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# Design and synthesis of luminescence chemosensors based on alkynyl phosphine gold(I)–copper(I) aggregates†

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Receptor-containing polynuclear mixed-metal complexes of gold(I)-copper(I) 1-3 based on a  $[{Au_3Cu_2(C = CPh)_6}Au_3{PPh_2-C_6H_4-PPh_2}_3]^2$  (Au\_6Cu\_2) core with benzo-15-crown-5, oligoether and urea binding sites were designed and synthesized, respectively. These complexes exhibited remarkably strong red emission at *ca*. 619–630 nm in dichloromethane solution at room temperature upon photoexcitation at  $\lambda > 400$  nm, with the emission quantum yield in the range 0.59–0.85. The cation-binding properties of 1 and 2 and the anion-binding properties of 3 were studied using UV-vis, emission and <sup>1</sup>H NMR techniques. Complex 1, with six benzo-15-crown-5 pendants, was found to show a higher binding preference for K<sup>+</sup>, with a selectivity trend of K<sup>+</sup>  $\gg$  Cs<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup>. The addition of metal ions ( $Li^+$ ,  $Na^+$ ,  $K^+$  and  $Cs^+$ ) to complex 1 led to a modest emission enhancement with a concomitant slight blue shift in energy and well-defined isoemissive points, which is attributed to the rigidity of the structure and the inhibited PET (photo-induced electron transfer) process from the oxygen to the aggregate as a result of the binding of the metal ion. The six urea receptor groups on complex 3 were found to form multiple hydrogen bonding interactions with anions, with the positive charge providing additional electrostatic interaction for anion-binding. The anion selectivity of 3 follows the trend  $F^- > Cl^- \approx H_2 PO_4^- > Br^-$  and the highest affinity towards  $F^-$  is attributed to the stronger basicity of F<sup>-</sup>, as well as its good size match with the cavity of the urea pocket.

# Introduction

In supramolecular host-guest chemistry, the design of selective and sensitive ion receptors is of great importance, due to their potential applications in ion transport, chemosensing and especially in the field of biomedical and environmental sciences.<sup>1,2</sup> Macrocyclic crown ether and oligoether units have been extensively utilized as the specific binding sites for alkali and alkaline earth metal ions.1 Urea has often been used as an excellent hydrogen bond donor in the design of anion receptors.<sup>2,3</sup> Signal transduction is also important in the design of specific chemosensors. Luminescence signaling has been widely used in the design of chemosensors due to its high sensitivity and the simplicity of its equipment requirements.<sup>4</sup> Although most studies on the design of luminescence probes for ion sensing in the past have been focused on organic receptors based on polyaromatic luminophores involving photoinduced electron transfer (PET) processes,5 the utilization of transition metal complexes as luminescent metal ion sensors has been relatively less explored, the main examples being of ruthenium(II),<sup>6</sup> rhenium(I),<sup>7</sup> iridium(III)<sup>8</sup> and platinum(II)<sup>9</sup> complexes utilizing MLCT excited states for luminescent signal transduction.

Luminescent polynuclear d<sup>10</sup> metal complexes have attracted increasing attention because of their potential applications in luminescence chemosensors, OLEDs or dopant emitters.<sup>10,11</sup> Gold(I) complexes are one of the important classes, due to their intriguing photoluminescence behaviour and their propensity to form aurophilic Au···Au interactions.12 Many studies showed that an increase in the  $Au\cdots Au$  interaction would lead to a shift of the emission to lower energy.<sup>13</sup> The ability of gold(I) to form heterometallophilic  $Au \cdots M$  (M = Cu or Ag) interactions is also interesting.14 Abu-Salah and coworkers reported a series of heteronuclear d<sup>10</sup> metal alkynyl complexes, demonstrating the presence and importance of both  $\sigma$ - and  $\pi$ -bonding modes in metal alkynyl systems.15 In these compounds, the emission can be modified not only by the aurophilic Au ··· Au interactions, but also by the presence of heterometallophilic Au...Cu or Au...Ag interactions. The photophysical properties of a series of pentanuclear Au(I)-Cu(I) and Ag(I) mixed-metal alkynyl complexes,  $[^{n}Bu_{4}N][Au_{3}M_{2}(C \equiv CC_{6}H_{4}R-p)_{6}]$ , (M = Cu, R = OMe,  $O^nBu$ ,  $O^nHex$ , Me, Et; M = Ag, R = Et,  $O^nHex$ ), have been studied by us.16 Eisenberg and coworkers reported interesting polymorphism of [PPN][Au<sub>3</sub>Cu<sub>2</sub>(1-ethynylcyclohexanol)<sub>6</sub>], and

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demonstrated that the polymorphs exhibit different emission energies as a result of the different Au $\cdots$ Au, Au $\cdots$ Cu and Cu $\cdots$ Cu distances.<sup>17</sup>

Recently, Koshevoy and coworkers reported an interesting series of alkynyl-phosphine gold(I)-copper(I) aggregates that have highly intense luminescence, with their luminescence quantum yields reaching a maximum value of 0.92.18 The metal-centered triplet state of the heterometallic alkynyl aggregate was suggested to play a key role in the observed phosphorescence. Variation of the substituents with different electronic groups was found to have relatively little effect on the structure, but displayed a significant influence on their photophysical properties. In addition, a decrease in the size of the metal aggregate has been found to lead to an increase in efficiency and photostability, which has been demonstrated by both experimental and theoretical studies. Amongst all of the alkynyl-phosphine gold(I)-copper(I) aggregates reported,  $[{Au_3Cu_2(C = CPh)_6}Au_3{PPh_2-C_6H_4-PPh_2}_3]^{2+}$ , with the smallest  $Au_6Cu_2$  cluster core, was found to be the most stable and effective luminophore.18b

