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Nanosphere $[Ag(SR)]_n$: coordination polymers of Ag^+ with a combination of hydrophilic and hydrophobic thiols†

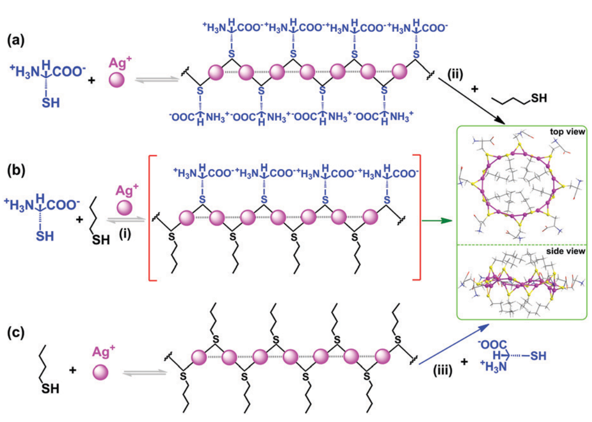
Yan Xu, Su-Li Dong, Xiao-Sheng Yan, Qian Wang, Zhao Li and Yun-Bao Jiang*

We propose to create nanospheres in aqueous solutions from coordination polymers of Ag^+ with a combination of a hydrophilic and a hydrophobic thiol, of diameter *ca.* 2.7 nm in the case of using cysteine and *n*-butanethiol. A spectral probe for the formation of the nanospheres is a reversal of the CD signal at 253 nm from negative in the case of cysteine alone to positive when cysteine and *n*-BuSH are both employed, together with an amplification.

The synthesis of macrocyclic compounds remains a challenge, despite many successful examples and sophisticated strategies.[1] We developed a variety of coordination polymers of Ag^+ with thiol ligands, in particular the cysteine derivatives (Scheme 1a) for spectral sensing[2–4] and characterizing supramolecular chirality.[5] Those coordination polymers are maintained by both the argentophilic interaction (the $Ag^+\cdots Ag^+$ interaction) along the polymeric backbone and the interactions between side-chains of ligands binding to Ag^+ ions in the backbone. The coordination polymers can be viewed as a kind of Ag^+-chain. It would be of significance to explore the cyclic version of those coordination polymers, in the context of the synthetic methodology towards macrocyclic species and the $Ag^+\cdots Ag^+$ interaction in a bent system. Compared with the chain-like counterparts, cyclic polymers or oligomers may exhibit unique properties, such as a reduced hydrodynamic volume and catalytic activity,[6] and interesting supramolecular chirality when using a chiral thiol ligand. A few cases of synthetic cyclic clusters and complexes based on $Ag^+\cdots Ag^+$ interaction have actually been reported,[7–10] despite the synthetic challenge.

We propose a strategy of building a cyclic oligomeric version of those chain-like $[Ag–SR]_n$ coordination polymers, by using a combination of a hydrophilic (HSR_L) and a hydrophobic (HSR_B) thiol ligand, where in the formed coordination polymers the hydrophilic and hydrophobic thiol ligands would locate respectively on the two sides of the polymeric backbone, being respectively repulsive and attractive and thereby pushing the chain-like coordination polymer into a cyclic structure, in which the "$\cdots(R_LS)Ag(SR_B)\cdots$" unit functions as a surfactant, while the $Ag^+\cdots Ag^+$ interactions link those "surfactants" within a cyclic structure (Scheme 1). Following the established surfactant chemistry,[11] for a given hydrophilic thiol ligand, the hydrophobic thiol $n\text{-}C_nH_{2n+1}SH$ shall bear an optimal chain length so that a good hydrophilic–hydrophobic balance could be maintained. We screened the combinations of chiral hydrophilic cysteine (Cys) and a series of hydrophobic $n\text{-}C_nH_{2n+1}SH$ (n = 2, 3, 4, 5, 6, 8, 10, 16) in aqueous solutions in the presence of Ag^+ and found that the *n*-butylmercaptan (BuSH)/cysteine pair is optimal to form the nanosphere structures of diameters around 2.7 nm, from the Ag^+–(Cys + BuSH) coordination polymers (Scheme 1).

