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A ratiometric luminescent sensing of Ag⁺ ion *via in situ* formation of coordination polymers†

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A ratiometric luminescent sensing of Ag⁺ ion is developed via the Ag(I)–NCys coordination polymeric luminophore *in situ* formed in aqueous solution upon mixing Ag⁺ ion with the designed fluorescent thiol ligand NCys.

Silver has been extensively employed in the photographic and imaging industry and pharmacy during the past decades. Approximately 2500 tonnes of silver are released into the environment every year, a portion of which enters surface water and results in high toxicity to aquatic organisms. For example, the Ag⁺ ion is considered to be one of the most toxic metals for rainbow trout, the most studied freshwater fish species.¹ Sensitive and selective chemosensing of Ag⁺ ion is thus highly demanded. Actually there are only a few sensing systems that have been reported for Ag⁺ ion. Available Ag⁺ ion chemosensors are in general represented in three kinds, (i) Ag⁺ coordination to the sensor molecule containing S and/or N coordination centre(s),² (ii) the C–Ag⁺–C or A–Ag⁺–A interaction,³ in which C and A represent cytosine and adenine, respectively, and (iii) Ag⁺ involved chemical reactions.⁴

Herein reported is a ratiometric luminescent sensing ensemble for Ag⁺ ion based on the Ag(I)–SR coordination polymers as the luminophore that are *in situ* formed in aqueous buffer solution upon mixing Ag⁺ ion with ligand RSH, in which Ag(I)···Ag(I) interaction may play a role. Argentophilic Ag(I)···Ag(I) interaction as a kind of metallophilic interaction of closed-shell d¹⁰ metal ions⁵ is much less investigated than that with the aurophilic Au(I)···Au(I) interaction, probably because it is much weaker in strength than the latter. Although switching on/off or modulating metallophilic interaction (M(I) = Ag(I)⁶ and Au(I)^{2f,7}) has been nicely applied for photoluminescent (PL) sensing of neutral species and metal ions, employing the metallophilic interactions for sensing of these M(I) cations themselves has not been explored. In the present sensing protocol, polymerization is involved with the

sensing species Ag⁺ during the formation of Ag(I)–SR coordination polymeric luminophore, a signal amplification is therefore expected.^{6c,8,9}

We previously showed that when Ag⁺ ion was mixed with cysteine (Cys) and glutathione (GSH) (Scheme 1) in aqueous solutions, Ag(I)–Cys and Ag(I)–GSH coordination polymers formed immediately, which is facilitated by the Ag(I)···Ag(I) interaction and the electrostatic interaction among the side-chains along the polymeric backbone.^{6c,9} In these two cases the coordination polymers are however weakly luminescent or nonluminescent. We therefore envisaged replacing the electrostatic interactions among the side-chains by π – π stacking by including an aromatic fluorophore in the RSH ligand so that the formed coordination polymers might also be luminescent. It was for this reason we designed NCys (Scheme 1),¹⁰ in which the amine group in Cys moiety was derived into 2-(1-naphthyl)-acetamide so that the aromatic fluorophore may afford the π – π stacking when the Ag(I)–NCys coordination polymers are formed in aqueous solution and make the polymers luminescent. Naphthalene moiety is our first choice as the aromatic component also because it may serve as an antenna to harvest excitation light to enhance the emission related to the Ag(I)···Ag(I) interaction in the coordination polymers (Scheme 2), since the emission of 1-methylnaphthalene at *ca.* 340 nm is close to the absorption maximum of the Ag(I)–Cys and Ag(I)–GSH polymers at *ca.* 350 nm,^{6c,9} so that a dual luminescent signaling could be created for Ag⁺ ion. Indeed, a ratiometric luminescent sensing selective to and sensitive for Ag⁺ ion was achieved in buffered EtOH–H₂O solution, which we show here to result from the Ag(I)–NCys coordination polymers *in situ* formed upon mixing Ag⁺ ion with NCys.

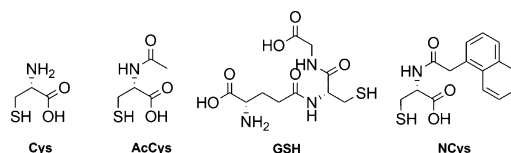
Absorption and emission of NCys itself originate from its naphthyl moiety (Fig. 1a and 2a). No circular dichroism (CD) signal is observed from NCys beyond 240 nm (Fig. 1b), indicating that the chirality of Cys moiety in NCys is not transferred to the naphthyl moiety. When it is mixed with Ag⁺ ion in aqueous buffer solution, stable spectral signals are

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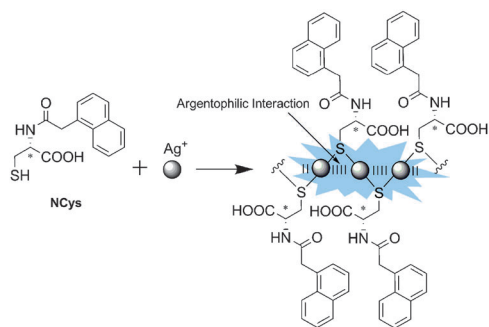
E-mail: ybjiang@xmu.edu.cn; Fax: +86 592 218 6401; Tel: +86 592 218 8372

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† Electronic supplementary information (ESI) available: Synthesis and characterization of NCys. Fig. S1–11, Table S1 and ¹H and ¹³C NMR spectra of NCys. See DOI: 10.1039/c0cc05519k



Scheme 1 Structure of cysteine and its derivatives.