It is believed that such kinds of strongly emissive luminophores could be explored for signal transduction in the design of luminescence chemosensors *via* the PET (photoinduced electron transfer) mechanism upon the introduction of some specific ion-binding groups to the [ $\{Au_3Cu_2(C \equiv CPh)_6\}Au_3\{PPh_2-C_6H_4-PPh_2\}_3\}^{2+}$  system. Herein, we report the design and synthesis of  $Au_6Cu_2$  aggregate-based complexes **1–3** with benzo-15-crown-5, oligoether and urea binding sites, respectively (Scheme 1). The photophysical and cation-binding properties of **1** and **2** and the anion-binding properties of **3** have been studied using UV-vis, emission and <sup>1</sup>H NMR techniques.

# **Results and discussion**

### Synthesis and characterization

Complexes 1–3 were synthesized according to a modification of previously reported procedures<sup>18</sup> and the synthetic route is summarized in Scheme 1. Complexes S1–S3 were synthesized according to a modification of the literature method by adding 1,4bis(diphenylphosphino)benzene to depolymerize [AuC $\equiv$ CR]<sub>\*</sub>, which was prepared *in situ* by reacting [Au(tht)Cl] with the corresponding HC $\equiv$ CR in the presence of Et<sub>3</sub>N. By adding a stoichiometric amount of [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> to the respective complexes S1–S3 in dichloromethane solution, bright orange to red solutions with intense red emissions were observed. Complexes 1–3 were obtained as orange to red solids upon recrystallization from dichloromethane–diethyl ether. All of the complexes were characterized by <sup>1</sup>H NMR, <sup>31</sup>P NMR and FAB-MS and gave satisfactory elemental analysis. The structure of complex 3 was established by X-ray structure determination.

#### X-Ray crystal structure determination of 3

The perspective drawing of the complex cation of **3** is depicted in Fig. 1. The structure of complex **3** is similar to the reported  $[{Au_3Cu_2(C = CPh)_6}Au_3{PPh_2-C_6H_4-PPh_2}_3]^{2+}$  with a Au\_6Cu<sub>2</sub> core,<sup>18</sup> which has a central  $[Au_3Cu_2(C = CR)_6]^-$  "rod" wrapped by a  $[Ph_2P-C_6H_4-PPh_2Au]_3^{3+}$  "belt". Six urea receptor groups are integrated into the luminescent Au\_6Cu<sub>2</sub> unit. It is expected that six urea receptor groups provide a pocket that form multiple hydrogen bonding interactions with anions.



Scheme 1 The synthetic route to 1–3.



Fig. 1 A perspective drawing of the complex cation of 3. Thermal ellipsoids are shown at the 30% probability level.

 Table 1
 Selected bond lengths [Å] and bond angles [deg] for complex 3

 with estimated standard deviations in parentheses

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Selected bond lengths [Å]				
	Cu(1)–Au(1) Cu(1)–Au(5) Cu(2)–Au(3) Au(1)–Au(5) Au(3)–Au(4) Au(5)–Au(6)	2.7691(15) 2.9329(15) 2.880415) 3.3363(8) 2.8594(9) 2.8654(7)	Cu(1)-Au(3) Cu(2)-Au(5) Au(1)-Au(2) Au(1)-Au(3) Au(3)-Au(5)	2.8830(15) 2.7821(14) 2.8656(7) 3.3684(8) 3.2645(10)	

The selected bond lengths are tabulated in Table 1. Three short Au  $\cdots$  Au contacts (2.8594, 2.8656 and 2.8654 Å) between the "rod" and "belt" were observed, suggesting the "rod-and-belt" structure is stabilized by the aurophilic interactions. The structure of the central [Au<sub>3</sub>Cu<sub>2</sub>(C=CR)<sub>6</sub>]- "rod" is very similar to the reported pentanuclear clusters [Au<sub>3</sub>Cu<sub>2</sub>(C=CPhR-4)<sub>6</sub>]<sup>-.15,16</sup> The metal atoms are arranged at the vertices of the trigonal bipyramid, in which two copper atoms occupy the apical positions, while the three gold atoms form a triangle. Each gold(I) atom is  $\sigma$ -bonded to two alkynyl groups in an almost linear fashion, with the C-Au-C angles in the range 1.946-2.036 Å. On the other hand, each copper(I) atom is unsymmetrically  $\pi$ -bonded to three alkynyl groups. Six short Au $\cdots$ Cu distances in the range 2.7691(15)-2.9329(15) were also observed, indicative of the presence of heterometallic Au...Cu interactions. Such short heterometallic Au...Cu contacts were also found in the previously reported pentanuclear clusters [Au<sub>3</sub>Cu<sub>2</sub>(C=CPhR-4)<sub>6</sub>]<sup>-.15,16</sup>

