the high-resolution 145° detector bank, by using the GSAS suite of programs.[16] Nitrogen content, measured from C,H,N analysis, showed the nitrogen stoichiometry to be 1.01(3), assuming a Ca:Au ratio of 2:1.

Received: April 20, 1998 [Z11753IE]
German version: *Angew. Chem.* **1998**, *110*, 3040–3041

Keywords: calcium · gold · neutron diffraction · nitrides · solid-state structures

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Proof of Potassium Ions by Luminescence Signaling Based on Weak Gold–Gold Interactions in Dinuclear Gold(I) Complexes[**]

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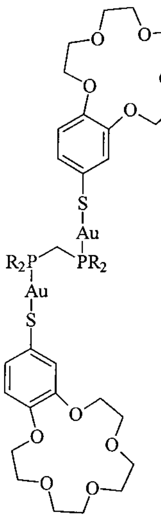
The search for host molecules that can selectively recognize specific guest molecules at their receptor site and produce a measurable physical change is currently of immense interest. Spectroscopic detection of metal ions or anions is of great importance both in classical analytical chemistry and in the molecular design of ion sensors that involve optical signal transformation. The utilization of sensitive luminescence signaling has always been an attractive and popular option, particularly when combined with a selective and specific complexing process involving the target species. Ion-controlled luminescence probes are of interest for ion sensing as well as for the construction of molecular optoelectronic switches.[1–3] A number of ion-binding organic receptors have been studied, most of which were based on polyaromatic luminophores[2a, c, 4] and the exploitation of photoinduced electron transfer (PET) processes.[1–3] Although there has been increased attention given to the design of metalloreceptors in recent years, most of it has focused on systems with metal-to-ligand charge-transfer (MLCT) excited states,[5] with relatively few studies of other systems.[5a, b, 6]

In recent years 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 gold–gold interactions.[7] Recent studies by us[8] and others[9] have shown that the presence of weak gold–gold interactions in a number of di- and polynuclear gold(I) complexes gives rise to unique electronic spectroscopic features; in particular many of them exhibit intense yellowish green to orange-red phosphorescence. In general, we and others observed that an increase in gold–gold interactions leads to a lower energy emission.

Herein, we describe a versatile luminescence ion probe for potassium ions based on the switching on and off of the gold–gold interactions. The present system not only serves as a molecular phosphorescent ion sensor and a molecular optoelectronic switch, but also provides spectroscopic evidence for potassium ion induced gold–gold interactions.

The complexes $[Au_2(dppm)(S\text{-benzo}[15]crown\text{-}5)_2]$ (**1**) and $[Au_2(dcpm)(S\text{-benzo}[15]crown\text{-}5)_2]$ (**2**) were synthesized by the reaction of $[Au_2(dppm)Cl_2]$ and $[Au_2(dcpm)Cl_2]$, respectively, with two equivalents of 4′-sulfanylmonobenzo[15]-crown-5 in the presence of triethylamine in dichloromethane under an inert atmosphere of nitrogen (dppm = bis(diphenylphosphanyl)methane; dcpm = bis(dicyclohexylphosphanyl)methane). The identities of **1** and **2** were confirmed by ^1H NMR spectroscopy, positive-ion FAB-mass spectrometry, and satisfactory elemental analyses,[10] and the structure of **2** was confirmed by an X-ray crystal structure determination; the Au–Au separation is 3.28 Å.[11]



1, R = phenyl
2, R = cyclohexyl

The electronic spectra of **1** and **2** in dichloromethane/methanol (1/1) containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte show spectral changes upon addition of K^+ ions (Figure 1). Isosbestic points were observed at 266, 335, and 390 nm for **1** and at 235 and 352 nm for **2**, which are indicative of a clean reaction. Control experiments with the crown-free analogues $[Au_2(dppm)\{S\text{-}3,4\text{-}(OMe)_2C_6H_4\}_2]$ (**3**) and $[Au_2(dcpm)\{S\text{-}3,4\text{-}(OMe)_2C_6H_4\}_2]$ (**4**) showed no UV/Vis spectral changes upon addition of K^+ ions under the

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[**] V.W.W.Y thanks the Research Grants Council, the Croucher Foundation, and The University of Hong Kong for financial support. C.L.C acknowledges the the Croucher Foundation and the Sir Edward Youde Memorial Fund Council for scholarships.

