A supramolecular sensing system for Ag^I at nanomolar levels by the formation of a luminescent Ag^I–Tb^{III}–thiacalix[4]arene ternary complex†

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The first example of the detection of Ag^I ions using supramolecular chemistry is demonstrated, in which two thiacalix[4]arene ligands are linked by analyte Ag^I ions and then coordinate to Tb^{III} ions to form a luminescent ternary complex, $Ag^I_2 \cdot Tb^{III}_2 \cdot TCAS_2$, enabling the detection of Ag^I at concentrations as low as 3.2×10^{-9} M.

One of the most significant contributions of supramolecular chemistry has been the development of a precise strategy to design fluorescent chemosensors with high selectivities and sensitivities for heavy metal ions.[1] This strategy involves the covalent joining of a specific binding unit of a metal ion and a signal-transducing unit (Fig. 1).[2] The former is a ligating group that is carefully selected after considering factors that will affect its selectivity, such as the affinity of donor atoms to analyte cations and the stereochemistry of the resulting complex. The latter is a fluorophore, whose photophysical properties are susceptible to changes such as excimer formation/dissociation, photoinduced electron transfer, charge transfer and energy transfer caused by metal binding. The validity of this strategy, termed the covalent strategy, has been demonstrated by many of the fluorescent sensors that have been synthesized.[2] For instance, a ratiometric sensor, where pyrene is attached as a signaling unit to a ligand having N,O donors, has been designed to enable the detection of Ag^I ions at micromolar levels in a 50 : 50 v/v EtOH–water mixture.[3] The strategy seems to have been derived on the premise that two different processes occurs in analyte sensing—recognition and signaling. Although this strategy is useful, it does not provide much scope for alternative methods of designing sensors or sensing systems. In this Letter, we present a system for sensing Ag^I ions by the formation of a luminescent complex using supramolecular chemistry,[4] where the analytes and components are synergistically assembled to function as a sensor.

Since the development of a facile one-step method to synthesize thiacalix[4]arene, we have been interested in its inherent complexing properties and applications.[5] For example, thiacalix[4]arene-*p*-tetrasulfonate (TCAS, Fig. 2) reacts with a Tb^{III} ion to form a 1 : 1 complex, $Tb^{III} \cdot TCAS$ (**1**), in an aqueous solution at pH > 8.5 by the ligation of a bridging sulfur and two adjacent phenol oxygen donors. Complex **1** exhibits strong luminescence due to the presence of the Tb^{III} ion, whose excitation energy is transferred from TCAS in a triplet excited state.[6] The luminescence of **1** allows the detection of the Tb^{III} ion at nanomolar levels.[7] Furthermore, TCAS, Tb^{III} and Ag^I ions form a luminescent ternary complex, $Ag^I_2 \cdot Tb^{III}_2 \cdot TCAS_2$ (**2**), at a pH of around 6.[8] In this pH region, only a small fraction of the Tb^{III} ions are complexed by TCAS.[6,8] This suggests that Ag^I can be detected by measuring the luminescence of complex **2**, which is formed in the presence of Tb^{III} ions and TCAS at a pH of 6 (see the graphical abstract).

Accordingly, when $[Tb^{III}]_T = 1.0 \times 10^{-6}$ and $[TCAS]_T = 2.0 \times 10^{-6}$ M at a pH of 6.1 (T = total), the dependence of the luminescence intensity at 544 nm, assigned as the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{III}, on the Ag^I concentration was investigated (Fig. 3). For a wide range of Ag^I concentrations, the intensity increased almost linearly as $[Ag^I]_T$ increased from nanomolar to sub-micromolar levels. This demonstrates that Ag^I can be detected by the formation of ternary complex **2**. For higher $[Ag^I]_T$ levels ($> 2.0 \times 10^{-7}$ M), the dependence showed a slight upward convex curve. This can be attributed to the fact that $[Ag^I]_T$ attains a concentration level equivalent to that of Tb^{III} and the availability of Tb^{III} ions to form complex **2** is low. When $[Ag^I]_T \leq 2.0 \times 10^{-8}$ M, a linear calibration curve was obtained by least-square fitting, as shown in eqn (1).