#### Electronic absorption and emission properties

In dichloromethane solution, complexes 1–3 exhibited yellow to orange–yellow colors. Intense high-energy absorption bands at 260–310 nm and low-energy absorption bands at *ca*. 400 nm, with tails to *ca*. 550 nm were observed (Fig. S1†). The photophysical data are collected in Table 2. With reference to a previous work on alkynylgold(1) and copper(1)<sup>16</sup> and the systematic study on the related Au<sub>6</sub>Cu<sub>2</sub> system by Koshevoy,<sup>18</sup> the high-energy absorption bands are tentatively assigned as the intraligand  $\pi \rightarrow \pi^*$  transitions

 Table 2
 Photophysical data for complexes 1–3

of the phosphine and alkynyl ligands, while the lower-energy absorption at *ca*. 400 nm and the tails extending to 550 nm are likely to be ascribed to metal cluster-centered ds/dp transitions due to the presence of the metal…metal interaction, with some mixing of metal to  $\pi^*(C \equiv CR)$  metal-to-ligand charge transfer (MLCT) transitions.

In addition, complexes **1–3** gave remarkably strong red emission at *ca*. 619–630 nm in dichloromethane solution at room temperature upon photoexcitation at  $\lambda > 400$  nm (Fig. S2†). The luminescence quantum yields of complexes **1–3** are in the range 0.59–0.85. The long-wavelength emission with high luminescence quantum yield make these complexes useful for application as chemosensors. The emission lifetimes are found to be in the microsecond range, which is suggestive of a triplet parentage. The intense red emission was tentatively assigned to the metal cluster (Au<sub>6</sub>Cu<sub>2</sub>)-centered triplet emission. Complex **3** showed a slight blue shift in emission energy compared to those of complexes **1** and **2**, which have strong electron-donating groups, similar to those reported previously.<sup>18c</sup>

# **Ion-binding studies**

Cation-binding of complexes 1 and 2. The cation-binding ability of complexes 1 and 2 was investigated by luminescence studies. In general, the addition of metal ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>) to complex 1 gave rise to a modest emission enhancement, with a concomitant slight blue shift in energy and well-defined isoemissive points. Fig. 2 shows the emission spectral changes of complex 1 upon the addition of K<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (1:1 v/v; 0.1 M "Bu<sub>4</sub>NPF<sub>6</sub>). The inset shows the changes in the emission intensity at 610 nm as a function of the added K<sup>+</sup> concentration. Such an enhancement in emission intensity could be rationalized



Fig. 2 Emission spectral traces of 1 ( $2.88 \times 10^{-7}$  M) in CH<sub>2</sub>Cl<sub>2</sub>–MeOH (1:1 v/v; 0.1 M "Bu<sub>4</sub>NPF<sub>6</sub>) upon the addition of K<sup>+</sup>. Excitation at 400 nm. Inset: A plot of the emission intensity at 610 nm as a function of K<sup>+</sup> concentration and its theoretical fit for the 1:1 binding of complex 1 with K<sup>+</sup>.

Complex	Absorption $\lambda/\text{nm}$ ( $\epsilon \times 10^{-5}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	Emission $\lambda_{em}/nm (\tau_0/\mu s)$	Ø <sub>em</sub>
1	264 (1.44), 310 (0.81), 400 (0.42)	630 (5.6)	0.85
2	264 (1.79), 290 (1.16), 402 (0.53)	630 (8.3)	0.72
3	266 (1.99), 304 (1.36), 398 (0.62)	619 (7.8)	0.59

**Table 3** Binding constants (log  $K_s$ ) of complex 1 for various metal ionsin CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (1:1, v/v) at 298 K

	Li+	Na <sup>+</sup>	K+	$Cs^+$
1	Too small to be determined	$3.67\pm0.04$	$6.81\pm0.03$	$4.66 \pm 0.10$

by the increased rigidity of the structure and the inhibited PET (photo-induced electron transfer) process from the oxygen to the aggregate upon binding of the metal ion. The addition of Na<sup>+</sup> and Cs<sup>+</sup> also produced similar emission enhancement, as shown in Fig. S3-S4.<sup>†</sup> However, few emission changes were observed for Li<sup>+</sup>, which may be due to the small binding affinity of 1 for Li<sup>+</sup> as a result of the poor size match. In our previous work on dinuclear gold(I) complexes with crown ether pendants and the trinuclear gold(I) complex with oligoether pendants, the metal binding could force the gold(I) atoms into close proximity, which can lead to a large emission response in the lower-energy wavelength region.<sup>10a-d</sup> However, in this work, no lower-energy emission bands were observed for complexes 1 and 2 upon metal ion binding. The reason might be due to the rather rigid structure of the aggregates, which would not allow the gold(I) and copper(I) atoms in 1 and 2 to change readily upon binding, as compared to our previous systems.10a-d

The emission titration data were found to show a close agreement with the theoretical fit based on a 1 : 1 binding model. The binding constants (log  $K_s$ ) of **1** toward Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> were determined to be 3.67 ± 0.04, 6.81 ± 0.03 and 4.66 ± 0.10, respectively, and are tabulated in Table 3. Complex **1** shows a higher binding preference for the binding of metal ions with large sizes (K<sup>+</sup> and Cs<sup>+</sup>), with a selectivity trend of K<sup>+</sup>  $\gg$  Cs<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup>. Despite the well-known selectivity of benzo-15-crown-5 (1.70–2.20 Å) for Na<sup>+</sup> (1.94 Å) due to the good size match between the crown cavity and the Na<sup>+</sup> ion, a trend that is not consistent with that expected was observed. The high binding preference for K<sup>+</sup> (2.66 Å) and Cs<sup>+</sup> (3.34 Å), which are too large to fit into the cavity size of benzo-15-crown-5, is suggestive of their binding to the benzocrown moieties in a sandwiched or caged fashion.