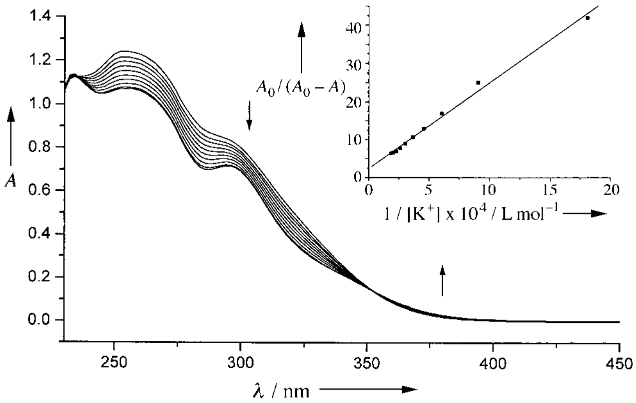

Figure 1. UV/Vis spectral changes of **2** (5.3×10^{-5} mol L^{-1}) upon addition of various concentrations of potassium ions in CH_2Cl_2/MeOH (1/1; 0.1 M nBu$_4$NPF$_6$). The insert shows the plot of $A_0/(A_0-A)$ versus 1/[K$^+$] at 290 nm

same conditions. This observation is supportive of the importance of the crown moieties in the specific association of **1** and **2** with K$^+$ ions rather than resulting from changes in the solvent polarity. A plot of $A_0/(A_0-A)$ versus $[K^+]^{-1}$ yielded a satisfactory straight line, which indicated that the complexation of a K$^+$ ion to the dinuclear Au^I complex was in a 1:1 ratio (A and A_0 refer to the absorbance at 290 nm with and without K$^+$ ions, respectively). Since the ionic radius of the K$^+$ ion is too large to fit into the cavity of a benzo[15]-crown-5, the 1:1 complexation ratio indicates that the K$^+$ ions are sandwiched between two benzo[15]crown-5 units within the dinuclear Au^I complex. The lg$K$ values for the binding of K$^+$ ions to **1** and **2** were 3.4 and 4.0, respectively.

The changes in the luminescence response of **1** and **2** towards K$^+$ ion binding were found to be more pronounced. The emission spectra of **1** (Figure 2) with excitation at 390 nm, the isosbestic wavelength, showed a drop in intensity at approximately 502 nm with the concomitant formation of a new long-lived, low-energy emission band at 720 nm upon addition of K$^+$ ions. An isoemissive point was obtained at about 600 nm. The lifetime of the excited state for the emission band at 720 nm was determined as 0.2 μs. Interestingly, in the absence of K$^+$ ions, the emissive lifetime of the band at 520 nm was less than 0.1 μs. Successive addition of free benzo[15]crown-5 to the mixture of **1** and K$^+$ led to the observation of a reverse trend, in which the low-energy emission at 720 nm dropped in intensity with a concomitant rise in the high-energy emission at 502 nm. This result is indicative of the reversible nature of the ion-binding process. A plot of $I_0/(I-I_0)$ versus $[K^+]^{-1}$ for **1** yielded a satisfactory straight line, which further confirmed that the complexation of K$^+$ ion to the dinuclear Au^I complex was in a 1:1 ratio; thedetermined lg$K$ value of 3.2 is in close agreement with that obtained from absorption measurements (I_0 and I refer to the emission intensity at 720 nm in the absence and in the presence of K$^+$ ions, respectively). The identity of the $\{\mathbf{1}\cdot K^+\}$ adduct was confirmed by electrospray-ionization mass spectrometry (ESI-MS). Similar to the absorption studies, control experiments with the crown-free analogues **3** and **4** under the same conditions showed no changes in the emission characteristics upon addition of K$^+$ ions, supportive of the importance of the crown moieties in the specific association of **1** and **2** with K$^+$ ions.

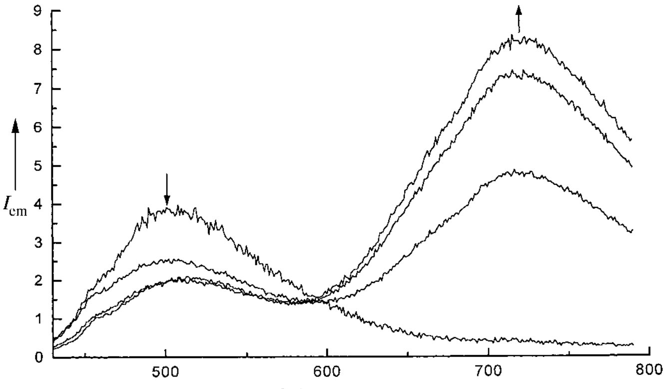

Figure 2. Emission spectra of **1** (1.7×10^{-3} mol L^{-1}) upon addition of various concentrations of potassium ions in CH_2Cl_2/MeOH (1/1; 0.1 M nBu$_4$NPF$_6$).