Fig. 1 shows CD spectra measured immediately upon mixing an aqueous solution of L-cysteine (L-Cys) and $n\text{-}C_nH_{2n+1}SH$ with Ag^+ of increasing concentration. A notable observation is the reversal of the CD signal at 253 nm in the case of cysteine and $n\text{-}C_nH_{2n+1}SH$ (n = 2, 3, 4, 5, 6, 8, 10), compared to that of cysteine only and the case of cysteine together with HexaSH. Detailed time profiles of the CD spectra show similar reversal of CD signals at



Scheme 1 Thiol ligand exchange to (a and c) and direct formation of (b) the Ag^+–(Cys + BuSH) coordination polymers.

Department of Chemistry, College of Chemistry and Chemical Engineering, the MOE Key Laboratory of Spectrochemical Analysis and Instrumentation and iChEM, Xiamen University, Xiamen 361005, China. E-mail: ybjiang@xmu.edu.cn; Fax: +86 592 218 6401; Tel: +86 592 218 8372

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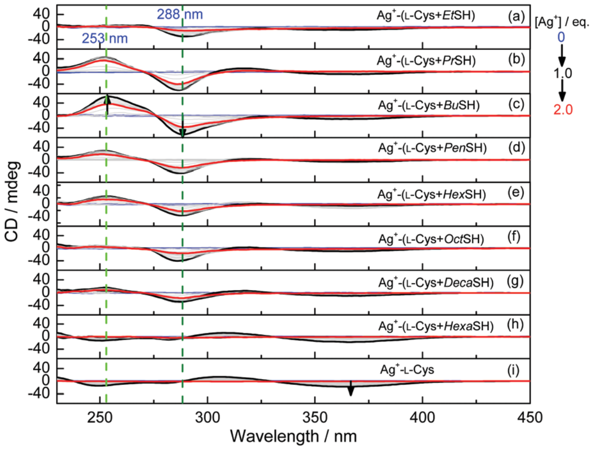

Fig. 1 Traces of CD spectra of Ag^+–(L-Cys + n-$C_nH_{2n+1}SH$) (a–h) and Ag^+–L-Cys (i) measured immediately after mixing with Ag^+ of increasing concentration in 10 mM pH 5.0 HAc-NaAc buffer solution. [n-$C_nH_{2n+1}SH$] = [L-Cys] = 50 μM, [Ag^+] = 0–2.0 equiv.

253 nm of cysteine and n-$C_nH_{2n+1}SH$ (n = 2, 3, 4, 5, 6, 8, 10), yet that of the combination of cysteine and BuSH gives the strongest signals (Fig. S1 and S2, ESI†). This confirms that an optimal hydrophilic and hydrophobic balance is maintained in the case of cysteine and BuSH in the presence of Ag^+, a fact that supports the assumption that the "$\cdots(R_LS)Ag(SR_B)\cdots$" unit acts as a supramolecular surfactant. The remaining investigations, therefore, focus on the characterization of the structures from the combination of cysteine and BuSH in the presence of Ag^+.

By varying the molar ratio of L-cysteine to BuSH, we find that this ratio has to be over 1 : 1 to guarantee the formation of the coordination polymers with the mixed ligands (Fig. S3, ESI†). Another piece of evidence is that in the Ag^+–(Cys + BuSH) system strong CD signals are observed only at pH below 7.0 (Fig. S4, ESI†) and the CD signals can be switched on and off multiple times by changing the solution pH (Fig. S5 and S6, ESI†), that the polar head group from the cysteine residue has to be made into a certain charged state to allow the hydrophilic–hydrophobic balance. The function of an optimal polar head group is further approved by testing several derivatives of cysteine in combination with BuSH, while they do not work as cysteine does (Fig. S7–S10, ESI†).

