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## COMMUNICATION

Highly sensitive and selective fluorescent chemosensor for Ag<sup>+</sup> based on a coumarin–Se<sub>2</sub>N chelating conjugate†Shanshan Huang,<sup>a</sup> Song He,<sup>a</sup> Yan Lu,<sup>\*a</sup> Fangfang Wei,<sup>a</sup> Xianshun Zeng<sup>\*a</sup> and Liancheng Zhao<sup>ab</sup>

Received 25th October 2010, Accepted 23rd November 2010

DOI: 10.1039/c0cc04589f

A highly sensitive and selective fluorescent chemosensor SC1 for Ag<sup>+</sup> based on a coumarin–Se<sub>2</sub>N chelating conjugate has been synthesized and characterized. Due to inhibiting a photoinduced electron transfer (PET) quenching pathway, a fluorescent enhancement factor of 4-fold is observed under the binding of the Ag<sup>+</sup> cation to the chemosensor SC1 with a detection limit down to the 10<sup>−8</sup> M range.

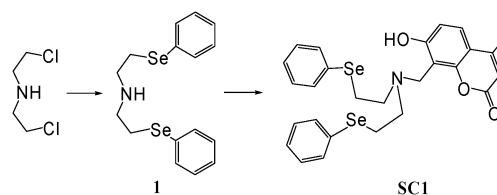
As heavy metal ions can cause severe risks for the environment and human health, highly selective cation sensing is imperative for many areas of technology, including environmental, biological, clinical, and waste management applications.<sup>1</sup> Silver ions are known to bind with various metabolites, including amine, imidazole, and carboxyl groups, and inactivate sulfhydryl enzymes.<sup>2</sup> There are also many reports on silver bioaccumulation and toxicity.<sup>3</sup> On the other hand, the widely used silver nanoparticles (AgNPs)<sup>4</sup> are also known to generate highly reactive oxygen species and may destroy the environmentally benign bacteria by inhibiting their growth and disturbing their reproductive ability.<sup>2</sup> Thus, development of sensitive and selective methods for the determination of trace amounts of silver ions (Ag<sup>+</sup>) in various media is of considerable importance for the environment and human health.

Traditional quantitative approaches,<sup>5</sup> such as atomic absorption spectroscopy and inductively coupled plasma-mass spectroscopy, have been reported for the trace-quantity determination of Ag<sup>+</sup>. Potentiometric methods for Ag<sup>+</sup> assay based on ion-selective electrodes (ISEs) are also reported with a detection limit down to the ppb range. But, most of these methods are expensive and time-consuming in practice. Therefore, in addition to the sophisticated methods, sensitive

and selective optical sensors for Ag<sup>+</sup> with simple instrumental implementation and easy-operation have received much attention.<sup>6–8</sup> But, Ag<sup>+</sup> belongs to the so-called “silent ions” since, unlike some biological metal ions (such as Cu<sup>2+</sup> or Fe<sup>2+</sup>), it does not have an intrinsic spectroscopic or magnetic signal because of its d<sup>10</sup> electronic configuration which is known as fluorescence quencher, discrimination between Ag<sup>+</sup> and chemically close ions presents a challenge. The fluorometric detection of such ions is based on the use of small-molecule fluorescent chemosensors that consist of an ionophore–chromophore system. These chemosensors may coordinate selectively to the target ion and respond to changes in ion levels with changes in their fluorescence profile that may be translated to accurate measurements of the ion concentrations. Most of the reported fluorescent chemosensors for Ag<sup>+</sup> are based on a fluorescence quenching mechanism.<sup>7</sup> Only a few fluorescence “turn on” chemosensors for Ag<sup>+</sup> have been described and developed by now.<sup>8</sup>

Herein, we report a new Ag<sup>+</sup>-ion-specific fluorescent chemosensor Silver Coumarin **1** (SC1), which takes advantage of both the high selenophilicity of Ag<sup>+</sup> and high photostability of coumarin fluorophore. The choice of the Se<sub>2</sub>N ionophore was based on our previous reports using similar pendant or crown ether systems for the coordination of heavy metals.<sup>9</sup> The chemosensor SC1 has excellent selectivity for Ag<sup>+</sup> ions over relevant competing metal ions with a fluorescent enhancement factor of 4-fold by inhibiting a photoinduced electron transfer (PET) quenching pathway, thus resulting in the enhancement of fluorescence,<sup>1c</sup> and with the detection limit reaching the 10<sup>−8</sup> M range in ethanol/water.