Despite the well known high affinity of benzo[15]crown-5 for sodium ions, addition of Na$^+$ ions to **1** did not give rise to the growth of a new emission band at 720 nm. This is consistent with our rationale for the design of complexes **1** and **2** as a photoswitch. In solution the Au–Au separation in **1** and **2** is large as a result of the floppy nature of their structures. Thus, an emission typical of monomeric Au^I–phosphane was observed at around 502 nm. Upon addition of K$^+$ ions, which have ionic radii too large to fit into the cavity size of benzo[15]crown-5, the K$^+$ ions would tend to sandwich between two crown ethers, thereby bringing the two Au^I centers into close proximity. Such Au–Au interactions that involve the overlap of the 5d, 6s, and 6p$_z$ orbitals on each Au atom with those of the other Au atom would give rise to bonding and antibonding combinations of dσ, dσ*, dπ, dπ*, dδ, dδ*, sσ, sσ*, pσ, and pσ* character (the z axis is taken to be the Au–Au bond axis). A net stabilization of the dinuclear Au acceptor orbitals sσ or pσ would result. Thus a red emission characteristic of the ligand-to-metal–metal bond charge transfer (LMMCT; from the thiolate ligand to the gold–gold bond)[12] is observed. Addition of an excess of free benzo[15]crown-5 to the mixture of **1** and K$^+$ ions extracted the sandwiched K$^+$ ions from **1**, with a breaking of the short Au–Au contact and a reversal of the emission trend. Similarly, addition of Na$^+$ ions to a mixture of **1** and K$^+$ ions also caused a drop in the intensity of the emission band at 720 nm, probably as a result of the high affinity of the benzo[15]crown-5 unit for Na$^+$ ions, which displace the K$^+$ ions. Similar findings were also observed for complex **2**. Although one cannot eliminate the possibility that the generation of the low-energy emission band at 720 nm in **1** and at 713 nm in **2** upon addition of K$^+$ ions is a result of the slowing down of the rate of nonradiative decay that arises from the interlocking of the two crown units by K$^+$ ions to render the complexes more rigid, we favor the assignment of the low energy emission band as derived from a LMMCT state resulting from the formation of a weak Au–Au interaction.

Received: April 7, 1998 [Z11697IE]
German version: *Angew. Chem.* **1998**, *110*, 3041–3044

Keywords: crown compounds · gold · luminescence · molecular switches · S ligands

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[10] **1:** ^{1}H NMR ($CDCl_3$): $\delta = 3.7-4.1$ (m, 34 H, CH_2 (crown ether) and PCH_2P); 6.6, 7.0–7.1 (m, 6 H, Ar-*H*); 7.2–7.4, 7.6–7.7 (m, 20 H, PPh_2); positive-ion FAB-MS: *m*/*z*: 1077 [$M -$ S-benzo[15]crown-5$^+$]; elemental analysis calcd for **1** · $2\,CH_2Cl_2$: C 42.71, H 4.14; found: C 42.89, H 3.91. **2:** ^{1}H NMR ($CDCl_3$): $\delta = 1.1-2.2$ (m, 46 H, dcpm); 3.7–4.1 (m, 32 H, CH_2 (crown ether)); 6.6, 7.0–7.1 (m, 6 H, Ar-*H*); positive-ion FAB-MS: *m*/*z*: 1101 [$M^+ -$ S-benzo[15]crown-5]; elemental analysis calcd for **2** · $1/2\,CH_2Cl_2$: C 44.53, H 5.89; found: C 44.28, H 5.88. **3:** ^{1}H NMR ($CDCl_3$): $\delta = 3.7-3.8$ (m, 14 H, OCH_3 and PCH_2P); 6.6, 7.0–7.1 (m, 6 H, Ar-*H*), 7.2–7.4, 7.6–7.7 (m, 20 H, PPh_2); positive-ion FAB-MS: *m*/*z*: 947 [$M^+ - SC_6H_4(OMe)_2$; elemental analysis calcd for **3**: C 44.11, H 3.58; found: C 43.94, H 3.67. **4**: ^{1}H NMR ($CDCl_3$): $\delta = 1.1-2.2$ (m, 46 H, dcpm), 3.8 (d, 12 H, OCH_3), 6.6, 7.0–7.1 (m, 6 H, Ar-*H*); positive-ion FAB-MS: $m/z = 971$ [$M - SC_6H_4(OMe)_2^+$]; elemental analysis calcd for **4** · CH_2Cl_2 · H_2O: C 40.57, H 5.47; found: C 40.21, H 5.21.

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Sensitivity Enhancement in Transverse Relaxation Optimized NMR Spectroscopy[**]

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Continuing efforts to study ever larger biologically relevant proteins by NMR spectroscopy have resulted in many advances over the past 10 years; one notable development is the introduction of multidimensional heteronuclear techniques for proteins labeled with ^{13}C and ^{15}N. These techniques have greatly facilitated NMR studies of the structure and function of proteins with molecular weights up to 30 kD. However, their application to larger proteins is hampered by the decrease in the molecular tumbling rate.[1] This shortens the transverse relaxation time of the protein, which in turn

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[**] The authors thank Dr. David Smith for helpful discussions and Dr. Mingjie Zhang for a sample of ^{15}N-labeled calmodulin. This work was supported by grants from the Research Grant Council of Hong Kong (HKUST 563/95M, 6197/97M, and 6038/98M), and the Hong Kong Biotechnology Research Institute is acknowledged for the purchase of the spectrometer.

1433-7851/98/3720-2859 $ 17.50+.50/0