Scheme 2 Formation of Ag(I)-NCys coordination polymer.

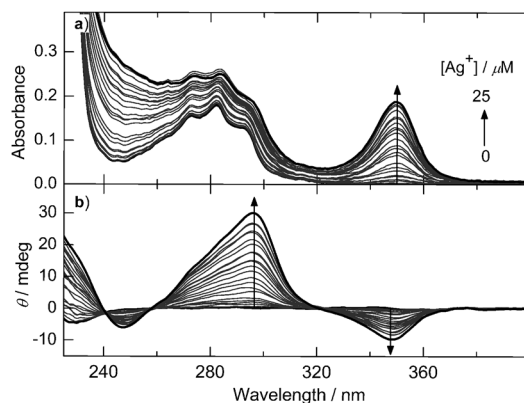


Fig. 1 (a) Absorption and (b) CD spectra of NCys (25 μM) in EtOH-H₂O (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0 in the presence of Ag⁺ of 0 to 25 μM .

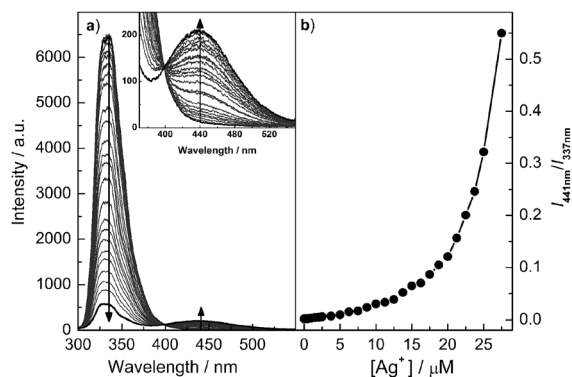


Fig. 2 (a) PL spectra of NCys (25 μM) in EtOH-H₂O (1:1, v/v) containing 5 mM NaAc-HAc of pH 5.0 in the presence of Ag⁺ of 0 to 25 μM and (b) plot of the dual emission intensity ratio against [Ag⁺]. λ_{ex} was 283 nm. Inset in (a) is an expansion of the portion of spectra around 441 nm.

observed in 20 min (Fig. S1, ESI[†]). A new absorption band at 350 nm is observed (Fig. 1), which is tentatively assigned to the ligand-to-metal charge transfer transition modified by the argentophilic interaction (LMMCT, S \rightarrow Ag(I)), by analogy to the reported assignment.^{6c,9,11} This observation is similar to the case of Ag(I)-Cys,⁹ implying the formation of Ag(I)-NCys coordination polymers. Hill plot suggests that the interaction of Ag⁺ with NCys is cooperative by a Hill coefficient of 1.37 (Fig. S2[†]),⁸ which means that a signal amplification for Ag⁺ sensing can be expected.^{6c,8,9} The absorbance of the

Ag(I)-NCys solution decreases sharply with increasing pH when -COOH in NCys undergoes deprotonation at higher pH, whereas it remains unchanged when pH is lowered (Fig. S3[†]). This could be understood in terms of the electrostatic repulsion among the -COO⁻ groups in the backbone of the Ag(I)-NCys polymers at high pH that enlarges the Ag-S-Ag angle. This observation could serve as a support of the occurrence of the argentophilic interaction since weakened or even diminished argentophilic interaction can be expected when the Ag-S-Ag angle in the Ag(I)-NCys polymers is enlarged.⁹ It was therefore proposed that the observed spectral response related to the argentophilic interaction.

Formation of the Ag(I)-NCys coordination polymers was supported by the dynamic light scattering (DLS) data that indicated a polydisperse size distribution of the polymers with a mean dynamic diameter at 10² nm order of magnitude (Fig. S4[†]). Scanning electron microscopy (SEM) images show continuous nanowire structures with a width of *ca.* 100 nm (Fig. S5[†]). Splitting CD signals observed from the Ag(I)-NCys polymers similarly probe a helical polymeric structure,^{9,12} as that concluded for the Ag(I)-Cys and Ag(I)-GSH polymers.^{6c,9} This is also supported by the structured CD signals around 280 nm originating from the naphthyl moiety when NCys was mixed with Ag⁺ ion (Fig. 1b). Since the chiral centre in NCys is by 3 atoms or 4 bonds away from the naphthyl moiety (Scheme 1) and NCys itself in aqueous buffer solution is CD silent beyond 240 nm (Fig. 1b), only the formation of the helical polymers could explain the observed CD signals from the naphthyl moiety.¹³ Actually, the chiroptical activity at 295 nm is amplified by 4-fold compared to that of the Ag(I)-Cys polymer.⁹ Spectral titrations and Job plot all indicate that Ag⁺ interacts with NCys in a 1:1 stoichiometry (Fig. S6 and S8[†]).