$$\text{Luminescence intensity} = 76.5 \times 10^8 \times ([Ag^I]_T/\text{M}) + 437 \quad (1)$$

Surprisingly, the detection limit (DL) at $S/N = 3$ was determined to be 3.2×10^{-9} M (0.35 ppb). This shows that

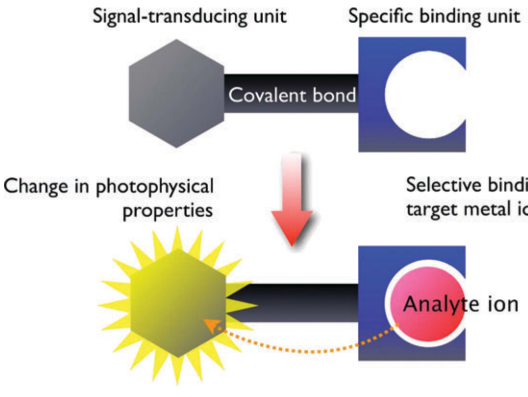

Fig. 1 Covalent strategy for designing metal sensors.

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† Electronic supplementary information (ESI) available: Experimental details for sample preparation and ESI-MS of complex 3.

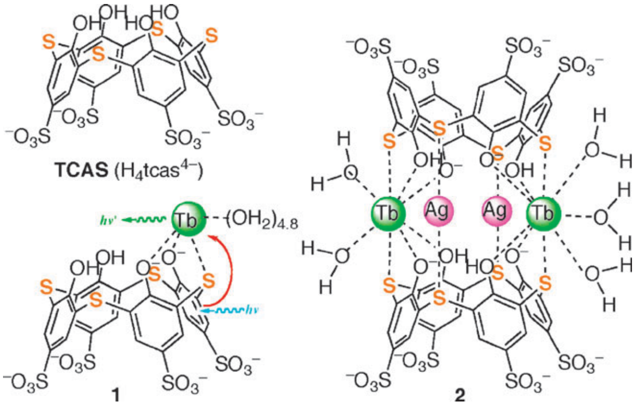

Fig. 2 The structure of TCAS, and complexes **1** and **2**.

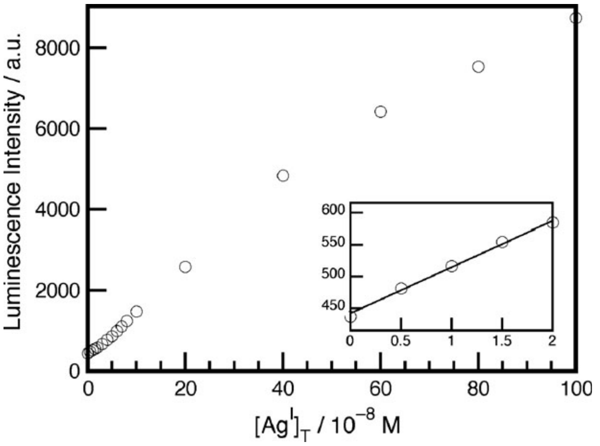

Fig. 3 Calibration graphs for Ag^I ions. The inset shows the calibration curve for the lowest Ag^I concentrations. Samples: $[Ag^I]_T$ = 0–100 × 10^{-8} M, $[Tb^{III}]_T$ = 1.0 × 10^{-6} M, $[TCAS]_T$ = 2.0 × 10^{-6} M and $[MES\ buffer]_T$ = 2 × 10^{-3} M (pH = 6.11). λ_{ex} = 323 and λ_{em} = 544 nm.