The UV-vis spectrophotometric method was also used to investigate the cation binding behavior of **1**. However, very small UV-vis spectral changes were observed for complex **1** upon the addition of alkali metal ions (Fig. S5<sup>†</sup>).

The cation-binding properties of complex 2 were also investigated by emission spectroscopy. However, a slight emission enhancement was observed upon the addition of metal ions. This may be ascribed to the non-specific binding and floppy nature of the oligoether receptors.

The cation-binding properties of **1** were also studied using <sup>1</sup>H NMR spectroscopy. Fig. 3 shows the <sup>1</sup>H NMR spectral changes of **1** upon the addition of an excess of different alkali metal ions in CDCl<sub>3</sub>–CD<sub>3</sub>OD (1:1, v/v) at room temperature. The aromatic protons of complex **1** displayed a set of low-field resonance signals ( $\delta$  (ppm): 7.85, 7.61 and 7.41) and a set of high-field resonance signals ( $\delta$  (ppm): 6.38 and 6.25). Based on the detailed NMR study by Koshevoy,<sup>18b</sup> the set of low-field signals can be assigned to the Ph<sub>2</sub>P–C<sub>6</sub>H<sub>4</sub>–PPh<sub>2</sub> moieties in the [Ph<sub>2</sub>P–C<sub>6</sub>H<sub>4</sub>–PPh<sub>2</sub>Au]<sub>3</sub><sup>3+</sup> "belt", in which the signals at  $\delta$  7.85 and 7.41 are assigned to the *ortho*-H and *meta*-H of the diphosphine ligand and the signal at  $\delta$  7.61 is assigned to the mixture of *para*-H of the diphosphine and the



Fig. 3  $^{-1}$ H NMR spectral changes of 1 (2.1 mM) in CDCl<sub>3</sub>–CD<sub>3</sub>OD (1:1 v/v) upon the addition of various metal ions at room temperature.

C<sub>6</sub>H<sub>4</sub> spacer. The set of high-field resonance signals are assigned to the benzo-15-crown-5 moieties in the  $[Au_3Cu_2(C \equiv CR)_6]^-$  "rod". The addition of metal ions was found to lead to large changes in the chemical shifts of the aromatic protons (H<sub>a</sub>-H<sub>c</sub>) of the benzo-15-crown-5 moieties, while almost no changes were observed on the [Ph<sub>2</sub>P–C<sub>6</sub>H<sub>4</sub>–PPh<sub>2</sub>Au]<sub>3</sub><sup>3+</sup> "belt", indicating that metal ions are bound to the crown units. Protons H<sub>b</sub> and H<sub>c</sub> were found to exhibit large downfield shifts with well-resolved doublet signals upon the addition of alkali metal ions. In addition, metal ions with a large size (K<sup>+</sup> and Cs<sup>+</sup>) showed more a significant effect on the downfield shifts. The downfield shift of H<sub>b</sub> and H<sub>c</sub> upon cation-binding could be ascribed to the electron-withdrawing effect of the cation. The more pronounced effect induced by larger size metal ions may be due to the higher binding constants, as shown in Table 3. On the contrary, the H<sub>a</sub> proton resonance was found to show interesting shifts. K<sup>+</sup> and Cs<sup>+</sup> with large sizes were found to lead to a large upfield shift of H<sub>a</sub>, while Na<sup>+</sup> with a smaller size gave rise to a large downfield shift instead. The different shift mode of H<sub>a</sub> may be attributed to the different binding mode of the metal ion to 1. The downfield shift of H<sub>a</sub> caused by Na<sup>+</sup> could be readily explained by the electron-withdrawing effect of Na<sup>+</sup> upon binding into the crown cavity. The unusual upfield shifts of H<sub>a</sub> induced by K<sup>+</sup> and Cs<sup>+</sup> are likely a consequence of the ring current effect resulting from  $\pi$ -stacking in the sandwiched or caged binding mode. Similar upfield shifts in related sandwiched structures have also been reported by us and Choi and Hamilton.<sup>19</sup>

In addition, a variable-temperature <sup>1</sup>H NMR study of complex 1 in the absence and presence of Cs<sup>+</sup> was also performed (Fig. S6<sup>†</sup>). Interestingly, in the presence of Cs<sup>+</sup>, the signal at  $\delta$  7.61 ppm (a mixture of *para*-H of the diphosphine and the C<sub>6</sub>H<sub>4</sub> spacer) split into two signals with nearly a 1:1 ratio at 258 K. However, such splitting was not observed in the absence of Cs<sup>+</sup>. This splitting in the presence of Cs<sup>+</sup> at low temperature could be a result of

**Table 4** Binding constants (log  $K_s$ ) of complex **3** for various anions in CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v) at 298 K

	F-	Cl⁻	Br−	$H_2PO_4^-$
3	$7.55\pm0.19$	$6.82\pm0.09$	$5.47\pm0.12$	$6.70\pm0.30$

the unsymmetrical binding of the cation to the crown units on one side and not the other, which caused the original signal at  $\delta$ 7.61 ppm to split into two well-resolved signals at low temperature, confirming the domination of the 1 : 1 binding mode. These signals, together with the nice agreement of the experimental data with the theoretical fit using the 1 : 1 binding model, are supportive of our assignment.

