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Helical nanofibers of N-(perfluorooctanoyl)cysteine ethyl ester in coordination polymers of Ag⁺
Helical nanofibers of $N$-(perfluorooctanoyl)cysteine ethyl ester in coordination polymers of Ag$^+$†

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We propose using the formation of coordination polymers of Ag$^+$ to probe differences between the perfluorinated alkyl chain and the alkyl chain by deriving a thiol ligand, $N$-(perfluoroalkanoyl)cysteine. Rapid formation in EtOH of $P$-/$M$-helical nanofibrils of high thermostability was found for $N$-(perfluorooctanoyl)-L-/D-cysteine ethyl esters at the µM level upon mixing with Ag$^+$, but not for the octanoyl counterpart. This difference was also observed in terms of circular dichroism-enantiomeric excess dependence.

Perfluorinated alkanes, in which all hydrogen atoms of the alkyl chains are substituted by fluorine atoms, differ considerably from their perhydrogenated alkane counterparts. For example, perfluorinated alkanes have a lower surface energy and dielectric constant, are more rigid and less miscible, and have poor affinity to both hydrophobic and hydrophilic solvents. The mechanisms for these characteristics remain to be clarified, partly because of the limited availability of perfluorinated compounds with diverse structures, despite the substantial recent progress in the synthetic context. An alternative route to create new species from the available perfluorinated compounds would be to form supramolecular aggregates of diverse structures, so that the differences can be seen in a variety of ways. However, the challenge is that perfluorinated compounds are both oleophobic and hydrophobic, which is not conducive to the formation of well-defined superstructures, especially in solution. In this context, assembly of building blocks containing perfluorinated components has been achieved on surfaces, and in specific fluorinated solvents. In some cases, however, it could take up to 1 month for the perfluorinated compound modified silica wafers to assemble into a helix. These extreme experimental conditions have, to some extent, limited the development of supramolecular assemblies of perfluorinated compounds.

Herein, we propose a method for forming supramolecular assemblies of perfluorinated compounds that can form coordination polymers with Ag$^+$ by deriving them into thiol ligands. Thus ($N$-perfluorooctanoyl)cysteine ethyl esters (L-1, Scheme 1) were created from perfluorooctanoic acid, in which the cysteine residue affords a thiol group that strongly coordinates to Ag$^+$ to form Ag$^+$-thiol coordination polymers. This approach also affords molecular chirality that could be transferred to the coordination polymers, promoting the formation of supramolecular helical assemblies. L-1 was found to form instantly at the micromolar concentration in EtOH helical nanofibers upon mixing with Ag$^+$. The nanofibers are of $P$- and $M$-senses, respectively, when the cysteine residues are of D- and L-configuration. The corresponding ($N$-octanoyl)cysteine ethyl esters (L-2, Scheme 1) do not form such fibres under the same conditions.

Fig. 1a shows the absorption spectra of L-1 in EtOH in the presence of increasing concentrations of Ag$^+$. A band at 280 nm develops, assigned to the ligand-to-metal–metal charge transfer

Scheme 1 Formation of (a) Ag$^+$-1 and (b) Ag$^+$-2 coordination polymers. Dashed lines indicate the Ag$^+$...Ag$^+$ interactions. Syntheses of 1 and 2 are described in the ESI.
(LMMCT) state from the in situ-generated chromophores, relating to the $\text{Ag}^+ \cdots \text{Ag}^+$ interaction in the $\text{Ag}^-\text{L}$ coordination polymers.$^{24-26}$ A 1 : 1 stoichiometry was found from the change in absorbance at 280 nm as a function of $\text{Ag}^+$ concentration (Fig. S1, ESI†), while dynamic light scattering (DLS) data showed the presence of large species in the solution (Fig. S2 and S3, ESI†). It was therefore concluded that the $\text{Ag}^-\text{L}$ coordination polymers were formed, as instantly observed experimentally upon mixing the two components in EtOH, even at a 1 : 1 concentration at the $\mu$M level. Absorption titrations also suggested the formation of $\text{Ag}^-\text{L}$ coordination polymers (Fig. 1c and Fig. S4, ESI†) with a 1 : 1 binding ratio, but of smaller sizes (Fig. S2 and S3, ESI†). It is noteworthy that a narrower absorption at 350 nm was observed, in addition to the 280 nm band; the former has previously also been assigned to narrow absorption at 350 nm was observed, in addition to the signals at $\delta_{\text{C}0}$ under-field shifts and were broadened upon the formation of coordination polymers.$^{19}$ $1^H$ NMR signals of protons related chromophores are brought into a chiral environment. The perfect mirror-image CD profiles of $\text{Ag}^-\text{L}$- polymers (Fig. 1a and b).$^{29}$ Again, the CD profiles of $\text{Ag}^-\text{L}$-polymers with a well-defined pitch were also observed by TEM (Fig. S14–S16, ESI†). The average pitch of the helical ribbons observed by SEM is ca. 330 nm, from more than 20 twisted ribbons in the $\text{Ag}^-\text{L}$-polymers have a non-helical nanostructure, but a linear chain morphology, as seen in the SEM (Fig. 2c and d) and AFM images (Fig. 2g and h). In the addition of $\text{Ag}^+$, suggesting an increasing hydrophobicity of the environment around the F-atoms, and thus indicative of the formation of coordination polymers.$^{16}$ $1^H$ NMR signals of protons in $\text{L}$ disappeared rapidly, but gradually broadened and weakened in the case of $\text{D}$ (Fig. S11–S13, ESI†), suggesting a stronger interaction in $\text{Ag}^-\text{L}$ polymers. This agrees with the higher binding constant of $\text{Ag}^-\text{L}$ (1.4 × 10$^7$ M$^{-1}$) than $\text{Ag}^-\text{D}$ (8.8 × 10$^5$ M$^{-1}$) from CD titrations (Fig. S14–S16, ESI†).