The synthesis of SC1, Scheme 1, began with SeN<sub>2</sub> receptor **1**, formed by the reaction of bis(2-chloroethyl)amine with the sodium salts of phenylselenenol, which was prepared *in situ* by the reaction of 1,2-diphenyldiselenide with NaBH<sub>4</sub> in the



Scheme 1 Synthesis of chemosensor SC1.

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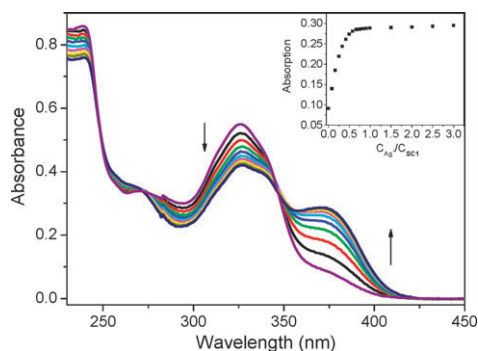
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† Electronic supplementary information (ESI) available: Experimental details; synthesis of **1** and SC1; the emission spectra of SC1 with Ag<sup>+</sup> salts with different counteranions (ClO<sub>4</sub><sup>−</sup>, NO<sub>2</sub><sup>−</sup>, PF<sub>6</sub><sup>−</sup>, AcO<sup>−</sup> and BF<sub>4</sub><sup>−</sup>); Job's plot; <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** and SC1 or other electronic format. See DOI: 10.1039/c0cc04589f

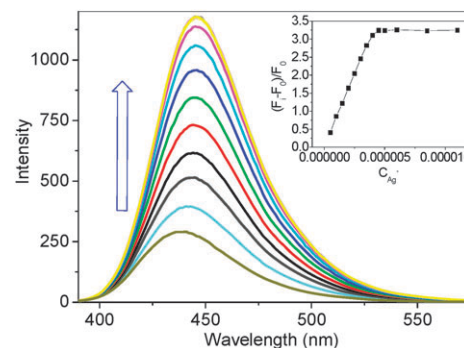
presence of NaOH. **SC1** was prepared successfully *via* a Mannich reaction by the condensation of **1** and Coumarin 4 with formaldehyde in THF/HOAc at 50 °C. All the reactions were achieved in reasonable yields and characterized by MS,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, and elemental analysis.

The spectroscopic properties of the chemosensor **SC1** were evaluated in an ethanol/water (1 : 1, v/v) solution. As shown in Fig. 1, the chemosensor **SC1** exhibits a maximal absorption at 320 nm ( $\epsilon = 1.035 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). Upon addition of silver ions (0–3 equiv.), the absorbance at 320 nm decreases gradually, and simultaneously, a significant absorption band like a shoulder at 375 nm increases. The presence of three clear isobestic points at 250, 271, 348 nm implies the conversion of the free chemosensor **SC1** to the only  $\text{Ag}^+$  complex. Moreover, the absorbance at 375 nm remains constant in the presence of more than 1 equiv. of silver ions, indicating the formation of a 1 : 1 complex between the chemosensor **SC1** and silver ion, which is in good agreement with 1 : 1 stoichiometry for the silver complex determined by Job's plot yielded from UV-vis absorption (Fig. S1, ESI†).