Data presented in Fig. 2 shows the formation of *pseudo* zero-dimensional nanosphere structures in the aqueous solution of Ag^+ with cysteine and BuSH. In the presence of Ag^+, absorptions develop at 280 nm and 360 nm in the Ag^+–Cys system (Fig. 2a), ascribed to the $Ag^+\cdots Ag^+$ interactions.[2,12,13] In Ag^+-BuSH solution there occurs new absorption between 250–320 nm suggesting the onset of $Ag^+\cdots Ag^+$ interaction too. In the absorption spectrum of Ag^+–(Cys + BuSH) new absorption bands are observed at 253 nm and 288 nm, assigned to the $Ag^+\cdots Ag^+$ interaction reported in the localized system in which two Ag^+ ions are bound by a bidentate ligand,[14] suggesting that coordination polymers of Ag^+ form with both thiol ligands.

L- and D-cysteine solutions show very weak CD signals below 250 nm (Fig. 2b). In the Ag^+-L-Cys and Ag^+-D-Cys solutions perfect mirror-imaged CD spectra are observed, suggesting that the supramolecular chirality originates from the cysteine residue. The Ag^+-BuSH solution is CD silent. In Ag^+–(L-Cys + BuSH) solution of the same concentration of cysteine, substantially enhanced splitting CD signals are observed at short wavelengths at which the argentophilic interaction related LMMCT transition absorbs (Fig. 2a), confirming that the coordination polymers are formed with mixed thiol ligands. The counter anion of Ag^+ appears to exert not much effect since Ag^+ with other counter anions such as $CF_3O_3S^-$, SbF_6^-, or BF_4^- led to similar spectral profiles (Fig. S11, ESI†) to those from $AgNO_3$, the Ag^+ source used in this work.

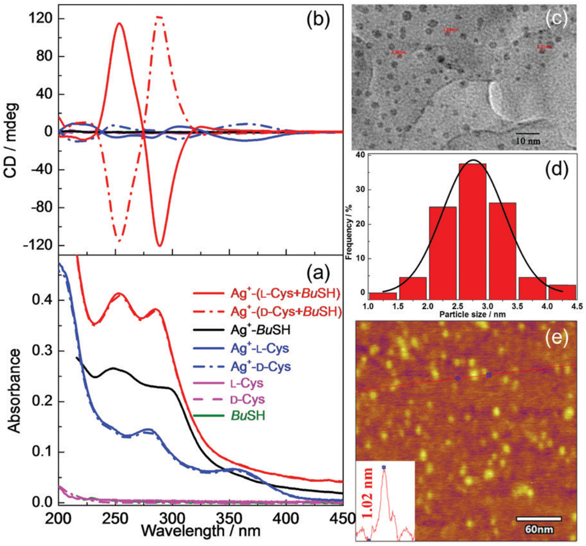

Fig. 2 Absorption (a) and CD (b) spectra of L-/D-Cys (25 μM, pink curve and dotted line), Ag^+–L-/D-Cys solution (25 μM, blue curve and dotted line), Ag^+-BuSH solution (25 μM, black curve), and Ag^+–(L-/D-Cys + BuSH) solution (50 μM, red curve and dotted line). High-magnification TEM image (c), size distribution from TEM data (d) and AFM image (e) of Ag^+–(L-Cys + BuSH) nanosphere structures. Inset in (e) shows the height profile along the red line. Note in (b) the sign of the CD signal at 253 nm of Ag^+–(L-Cys + BuSH) or Ag^+–(D-Cys + BuSH) is opposite to that of Ag^+–L-Cys or Ag^+-D-Cys.

TEM images of the Ag^+–(L-Cys + BuSH) coordination polymers (Fig. 2c and Fig. S12a, ESI†) show uniform nanosphere structures. The diameters of these nanostructures are estimated to be 2.76 ± 0.52 nm (Fig. 2d), which agrees with the value of 2.65 nm (Fig. S12c, ESI†) based on Gaussian structural modelling assuming 16 Ag^+ ions on the cyclic backbone, assuming a low limit of $Ag^+\cdots Ag^+$ distance of 2.8–3.4 Å that defines the argentophilic interaction.[15] The fact that the size of the objects does not change over the total thiol concentration of 2–10 μM (Fig. S13, ESI†), again supports the nanosphere structure. The height of the nanospheres obtained from the AFM image is *ca.* 1.02–1.12 nm (Fig. 2e and Fig. S12b, ESI†), agreeing with the value of 1.15 nm (Fig. S12d, ESI†) based on Gaussian structural modelling that the n-butyl groups locate inwardly, alternately up and down the backbone plane. TEM and AFM images of the Ag^+-L-Cys coordination polymers show chain-like structures (Fig. S14, ESI†). Attempts at using TEM mapping and STM to characterize the nanosphere structures failed because of the too small sizes and the lack of conductivity, respectively. Yet the observation of strong CD signals at short wavelengths from the Ag^+–(L-Cys + BuSH) or Ag^+–(D-Cys + BuSH) nanosphere structure is of significance; it means that the chiral ligands are helically bound to the Ag^+-ion backbone.