Anion-binding of complex 3. The anion-binding ability of complex 3 was investigated by luminescence and UV-vis spectrophotometric methods. Fig. 4 shows the UV-vis spectral changes of 3 upon the addition of  $F^-$  in  $CH_2Cl_2$ . The addition of  $F^$ produced an observable absorbance enhancement at 274-450 nm, with a clean isosbestic point at 274 nm, while the low-energy tail at 450-550 nm remained unchanged. Fig. 5 shows the emission spectral changes of 3 upon addition of F- in CH<sub>2</sub>Cl<sub>2</sub>. The addition of F- also led to a modest enhancement of the emission intensity. This enhancement in the emission intensity could also be attributed to the increased rigidity of the molecule upon F- binding to the urea units. Similar emission changes were also observed upon the addition of  $H_2PO_4^-$  and Cl<sup>-</sup>. For Br<sup>-</sup> and I<sup>-</sup>, only slight emission changes were observed as a result of the weak hydrogen bonding interaction. The emission titration data showed a nice fit to a 1:1 binding model. Table 4 shows the binding constants of complex 3 for various anions. The binding constants (log  $K_s$ ) of 3 toward F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and  $H_2PO_4^-$  were determined to be 7.55 ±  $0.19, 6.82 \pm 0.09, 5.47 \pm 0.12$  and  $6.70 \pm 0.30$ , respectively. The anion selectivity of 3 follows the trend of  $F^- > Cl^- \approx H_2 PO_4^- >$ Br<sup>-</sup>, suggesting that 3 can serve as a selective receptor for F<sup>-</sup>. The highest affinity towards F- could be attributed to the stronger basicity of F<sup>-</sup>, which can establish a stronger hydrogen bonding interaction with urea group, as well as its good size match with the cavity of the urea pocket. Fabbrizzi and coworkers studied the correlation of selectivity with basicity in detail, revealing that anion basicity plays an important role in determining the anion selectivity.3a



Fig. 4 UV-vis spectral changes of complex 3 ( $7.45 \times 10^{-6}$  M) in CH<sub>2</sub>Cl<sub>2</sub> upon the addition of "Bu<sub>4</sub>NF at 298 K.



**Fig. 5** Emission spectral traces of **3**  $(3.72 \times 10^{-7} \text{ M})$  in CH<sub>2</sub>Cl<sub>2</sub> upon the addition of F<sup>-</sup>. Excitation at 400 nm. Inset: A plot of the emission intensity at 600 nm as a function of F<sup>-</sup> concentration and its theoretical fit for the 1:1 binding of complex **3** with F<sup>-</sup>.

<sup>1</sup>H NMR spectroscopic experiments were also carried out. Fig. 6 shows the <sup>1</sup>H NMR spectral changes of **3** in CD<sub>2</sub>Cl<sub>2</sub> upon the addition of F<sup>-</sup> and CD<sub>3</sub>OD. In CD<sub>2</sub>Cl<sub>2</sub>, the <sup>1</sup>H NMR signals of the urea moieties were not well-resolved and the two NH peaks were found to be masked by the aromatic signals of the urea moiety. Large <sup>1</sup>H NMR spectral changes of the urea moiety were observed upon the addition of protic solvent CD<sub>3</sub>OD and F<sup>-</sup> ions to **3** in CD<sub>2</sub>Cl<sub>2</sub> solution, while the proton signals of the urea moieties and the disappearance of the NH signals as a result of the fast exchange with the solvent. The addition of F<sup>-</sup> also led to large downfield shifts of the two NH protons, suggesting that F<sup>-</sup> would interact with **3** through hydrogen bonding interactions.

However, complex **3** is not very stable in the presence of a large excess of anions (*ca.* 1000 equiv.) for a long period of time (*ca.* 12 h). Large emission quenching was observed. This may be due to the extraction of the Cu<sup>+</sup> ion by the large excess of anions and the decomposition of the Au<sub>6</sub>Cu<sub>2</sub> cluster **3** to dinuclear gold(1) complex **S3**, which can be confirmed by <sup>1</sup>H NMR study. A similar decomposition process for **3** can also be found in the <sup>1</sup>H NMR experiment using  $d_6$ -DMSO as the solvent.

# Conclusion

In summary, we designed and synthesized three receptorcontaining polynuclear mixed-metal complexes of gold(I)copper(I) 1-3 based on the  $[{Au_3Cu_2(C = CPh)_6}Au_3{PPh_2-}$  $C_6H_4$ -PPh<sub>2</sub>}<sub>3</sub>]<sup>2+</sup> (Au<sub>6</sub>Cu<sub>2</sub>) core with benzo-15-crown-5, oligoether and urea binding sites, respectively. Their photophysical and ion-binding properties were studied. These complexes exhibited remarkably strong red emission at ca. 619-630 nm in dichloromethane solution at room temperature, with the emission quantum yield in the range 0.59-0.85. The highly emissive Au<sub>6</sub>Cu<sub>2</sub> aggregate luminophore has proved to be an effective signal transduction unit in the design of luminescence chemosensors. Through the judicious introduction of specific ion-binding groups to the strongly emissive Au<sub>6</sub>Cu<sub>2</sub> aggregate, different selective luminescence chemosensors could be realized. Complex 1, with six benzo-15-crown-5 pendants, was found to show a higher binding preference for  $K^+$ , while complex 3, with six urea receptor groups, showed the highest binding affinity towards F<sup>-</sup>.



