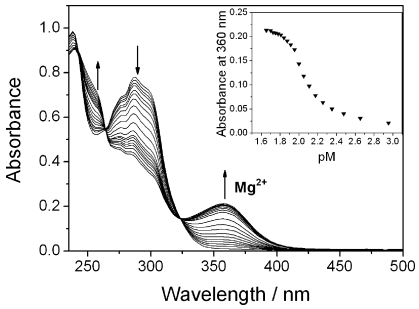
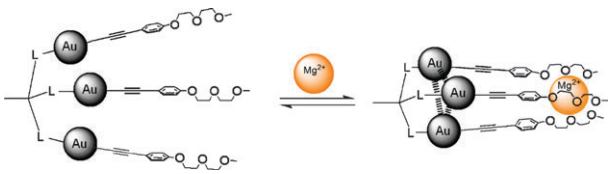


Fig. 2 UV-Vis spectral changes of complex **1** (1.1×10^{-5} M) in CH_2Cl_2–MeOH (1 : 1 v/v; 0.1 M ^{n}Bu$_4$NPF$_6$) upon addition of Mg(ClO$_4$)$_2$. Inset shows the absorbance changes at 360 nm of **1** upon titration of Mg^{2+}.

The binding abilities of complex **1** with other alkaline earth (Ca^{2+}, Ba^{2+}) and alkali (Li^+, Na^+, K^+) metal ions were also examined in CH_2Cl_2–MeOH (0.1 M ^{n}Bu$_4$NPF$_6$). Only Ca^{2+} shows a similar UV-vis change, but this is to a much lesser extent, and the addition of other ions essentially leads to no changes in the electronic absorption spectra.

The charge density and the metal ion size may account for the selectivity for Mg^{2+}. Among all alkali and alkaline earth metal ions, magnesium ion has the highest charge and the smallest size, and therefore has the highest charge density,[12] rendering the highest binding affinity to the oligoether pendants that brings the three Au atoms into close proximity (Scheme 1).[13]

To further elucidate the binding event, two control analogues without the oligoether tethers have been designed, in which **2** has a methoxy substituent on each of the phenyl rings of the alkynyl units to reproduce the electronic environment in **1**. The UV-vis spectrum of **3** essentially showed no spectral changes upon treatment with Mg^{2+} even in the presence of a large excess of Mg^{2+} salt. Upon addition of Mg^{2+} to complex **2**, the absorption band at *ca.* 290 nm did show a drop in absorbance, however, the absorbance of the band at *ca.* 350 nm only showed a slight increase initially that then disappeared completely upon addition of more Mg^{2+}



Scheme 1 Proposed binding mode for **1** and Mg^{2+}.

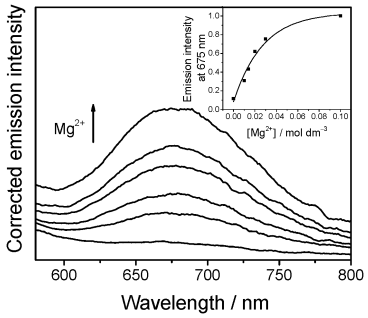


Fig. 3 Corrected emission spectral changes of complex **1** (1.0×10^{-4} M) in CH_2Cl_2–MeOH (1 : 1 v/v; 0.1 M $^nBu_4NPF_6$) upon addition of $Mg(ClO_4)_2$. Inset shows the plot of emission intensity at 675 nm as a function of Mg^{2+} concentration.

ion, indicating the instability of the tris-methoxy bound Mg^{2+} ion-encapsulated adduct.

Fig. 3 shows the emission spectral changes of **1** in CH_2Cl_2–MeOH (1 : 1 v/v; 0.1 M $^nBu_4NPF_6$) solution upon addition of Mg^{2+}. A new low-energy band at *ca.* 675 nm appeared. The excitation spectra of **1** in the absence and in the presence of Mg^{2+} ion revealed that the low-energy and the high-energy bands were derived from different excited state origin. The excitation spectrum in the presence of Mg^{2+} shows a low-energy shoulder at 360 nm, which coincides with the new absorption band at *ca.* 360 nm in the UV-vis spectrum resulting from the switching on of the Au···Au interaction upon Mg^{2+} binding. Thus, the low energy emission band at 675 nm has been attributed to originate from an excited state associated with the switching on of the Au···Au interaction upon the binding of Mg^{2+}, that gives rise to a reduced HOMO–LUMO energy gap.

In summary, a novel tripodal alkynylgold(I) complex with three oligoether pendants that shows selective binding towards Mg^{2+}, has been designed and synthesized. Optical reporting based on the switching on of Au···Au interactions was demonstrated and utilized as the mode of signal transduction.

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Notes and references

‡ *Crystal data* for **3**: $C_{65}H_{55}Au_3O_{0.5}P_3$, M = 1527.90, monoclinic, $P2_1/c$, a = 29.200(6), b = 13.992(2), c = 28.986(6) Å, β = 96.25(2)°, V = 11772 (4) Å^3, Z = 8, D_c = 1.724 g cm^{-3}, μ = 7.579 mm^{-1}, T = 301 K, 22 320 independent reflections, final R indices [$I > 2\sigma(I)$], $R1$ = 0.0498, w$R2$ = 0.1189, R_{int} = 0.0452, GoF = 1.043.

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