From chain-like Ag^+–L-Cys coordination polymers to spherical Ag^+–(L-Cys + BuSH), the $Ag^+\cdots Ag^+$ interactions underwent a change from the flexible delocalized helical version to the rigid localized bent version, which may contribute to the reversal of the CD signals around 253 nm (Fig. 2).

DLS diameters of Ag^+–(L-Cys + BuSH) polymers are smaller than those of Ag^+–L-Cys polymers up to 1.0 equiv. Ag^+ at a total thiol concentration of 5 μM (Fig. 3a), being 295 nm and 1281 nm, respectively at 1.0 equiv. Ag^+. The Ag^+–(L-Cys + BuSH) polymers of increasing concentration are also of smaller sizes than those of Ag^+–L-Cys polymers too (Fig. S15, ESI†). Both support the nanosphere structure of Ag^+–(L-Cys + BuSH) polymer, because of the constrained conformations and reduced entanglement relative to the linear polymers.[6a,16] Moreover, while the hydrodynamic diameters of Ag^+–L-Cys polymers measured at different scattering angles varied much, those of Ag^+–(L-Cys + BuSH) polymers are weakly fluctuant (Fig. S16, ESI†), in line with the chain-like structure of Ag^+–L-Cys polymers[17a] and the nanosphere structure of Ag^+–(L-Cys + BuSH) polymers.[17b]

^1H NMR of $-CH_2$ and –CH protons of L-Cys and $-CH_2$ and $-CH_3$ protons of BuSH in the Ag^+–(L-Cys + BuSH) system was followed. The resonances of all those protons in the ligand molecules disappear gradually upon the addition of Ag^+, indicative of the formation of the coordination polymers (Fig. S17, ESI†).[18] Similar observations were made for $-CH_2$ and –CH protons of L-Cys in Ag^+-L-Cys polymers (Fig. S18, ESI†) and $-CH_2$ and $-CH_3$ protons of BuSH in Ag^+-BuSH polymers (Fig. S20, ESI†), respectively. It is found that in the Ag^+–(L-Cys + BuSH) system, the disappearing rate of the resonances of those protons in BuSH is much faster than those in L-Cys at Ag^+ concentration below 0.75 equiv. (Fig. 3b), which supports the nanosphere structure that the hydrophilic L-Cys ligands locate loosely outside the backbone, while the hydrophobic BuSH ligands are more tightly packed inside the backbone (Scheme 1). This is backed up by the observations that the resonance of $-CH_2$ protons of L-Cys in Ag^+–L-Cys polymers disappears more quickly than that in the Ag^+–(L-Cys + BuSH) polymers (Fig. S19, ESI†), while those of $-CH_2$ protons of BuSH in Ag^+–(L-Cys + BuSH) polymers disappear more quickly than those in the Ag^+-BuSH polymers (Fig. S21, ESI†). The former is likely ascribed to the dynamical interconversion of more possible conformations of L-Cys ligand in chain-like Ag^+–L-Cys polymers than in the spherical Ag^+–(L-Cys + BuSH),[19] while the latter presumably results from tight packing of the hydrophobic BuSH ligands inside the nanosphere.