Fig. 6 <sup>1</sup>H NMR spectral changes of 3 in  $CD_2Cl_2$  (a) in the absence and the presence of (b) F<sup>-</sup> and (c)  $CD_3OD$ .

# **Experimental section**

#### Materials and reagents

Tetra-*n*-butylammonium fluoride, tetra-*n*-butylammonium chloride, tetra-*n*-butylammonium bromide, and tetra-*n*-butylammonium phosphate were purchased from Fluka. Lithium perchlorate, sodium perchlorate, potassium hexafluorophosphate, phenyl isocyanate and tetra-*n*-butylammonium hexafluorophosphate were purchased from Aldrich Chemical Company and the latter was recrystallized three times from hot absolute ethanol and dried under vacuum for 12 h prior to use. 1,4-Bis(diphenylphosphino)benzene,<sup>20</sup> 4-ethynylbenzo-15-crown-5 (L1),<sup>96</sup> 1-ethynyl-4-(2-(2-methoxyethoxy)ethoxy)benzene) (L2),<sup>10c</sup> 4-ethynyaniline, cesium triflate,<sup>21</sup> [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub>,<sup>22</sup> gold(1) acetylene polymer [AuC=CR]<sup>23</sup> and complexes S1–S3 and 1–3<sup>18</sup> were synthesized according to modified reported procedures.

All solvents were purified and distilled using standard procedures before use.<sup>24</sup> All other reagents were of analytical grade and were used as received. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques.

#### Synthesis

**HC**≡**CC**<sub>6</sub>**H**<sub>4</sub>**NHCONHC**<sub>6</sub>**H**<sub>5</sub> **(L3).** To a solution of HC≡**CC**<sub>6</sub>**H**<sub>4</sub>**NH**<sub>2</sub> (0.3 g, 2.56 mmol) in 40 ml of anhydrous CH<sub>2</sub>Cl<sub>2</sub> was slowly added phenyl isocyanate (0.3 g, 2.56 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 ml) over a period of 10 min and the mixture was heated to reflux overnight under a nitrogen atmosphere. The precipitate was collected by filtration and washed twice with CH<sub>2</sub>Cl<sub>2</sub> to yield the product as a yellow solid. Yield: 0.45 g, 75%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K, relative to Me<sub>4</sub>Si):  $\delta$  4.04 (s, 1 H; C≡CH), 6.98 (t, *J* = 7.4 Hz, 1 H; −C<sub>6</sub>H<sub>5</sub>−), 7.29 (t, *J* = 7.4 Hz, 2 H; −C<sub>6</sub>H<sub>5</sub>−), 7.35 (d, *J* = 7.8 Hz, 2 H; −C<sub>6</sub>H<sub>4</sub>−), 7.46 (m, 4 H; −C<sub>6</sub>H<sub>4</sub>− and −C<sub>6</sub>H<sub>5</sub>−), 8.72 (s, 1 H; −NH), 8.88 (s, 1 H; −NH). FAB-MS: *m/z* 236 [M]<sup>+</sup>.

 $[(PPh_2C_6H_4PPh_2)(AuC \equiv CB15C5)_2]$  (S1). [Au(tht)Cl] (55 mg, 0.17 mmol) was added to a dichloromethane solution of 4ethynylbenzo-15-crown-5 (L1) (50 mg, 0.17 mmol) and Et<sub>3</sub>N (120 ul, 0.85 mmol) under a nitrogen atmosphere, and the mixture was stirred at 0 °C for 2 h. 1,4-Bis(diphenylphosphino)benzene (38.2 mg, 0.085 mmol) was then added to the solution and the reaction mixture was allowed to stir for 2 h. The solvent was then removed under reduced pressure and the residue was recrystallized from dichloromethane-diethyl ether to give S1 as a pale yellow solid. Yield: 61 mg, 50%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si):  $\delta$  3.76 (m, 16 H; -OCH<sub>2</sub>-), 3.88 (m, 8 H;  $-OCH_{2}$ -), 4.10 (m, 8 H;  $-OCH_{2}$ -), 6.74 (d, J = 8.3 Hz, 2 H; - $C_6H_{3-}$ , 7.02 (d, J = 1.8 Hz, 2 H;  $-C_6H_{3-}$ ), 7.07 (dd, J = 8.3and 1.8 Hz, 2 H; -C<sub>6</sub>H<sub>3</sub>-), 7.46-7.60 (m, 24 H; -C<sub>6</sub>H<sub>4</sub>- and -PPh<sub>2</sub>). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, relative to 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$ 42.5. FAB-MS: m/z 1131 [M – L]<sup>+</sup>, 1423 [M]<sup>+</sup>, 1446 [M + Na]<sup>+</sup>. Elemental analysis, anal. found (%): C, 50.66; H, 4.20. Calcd for  $C_{62}H_{62}Au_2O_{10}P_2{\cdot}CH_2Cl_2{:}\ C,\ 50.18;\ H,\ 4.28.$ 