Previously we showed that the Ag(I)···Ag(I) interaction in Ag(I)-Cys and Ag(I)-GSH coordination polymers in aqueous solution is facilitated by the electrostatic interactions among the Cys or GSH side-chains in the polymeric backbones.^{6c,9} This is also confirmed by the fact that practically no spectral signal, absorption, CD or luminescence (Fig. S9[†]), was observed when Ag⁺ was mixed with AcCys (Scheme 1), the acetamide of Cys, that provides no such electrostatic interactions. Therefore, the observed spectral signals in the Ag(I)-NCys solution confirm that the π - π stacking among the naphthyl moieties along the polymeric backbone promotes the formation of the Ag(I)-NCys coordination polymers.

Excited at 283 nm the strong emission of NCys in the aqueous buffer solution from its naphthyl moiety at 337 nm is substantially quenched by Ag⁺ ion, while a new emission develops at 441 nm together with an isoemissive point at 399 nm (Fig. 2a). This means that in the Ag(I)-NCys solution there are two excited-states in equilibrium, an indication of the energy transfer from the naphthyl donor to an emissive state for the 441 nm emission, likely the LMMCT state.^{5a,6a,c,9,12,14} Although the naphthalene excimer or its exciplex with Ag⁺ may also lead to a red-shifted emission, the 441 nm emission originates likely from the LMMCT excited state. This was supported by the fact that the 441 nm emission can also be observed under excitation at 350 nm at which the naphthyl moiety in NCys does not absorb, while the Ag(I)···Ag(I) interaction related LMMCT state absorbs (Fig. 1).

Since the π - π interactions of the naphthalene moieties in Ag(I)-NCys coordination polymers are complementarily induced or enhanced by the Ag(I)··Ag(I) interactions or *vice versa*, the possibility of the excimer or exciplex origin of the 441 nm emission could not be completely ruled out, further experiments are therefore needed to clarify its origin. It is noteworthy that the 441 nm luminophore is polymeric since it exists only when the Ag(I)-NCys coordination polymers form *in situ* in the solution. An immediate support to this conclusion is the high value of polarization (0.40) of the 441 nm emission. Since the Ag(I)-NCys polymers can be viewed as being covered by a layer of naphthyl groups (Scheme 2), antenna effect of the naphthyl energy donors¹⁵ was expected to enhance the LMMCT emission from the polymeric luminophore. This is supported by the fact that, whereas the Ag(I)-Cys polymer is nonemissive and the Ag(I)-GSH polymer weakly emissive,^{6c,9} the Ag(I)-NCys polymer is relatively highly emissive with a quantum yield of *ca.* 0.004 for the 441-nm emission (Fig. 2).

The dual emission observed upon mixing Ag⁺ ion with NCys therefore allows for a ratiometric luminescent sensing of Ag⁺ in buffered aqueous solution, with a sub- μ M sensitivity (Fig. 2b). Other metal ions such as Al³⁺, Ba²⁺, Ca²⁺, Cd²⁺, Cr³⁺, Cu²⁺, Fe²⁺, Fe³⁺, Hg²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Pb²⁺ and Zn²⁺, do not show significant spectral response (Fig. S10†). Only slightly increased absorbance was observed in the cases of Fe²⁺, Fe³⁺ and Pb²⁺. Competition experiments showed that in the presence of 1 mM EDTA, the tested foreign cations did not exert interference except Hg²⁺ (Fig. S11†). The observed excellent sensitivity and selectivity of NCys in its spectral responses toward Ag⁺ ion are assumed to result from the polymeric sensory ensemble that would afford signal amplification,^{6c,8,9} which is supported by the Hill coefficient of *ca.* 1.4 (Fig. S2 and Table S1†).

With a rationally designed simple thiol ligand NCys we succeeded in establishing a ratiometric luminescent sensing ensemble for Ag⁺ ion in aqueous solutions. We show that this is realized *via*, probably the Ag(I)··Ag(I) interaction facilitated, *in situ* formed Ag(I)-NCys polymeric luminophore that is surrounded by a "layer" of naphthyl fluorophores as the energy donors. Inserting a naphthyl fluorophore in the RSH ligand appears to be critical for creating both the π - π stacking interaction in the Ag(I)-NCys coordination polymers and an energy transfer pathway for the observation of the dual emission. It turns to be promising to extend the current strategy by modifying the aromatic fluorophore and/or its linkage to the -SH binding site in the RSH ligand.

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