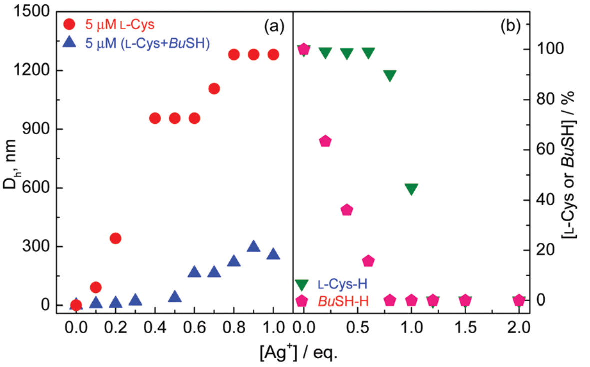

Fig. 3 (a) DLS measured hydrodynamic diameters of Ag^+–L-Cys and Ag^+–(L-Cys + BuSH) and (b) contents of L-Cys and BuSH calculated by ^1H NMR integrals of the Ag^+–(L-Cys + BuSH) system in 10 mM pH 5.0 HAc-NaAc buffer *versus* the equivalent of added Ag^+. [RSH] = 5 μM (a) [L-Cys] = [BuSH] = 50 μM (b). Buffer in (b) was prepared in D_2O and acetone was taken as an internal standard.

As shown in Scheme 1, the Ag^+–(L-Cys + BuSH) nanosphere polymers can in principle be formed in three ways, *i.e.* (i) direct mixing of Ag^+ with cysteine and BuSH in aqueous solution or by later adding (ii) BuSH or (iii) L-cysteine, respectively, into an aqueous solution containing Ag^+–L-Cys or Ag^+-BuSH coordination polymers. Time evolution traces of the absorption and CD spectra (Fig. S22, ESI†) show that the absorption at 360 nm of the Ag^+–(L-Cys + BuSH) system, attributed to the extended $Ag^+\cdots Ag^+$ interactions in the Ag^+–L-Cys coordination polymers,[2–5] decreases while those at shorter wavelengths of 253 nm and 285 nm increase. The latter has been assigned to the localized $Ag^+\cdots Ag^+$ interaction.[14] CD signals undergo similar profiles of variations. These suggest that the coordination polymers of Ag^+–(L-Cys + BuSH) experience an evolution from chain-like to the cyclic nanosphere structure, in 40 minutes to reach the equilibrium (Fig. S23 and S24, ESI†). It is worth noting that during the evolution, the CD signal at 253 nm undergoes a reversal in sign, from negative to positive. It appears that in the Ag^+–(Cys + BuSH) system, linear polymeric structures first quickly form, with characteristic absorption and CD signals at 366 nm (Fig. S22, ESI†), which evolve into nanospheres with dominant absorption and CD signals at 253 nm and 288 nm (Fig. S22, ESI†). This evolution was found to be accelerated when the solution was heated (Fig. S25, ESI†).

Upon adding BuSH into the aqueous solution of Ag^+–L-Cys coordination polymers, the CD signals of Ag^+–L-Cys instantly decrease to half of the original values (Fig. S26, ESI†), suggesting that the exchange of the ligands is quick. After standing, the CD signals at 253 nm and 288 nm gradually increase, levelling off in 80 min (Fig. S27, ESI†), leading to a CD spectrum that is the same as that of the equilibrated Ag^+–(L-Cys + BuSH) (Fig. S22b, ESI†). A similar evolution was found in the absorption spectrum of Ag^+–L-Cys polymers after adding BuSH, that the absorption at 360 nm, ascribed to the $Ag^+\cdots Ag^+$ interaction in chain-like Ag^+–L-Cys coordination polymers, disappears (Fig. S28, ESI†), while those at 253 nm and 283 nm increase. The eventual formation of the nanospheres is confirmed by the TEM image (Fig. S29, ESI†). Similar conclusions are drawn from the time evolution of the CD spectrum of Ag^+-BuSH solution after adding L-Cys (Fig. S30 and S31, ESI†).

The chemical state of Ag species in the nanospheres can be determined by examining the absorption spectra of Ag^+–(L-Cys + BuSH) solutions upon reducing by $NaBH_4$. Absorption of Ag^+–(L-Cys + BuSH) disappears while a new band at a longer wavelength 450 nm develops (Fig. S32, ESI†), a sign of the metallic Ag nanostructures.[20,21] During reduction, CD signals of the Ag^+–(L-Cys + BuSH) system in acidic aqueous solution disappear too (Fig. S32b, ESI†). We, therefore, conclude that in the Ag^+–(Cys + BuSH) backbone Ag species exist in the +1 state.