[(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)]AuC=CC<sub>6</sub>H<sub>4</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub>]<sub>2</sub>] (S2). This was synthesized according to the procedure for S1, except L2 (37.7 mg, 0.17 mmol) was used instead of L1. Recrystallization from dichloromethane–diethyl ether gave S2 as a white solid. Yield: 98 mg, 90%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si):  $\delta$  3.38 (s, 6 H; –OCH<sub>3</sub>), 3.57 (m, 4 H; –OCH<sub>2</sub>–), 3.71 (m, 4 H; –OCH<sub>2</sub>–), 3.84 (m, 4 H; –OCH<sub>2</sub>–), 4.12 (m, 4 H; –OCH<sub>2</sub>–), 6.80 (d, *J* = 8.8 Hz, 4 H; –C<sub>6</sub>H<sub>4</sub>C=C-), 7.40–7.60 (m, 28 H; –PC<sub>6</sub>H<sub>4</sub>P–, –C<sub>6</sub>H<sub>4</sub>C=C- and –PPh<sub>2</sub>). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, relative to 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  42.5. FAB-MS: *m/z* 1059 [M – L]<sup>+</sup>, 1278 [M]<sup>+</sup>, 1475 [M + Au]<sup>+</sup>. Elemental analysis, anal. found (%): C, 50.44; H, 4.19. Calcd for C<sub>56</sub>H<sub>54</sub>Au<sub>2</sub>O<sub>6</sub>P<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 50.20; H, 4.14.

 $[(PPh_2C_6H_4PPh_2)(AuC \equiv CC_6H_4NHCONHC_6H_5)_2]$  (S3). This was synthesized according to the procedure for S1, except L3 (40 mg, 0.17 mmol) was used instead of L1. Recrystallization from dichloromethane–diethyl ether gave S3 as a pale yellow solid. Yield: 89 mg, 80%. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , 298 K, relative to Me<sub>4</sub>Si):  $\delta$  6.97 (t, J = 7.3 Hz, 2 H; -C<sub>6</sub>H<sub>5</sub>), 7.22 (d, J = 8.6 Hz, 4 H; -C<sub>6</sub>H<sub>4</sub>), 7.28 (t, J = 7.6 Hz, 4 H; -C<sub>6</sub>H<sub>5</sub>), 7.38 (d, J = 8.6 Hz, 4 H; -C<sub>6</sub>H<sub>4</sub>), 7.44 (d, J = 7.6 Hz, 4 H; -C<sub>6</sub>H<sub>5</sub>), 7.57–7.72 (m, 24 H; PPh<sub>2</sub> and -C<sub>6</sub>H<sub>4</sub>–), 8.69 (s, 2 H; –NH), 8.74 (s, 2 H; –NH). <sup>31</sup>P NMR (202 MHz,  $d_6$ -DMSO, relative to 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  42.1. FAB-MS: m/z 1312 [M]<sup>+</sup>, 1075 [M – L]<sup>+</sup>. Elemental analysis, anal. found (%): C, 53.35; H, 3.53; N, 4.17. Calcd for C<sub>60</sub>H<sub>46</sub>Au<sub>2</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 53.69; H, 3.50; N, 4.14.

 $[(PPh_2C_6H_4PPh_2)_3Au_3[Au_3Cu_2(C \equiv CB15C5)_6]][PF_6]_2$ (1). This was synthesized according to a modification of a reported procedure.<sup>18</sup> [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (10 mg, 0.027 mmol) in dichloromethane (3 ml) was added dropwise to a solution of S1 (58 mg, 0.18 mmol) in dichloromethane (8 ml) to afford a transparent red solution. The solution was removed under vacuum and product was recrystallized from dichloromethanediethyl ether to give 1 as a red crystal. Yield: 41 mg, 65%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si):  $\delta$ 3.26 (m, 12 H; -OCH<sub>2</sub>-), 3.66 (m, 12 H; -OCH<sub>2</sub>-), 3.73 (m, 48 H; -OCH<sub>2</sub>-), 3.87 (m, 12 H; -OCH<sub>2</sub>-), 4.02 (m, 12 H; -OCH<sub>2</sub>-), 6.19 (6 H; -C<sub>6</sub>H<sub>3</sub>-), 6.30 (m, 12 H; -C<sub>6</sub>H<sub>3</sub>-), 7.35  $(t, J = 7.7 \text{ Hz}, 24 \text{ H}; Ph_2PC_6H_4PPh_2), 7.50-7.58 (m, 24 \text{ H};$  $Ph_2PC_6H_4PPh_2$ ), 7.82 (m, 24 H;  $Ph_2PC_6H_4PPh_2$ ). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, relative to 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  44.3. FAB-MS: m/z 1620. Elemental analysis, anal. found (%): C, 46.87; H, 3.85. Calcd for  $C_{186}H_{186}Au_6O_{30}P_8Cu_2F_{12}$ ·CH<sub>2</sub>Cl<sub>2</sub>: C, 47.08; H, 3.97.