Fig. 2 shows the fluorescence spectrum of compound **SC1** and those in the presence of different amounts of  $\text{Ag}^+$  in  $\text{H}_2\text{O}/\text{ethanol}$  (1 : 1, v/v). As displayed in Fig. 2, the titration of  $\text{Ag}^+$  into **SC1** gave a new emission band centered at 445 nm which showed a linear enhancement with the increase of  $[\text{Ag}^+]_{\text{total}}$  when the ratio of  $[\text{Ag}^+]_{\text{total}}/[\text{SC1}]$  is below or equal to 1 : 1. When the ratio reached 1 : 1, however, higher  $[\text{Ag}^+]_{\text{total}}$  did not lead to any further emission enhancement as shown in the inset of Fig. 2. The enhancement of emission intensity in  $\text{Ag}^+$ -binding titrations saturated at the addition of one equivalent of  $\text{AgNO}_3$  suggested that **SC1** forms a 1 : 1 complex with  $\text{Ag}^+$  in  $\text{H}_2\text{O}/\text{ethanol}$  (1 : 1, v/v), which is in agreement with the UV-vis titration results. The association constant is calculated as  $1.61 \times 10^8 \text{ M}^{-1}$  ( $R = 0.999$ ) by using nonlinear least-square analysis (Fig. S2, ESI†). From the changes in  $\text{Ag}^+$ -dependent fluorescence intensity (Fig. S3, ESI†), the detection limit was estimated to be  $5.2 \times 10^{-8} \text{ M}$ .<sup>10</sup> Similar fluorescence enhancement was observed for **SC1** after the addition of  $\text{Ag}^+$  salts with different counteranions ( $\text{ClO}_4^-$ ,  $\text{NO}_2^-$ ,  $\text{PF}_6^-$ ,  $\text{AcO}^-$  and  $\text{BF}_4^-$ ) (Fig. S4, ESI†). Reversible binding of **SC1** with  $\text{Ag}^+$  was also carried out. Addition of  $\text{Na}_2\text{S}$  to a mixture of **SC1**– $\text{Ag}^+$  results in diminishing of the fluorescence intensity at 445 nm, which



**Fig. 1** UV-vis spectra of chemosensor **SC1** (10.6  $\mu\text{M}$ ) upon titration of  $\text{Ag}^+$  (0–3 equiv.) in ethanol/water (1 : 1, v/v),  $[\text{Ag}^+]/[\text{SC1}] = 0, 0.08, 0.16, 0.25, 0.32, 0.42, 0.5, 0.58, 0.66, 0.75, 0.83, 0.92, 1, 1.5, 2, 2.5, 3$ . Inset: absorbance of **SC1** at 375 nm as a function of  $C_{\text{Ag}^+}/C_{\text{SC1}}$ .

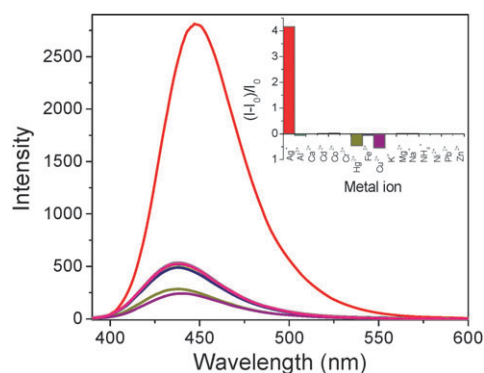


**Fig. 2** Fluorescent titration spectra of **SC1** (4  $\mu\text{M}$ ) in the presence of different concentrations of  $\text{Ag}^+$  in ethanol/water (1 : 1, v/v),  $[\text{Ag}^+]/[\text{SC1}] = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.7, 2.2$ . Inset: the fluorescence at 445 nm of **SC1** (4  $\mu\text{M}$ ) as a function of the  $\text{Ag}^+$  concentration.  $\lambda_{\text{ex}} = 360 \text{ nm}$ .

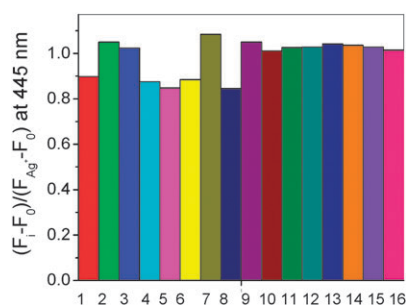
signifies the regeneration of the free **SC1**. The fluorescence can be recovered by adding  $\text{Ag}^+$  again (Fig. S5, ESI†).