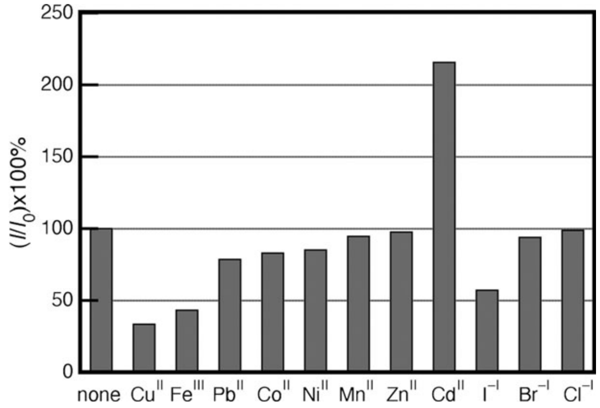

Fig. 4 The effect of a five-fold increase in concentration of "foreign ions" added to Ag^I on the luminescence signal. I and I_0 indicate the luminescence intensity for samples with and without foreign ions, respectively. Samples: $[foreign\ ion]_T$ = 0 or 5.0 × 10^{-7} M, $[Ag^I]_T$ = 1.0 × 10^{-7} M, $[Tb^{III}]_T$ = 1.0 × 10^{-6} M, $[TCAS]_T$ = 2.0 × 10^{-6} M and $[MES\ buffer]_T$ = 4 × 10^{-3} M (pH = 5.9). λ_{ex} = 323 and λ_{em} = 544 nm.

the system is more sensitive than covalently designed fluorescent sensors, which afford the detection of Ag^I at the 10^{-6} M level.[3,9] Notably, the DL of Ag^I with **2** is lower than that of flame atomic absorption spectrometry (DL 3 ppb) and as low as that of inductively-coupled plasma atomic emission spectroscopy (DL 0.2 ppb).[10]

The selectivity of this system with regard to Ag^I ions was investigated by adding five times the amount of transition metal cations (M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II}) and halide anions (X^- = Cl^-, Br^- and I^-) to a 1.0 × 10^{-7} M Ag^I ion solution. The luminescence intensity (at 544 nm), I, was measured and compared to the intensity measured in the absence of M or X^-, I_0. As shown in Fig. 4, the five-fold increase in Mn^{II} and Zn^{II} concentration did not affect the signal intensity of complex **2**; however, Pb^{II}, Co^{II} and Ni^{II} caused a slight change in its intensity. Notably, Cu^{II} and Fe^{III} ions caused negative interference (−67% and −57%, respectively). In the TCAS–metal binary systems, Cu^{II} and Fe^{III} ions formed complexes with M : TCAS ratios of 2 : 1 and 1 : 1, respectively, at a pH of 6. If these complexes had been formed in the present system, 1.75 × 10^{-7} and 1.5 × 10^{-7} M of TCAS would have been available to Ag^I (1.0 × 10^{-7} M) to form complex **2**. Therefore, it is likely that Cu^{II} and Fe^{III} ions formed ternary complexes with TCAS and Tb^{III} ions, thereby reducing the availability of Tb^{III} ions; this results in the formation of an insufficient amount of **2**. In addition, such an M–Tb^{III}–TCAS ternary complex would be non-luminescent because paramagnetic Cu^{II} and Fe^{III} ions readily quench the excited states of the TCAS ligand. In contrast, Cd^{II} caused a positive deviation (+116%) in the signal. Thus, it follows that Cd^{II} should have formed a luminescent Cd^{II}–Tb^{III}–TCAS ternary complex that is luminescent, since Cd^{II} is a non-quenching ion due to its d^{10} electronic configuration. In fact, the Cd^{II}–Tb^{III}–TCAS ternary system ($[Cd^{II}]_T$ = $[Tb^{III}]_T$ = 1.0 × 10^{-6} M, [TCAS] = 2.0 × 10^{-6} M; pH = 6.5) yielded a luminescent complex, whose composition was $Cd^{II}_2{\cdot}Tb^{III}_2{\cdot}TCAS_2$ (**3**), as suggested by electrospray ionization-mass spectroscopy (ESI-MS) measurements, yielding a peak at m/z = 1101.5983 that is assignable to $[2Cd^{2+} + 2Tb^{3+} + Na^+ + 3H^+ + 2TCAS^{8-} + H_2O]^{2-}$ (Fig. 5; also see ESI†). In the present system, complex **3**, which was formed concomitantly, caused an increase in the luminescence. Among the halide ions, iodide caused a negative (−43%) deviation from the original intensity, I_0, which can be attributed to its strong ability to form the halo complexes $[AgX_n]^{(n-1)-}$ (n = 1–4), as indicated by their stability constants.[11]