[(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>3</sub>Au<sub>3</sub> { Au<sub>3</sub>Cu<sub>2</sub> [ C=C<sub>6</sub>H<sub>4</sub>O ( CH<sub>2</sub>CH<sub>2</sub>O )<sub>2</sub>-CH<sub>3</sub>]<sub>6</sub>}][PF<sub>6</sub>]<sub>2</sub> (2). This was synthesized according to the procedure for 1, except S2 (52 mg, 0.18 mmol) was used instead of S1. Recrystallization from dichloromethane–diethyl ether gave 2 as a red plate crystal. Yield: 35%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si): δ 3.41 (s, 18 H; –OCH<sub>3</sub>), 3.61 (m, 12 H; –OCH<sub>2</sub>–), 3.73 (m, 12 H; –OCH<sub>2</sub>–), 3.86 (m, 12 H; – OCH<sub>2</sub>–), 4.04 (m, 12 H; –OCH<sub>2</sub>–), 6.34 (d, *J* = 8.7 Hz, 12 H; –C=CC<sub>6</sub>H<sub>4</sub>–), 6.53 (d, *J* = 8.7 Hz, 12 H; –C=CC<sub>6</sub>H<sub>4</sub>–), 7.33 (t, *J* = 7.7 Hz, 24 H; –Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>–), 7.55 (m, 24 H; – Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>–), 7.81 (m, 24 H; –Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>–). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, relative to 85% H<sub>3</sub>PO<sub>4</sub>): δ 44.1. FAB-MS: *m/z* 1982 [M – 2PF<sub>6</sub>]<sup>2+</sup>. Elemental analysis, anal. found (%): C, 46.97; 3.85. C<sub>168</sub>H<sub>162</sub>Au<sub>6</sub>Cu<sub>2</sub>F<sub>12</sub>O<sub>18</sub>P<sub>8</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 46.78; H, 3.81.

[(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>3</sub>Au<sub>3</sub>{Au<sub>3</sub>Cu<sub>2</sub>(C=CC<sub>6</sub>H<sub>4</sub>NHCONHC<sub>6</sub>H<sub>5</sub>)<sub>6</sub>]-[PF<sub>6</sub>]<sub>2</sub> (3). This was synthesized according to the procedure for 1, except S3 (53 mg, 0.18 mmol) was used instead of S1. Recrystallization from dichloromethane–diethyl ether gave 3 as a red crystal. Yield: 70%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>–CD<sub>3</sub>OD (2:1, v/v), 298 K, relative to Me<sub>4</sub>Si):  $\delta$  6.54 (d, *J* = 8.5 Hz, 2 H;), 6.87 (d, *J* = 8.5 Hz, 2 H;), 7.01 (t, *J* = Hz, 1 H;), 7.20–7.28 (m, 4 H;), 7.38 (t, *J* = 7.5 Hz, 4 H;), 7.57 (t, *J* = 7.6 Hz, 2 H;), 7.62 (m, 2 H;), 7.84 (m, 4 H;). FAB-MS: *m/z*. 2030 [M–2PF<sub>6</sub>]<sup>2+</sup>. Elemental analysis, anal. found (%): C, 49.42; H, 3.35; N, 3.89. Calcd for C<sub>180</sub>H<sub>138</sub>Au<sub>6</sub>Cu<sub>2</sub>N<sub>12</sub>O<sub>6</sub>P<sub>8</sub>F<sub>12</sub>·CH<sub>3</sub>OH·2H<sub>2</sub>O: C, 49.21; H, 3.33; N, 3.80.

# Physical measurements and instrumentation

The UV-vis spectra were recorded on a Hewlett–Packard 8452 A diode array spectrophotometer. <sup>1</sup>H NMR spectra with chemical shifts relative to tetramethylsilane (Me<sub>4</sub>Si) were recorded on a Bruker Avance 400 FT-NMR spectrometer. <sup>31</sup>P NMR spectra

were recorded on a Bruker Avance 400 FT-NMR spectrometer with chemical shifts reported relative to 85% H<sub>3</sub>PO<sub>4</sub>. Positive-ion fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analysis of the new complexes was performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry of the Chinese Academy of Sciences in Beijing.

Steady-state excitation and emission spectra were recorded on a Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. All solutions for photophysical studies were prepared under a high vacuum in a 10-cm<sup>3</sup> round-bottomed flask equipped with a sidearm 1-cm fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than four successive freeze-pump-thaw cycles. The excitation source used was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube, recorded on a Tektronix Model TDS-620 A (500 MHz, 2 GS s<sup>-1</sup>) digital oscilloscope, and analyzed by using a program for exponential fits.

#### **Binding constant determination**

The emission spectral titration for binding constant determination was performed on Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer. Binding constants for 1:1 complexation were obtained by a nonlinear least-squares fit<sup>25</sup> of the emission intensity (*I*) versus the concentration of ions added ( $C_A$ ) according to the following equation:

$$I = I_0 + \frac{I_{\rm lim} - I_0}{2C_0} [C_0 + C_{\rm M} + 1/K_{\rm s} - [(C_0 + C_{\rm M} + 1/K_{\rm s})^2 - 4C_0C_{\rm M}]^{1/2}]$$

where  $I_0$  and I are the emission intensity the complex at a selected wavelength in the absence and presence of the ions, respectively,  $[C_0]$  is the total concentration of the complex,  $[C_M]$  is the concentration of the ion,  $I_{\rm lim}$  is the limiting value of emission intensity in the presence of excess ion and  $K_s$  is the stability constant.

#### X-Ray crystallography

A single crystal of **3** was obtained by vapor diffusion of diethyl ether into a concentrated solution of **3** in dichloromethanemethane (3:1, v/v). The structure was solved by direct methods employing SHELXS-97 program on PC.<sup>26</sup> Au, Cu, P and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97<sup>26</sup> on PC. There was one formula unit in the asymmetric unit. Two PF<sub>6</sub> anions were located. Two halves of methanol and two water O atoms were located, in which the two water O atoms may form H-bonding to NH groups and the two halves of methanol located inside the "cages". All benzene rings were constrained to be regular hexagon rings with edges of 1.39 Å.

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