Subsequently, we evaluated the response of the chemosensor **SC1** to other metal ions. As shown in Fig. 3, the addition of 2 equiv. of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  has no obvious effect on the fluorescence emission, whereas  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$  responded with a significant decrease in the fluorescent intensity. In contrast, the addition of  $\text{Ag}^+$  resulted in an enhancement of the emission intensity (with an enhancement factor of 4-fold) positioned around 445 nm as shown in Fig. 3. On the other hand, upon the addition of 50 equiv. of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  to the chemosensor **SC1** solution, only  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  produced a much weaker fluorescence enhancement compared to  $\text{Ag}^+$ .  $\text{Pb}^{2+}$  and most of transition metal ions responded with a significant decrease in the fluorescent intensity (Fig. S6, ESI†); thus, **SC1** can function as an highly selective fluorescence chemosensor for the  $\text{Ag}^+$  cation.

To explore further the utility of **SC1** as an ion-selective fluorescent chemosensor for  $\text{Ag}^+$ , the competition experiments are conducted in which **SC1** (5.0  $\mu\text{M}$ ) is first mixed with five



**Fig. 3** Fluorescence spectra of **SC1** (5.0  $\mu\text{M}$ ) upon the addition of the nitrate salts (2.0 equiv.) of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ag}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  in ethanol/ $\text{H}_2\text{O}$  (1 : 1, v/v). Inset: histogram representing the fluorescence enhancement and quenching of **SC1** in the presence of metal ions. For the entire test, excitation and emission were performed at 360 and 445 nm.



**Fig. 4** Change ratio  $((F_i - F_0)/(F_{Ag^+} - F_0))$  of fluorescence intensity of SC1 upon the addition of 1 equiv.  $Ag^+$  in the presence of 5 equiv. background metal ions. 1:  $Ag^+ + Al^{3+}$ ; 2:  $Ag^+ + Ca^{2+}$ ; 3:  $Ag^+ + Cd^{2+}$ ; 4:  $Ag^+ + Co^{2+}$ ; 5:  $Ag^+ + Cr^{3+}$ ; 6:  $Ag^+ + Cu^{2+}$ ; 7:  $Ag^+ + Fe^{3+}$ ; 8:  $Ag^+ + Hg^{2+}$ ; 9:  $Ag^+ + K^+$ ; 10:  $Ag^+ + Mg^{2+}$ ; 11:  $Ag^+ + Na^+$ ; 12:  $Ag^+ + NH_4^+$ ; 13:  $Ag^+ + Ni^{2+}$ ; 14:  $Ag^+ + Pb^{2+}$ ; 15:  $Ag^+ + Zn^{2+}$ ; 16:  $Ag^+$  in EtOH/H<sub>2</sub>O (1 : 1, v/v) solution.

equivalent of various metal ions, and then one equivalent of  $Ag^+$  is added. The fluorescence spectra are exploited to monitor the competition events. As can be seen from Fig. 4, no strong interference was observed in the presence of 5 equiv. of a series of metal ions. In the presence of  $Ca^{2+}$ ,  $Cd^{2+}$ ,  $Fe^{3+}$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $NH_4^+$ ,  $Ni^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ , the emission spectra are almost identical to that obtained in the presence of  $Ag^+$  alone. In the case of  $Al^{3+}$ ,  $Co^{2+}$ ,  $Cr^{3+}$ ,  $Cu^{2+}$  and  $Hg^{2+}$ , the emission intensities are about 10% diminished to that obtained in the presence of  $Ag^+$  alone. The results demonstrated that the chemosensor SC1 is able to discriminate between  $Ag^+$  and chemically close ions, especially  $Cu^{2+}$  and  $Hg^{2+}$  which are common interfering anions in many cases<sup>7f-i,8a-c</sup> are eliminated.

In summary, we have prepared a fluorescence chemosensor SC1 for silver ions in ethanol/water, which demonstrates a unique ability to discriminate between  $Ag^+$  and chemically close ions and with a detection limit down to the  $10^{-8}$  M range. The highly selective and sensitive  $Ag^+$ -chemosensor SC1 may have wide applications for quantitative measurement of silver ions.

This work was sponsored by the NCET-09-0894, NNSFC (20972111, 21074093, 21004044), the NSFT (08JCYBJC-26700), SRF for ROCS, SEM and the State Key Lab. Elemental-Organic Chemistry at Nankai University (NO. 0802, 0908).

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