In metal–ion sensors designed using a covalent strategy, the roles of each functional group are different (Fig. 1). On the other hand, in the present Ag^I sensing system, it is ambiguous which moiety of **2** is responsible for the functions of binding and signaling. As shown in the schematic drawing of **2** (Fig. 2), TCAS has four O and four S donors that form the tetrametal core, $Ag^I_2Tb^{III}_2$. Furthermore, there is an antenna present to absorb photons, the energy from which is eventually transferred to the Tb^{III} center. Upon excitation, the Tb^{III} center emits light *via* an f–f transition. From a structural point of view, Tb^{III} ions accept two sets of O,S,O donations from the TCAS ligands. However, it is important to consider that in the Tb^{III}–TCAS binary system, Tb^{III} does not form a complex with TCAS at a pH of 6. Thus, analyte Ag^I is indispensable in

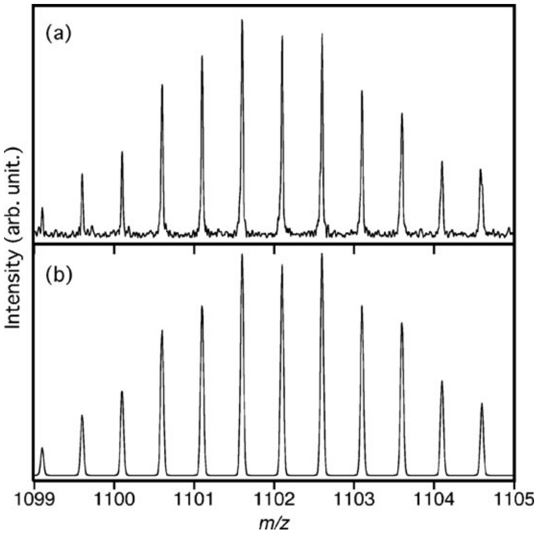

Fig. 5 Part of the ESI mass spectrum of complex **3**, showing the isotopomer pattern for $[2Cd^{2+} + 2Tb^{3+} + Na^{+} + 3H^{+} + 2TCAS^{8-} + H_2O]^{2-}$. (a) Observed pattern for a sample ($[TCAS]_T = [Cd^{II}]_T = [Tb^{III}]_T = 2.5 \times 10^{-5}$ M, $[HCl]_T = 5 \times 10^{-5}$ M; pH 5.82 (adjusted with NH_3)) and (b) simulated pattern.

linking two TCAS ligands *via* $S–Ag^{I}–S$ bridges to promote the coordination of TCAS to Tb^{III}, to form **2**. In fact, TCAS formed a 4 : 2 complex, $Ag^{I}_4{\cdot}TCAS_2$, in the binary system at pH 6.[8] In conclusion, multidentate and photon-absorbing TCAS, luminescent Tb^{III} and analyte Ag^{I}, with a linear coordination geometry, were synergistically assembled to form a supramolecular structure that is capable of sensing Ag^{I} ions at nanomolar concentrations (see graphical abstract). Since the sensing function of this system originates from the supramolecular nature of complex **2**, and not from TCAS and Tb^{III} individually, complex **2** truly demonstrates the "supramolecular strategy." Here, it is very important to rationally design molecules so that they form supramolecular assemblies that display functionalities absent from their individual components.

Experimental

Procedure for the detection of Ag^{I} ions

To a sample solution containing silver(I) nitrate and a particular foreign ion, if any, appropriate amounts of aqueous solutions of terbium(III) nitrate, TCAS, pH buffer (2-morphorinoethanesulfonic acid (MES)) and doubly-distilled water were added. Before the measurement of its luminescence spectrum, each sample solution was allowed to stand for 1 h at room temperature to ensure equilibration. The luminescence spectra were measured using a Hitachi F-4500 fluorescent spectrometer.

Mass spectrometry

ESI-MS experiments were performed using a Fourier transform ion cyclotron resonance mass spectrometer APEX III (Bruker). Mass spectra were simulated using the program iMass for Mac OS X version 1.1.[12]

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