Properties of the nanospheres were examined by observing CD spectra of Ag^+–(Cys + BuSH) solutions as a function of the

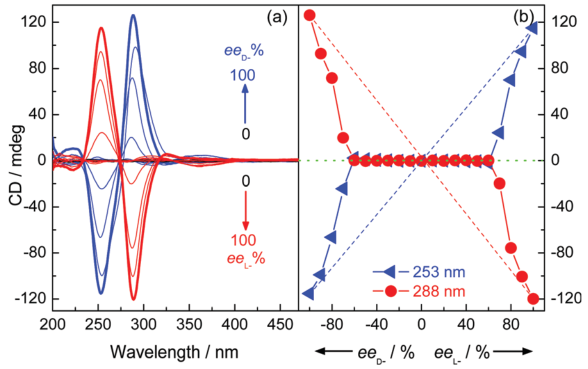

Fig. 4 CD spectra (a) and plots of the CD signals at 253 nm and 288 nm (b) of the Ag^+–(Cys + BuSH) system of varying ee of cysteine component in 10 mM pH 5.0 HAc-NaAc buffer. [BuSH] = 25 μM, [L-Cys] + [D-Cys] = 25 μM, [Ag^+] = 35 μM, time = 80 min.

enantiomeric excess (ee) of the chiral ligand component, cysteine (Fig. 4). CD signals at 253 nm and 288 nm plotted against ee exhibit an anti-*Z*-shaped dependence (Fig. 4b), suggesting a racemate rules effect (RRE).[22] For the Ag^+–Cys system, it is also the anti-*Z*-shaped dependence (Fig. S33, ESI†), despite much weaker CD signals. The CD-ee curvature is larger in the Ag^+–(Cys + BuSH) nanospheres than in the Ag^+–Cys chain polymer (Fig. S34, ESI†), a fact good for measuring ee at high value ends. The nanosphere structure is therefore shown to promote heterochiral selectivity.[5,22b] As we showed earlier, during the evolution of the chain-like Ag^+–L-Cys coordination polymers into the Ag^+–(L-Cys + BuSH) polymers, the CD signal at 366 nm disappears while that at 288 nm is enhanced (Fig. S22b, ESI†). The latter is actually amplified when the *g* factor at 288 nm of the nanosphere structure is -9.8×10^{-3}, which is 2 times higher than that at 366 nm of the Ag^+–L-Cys coordination polymers, -4.7×10^{-3} (Fig. S35, ESI†).

In conclusion, we developed a new strategy for building nanosphere structures in aqueous solution from the chain-like coordination polymers of Ag^+ with a hydrophilic chiral thiol ligand, cysteine, by introducing a hydrophobic thiol ligand, BuSH of an optimal *n*-butyl length. Combination of cysteine and BuSH in pH 5.0 acidic solution allows the ready formation of Ag^+–(Cys + BuSH) nanospheres of diameter *ca.* 2.7 nm, with Ag^+ ions on the backbone linked by localized $Ag^+ \cdots Ag^+$ interaction that is characterized by absorption at 285 nm. The hydrophilic and hydrophobic thiol ligands locate respectively outward and inward of the backbone, such that "$\cdots(R_LS)Ag(SR_B)\cdots$" unit functions like a *pseudo*-amphiphile. The evolution of the chain-like structure into nanospheres is indicated by the disappearance of the absorption and CD signals at 360 nm with the enhancement of those at 288 nm, together with a reversal of the CD signal at 253 nm. During the structural evolution, the CD signal at short-wavelength is amplified, with an enhanced anti-*Z* shaped dependence of the CD signals *versus* ee of the chiral thiol component in the nanospheres than in the chain-like coordination polymers. Ongoing experiments show that this strategy is applicable to other systems. As metal–metal interactions exist between many d^8 or d^{10} metal ions such as Cu^+, Au^+, Pt^{2+} and Pd^{2+},[15,23] nanospheres can be similarly built of structural diversity and functions.

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Conflicts of interest

There are no conflicts to declare.

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