To investigate further the supramolecular structures of the $\text{Ag}^-\text{thiol}$ coordination polymers, scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscopy (AFM) images were taken. The $\text{Ag}^-\text{L}$ polymers are right-handed twisted ribbons (Fig. 2a and e), while the $\text{Ag}^-\text{D}$-polymers are left-handed twisted ribbons (Fig. 2b and f). The average pitch of the helical ribbons observed by SEM is ca. 330 nm, from more than 20 twisted ribbons in the $\text{Ag}^-\text{L}$-images (Fig. S17, ESI†). The helical ribbons of $\text{Ag}^-\text{L}$ and $\text{Ag}^-\text{D}$ exhibited AFM heights of 31 nm and 33 nm, respectively (Fig. 2e and f). The helicities observed in SEM and AFM are the same as those indicated by CD profiles (Fig. 1b). Those well-defined helical nanoribbons should originate from the supramolecular chirality of the $\text{Ag}^-\text{L}$-polymers, since the patterns of $\text{L}$ and $\text{D}$ are microgranular of ca. 1 nm diameter (Fig. S18, ESI†). Moreover, the chain structures of the $\text{Ag}^-\text{L}$-polymers with a well-defined pitch were also observed by TEM (Fig. S19, ESI†). In contrast, the $\text{Ag}^-\text{D}$-polymers have a non-helical nanostructure, but a linear chain morphology, as seen in the SEM (Fig. 2c and d) and AFM images (Fig. 2g and h). In the
latter, the heights were determined to be 3.2 nm and 3.1 nm, respectively, which are much smaller than those of the Ag⁺−1/0-1 coordination polymers (Fig. 2e and f).

Temperature-dependent CD measurements show that the Ag⁺−1 polymers are much more thermally stable than the Ag⁺−2 polymers (Fig. 3). Upon heating at a rate of 5 K min⁻¹, the CD signal of the Ag⁺−1 polymers changed a little below 308 K, followed by a slight increase (Fig. 3c). The Ag⁺−1 coordination polymers underwent a transition from kinetic to thermodynamic control, a slow cooling at −5 K min⁻¹ was applied subsequently. No apparent change was observed (Fig. 3d), thus confirming that the Ag⁺−1 polymers are of high thermal stability. For the Ag⁺−2 polymers, the CD signal undergoes a substantial decline upon heating (Fig. 3g) and the signal is not restored in the next cooling cycle (Fig. 3h).

The difference in thiol ligand side-chain composition (perfluoroalkyl versus hydrocarbon alkyl) also leads to an opposite dependence of the CD signals of the coordination polymers on the enantiomeric excess (ee) of ligands 1 and 2. The Ag⁺−1 coordination polymers exhibit a negative nonlinear CD-ee dependence (Fig. 4a and b),²⁰,³¹−³³ in contrast with a positive nonlinear dependence for the Ag⁺−2 polymers. This suggests a chiral amplification governed by the majority-rules effect (MRE),¹⁴ although the effect is only small (Fig. 4c and d).

The mechanisms for the differences between Ag⁺−1 and Ag⁺−2 coordination polymers were then analysed. The heights of the Ag⁺−2 coordination polymers observed in AFM images (3.2 nm and 3.1 nm, respectively; Fig. 2g and h), are consistent with those of a single chain of the Ag⁺−2 coordination polymers calculated from the Materials Studio structural modelling (3.1 nm, Fig. S20, ESI†). The Ag⁺−2 coordination polymers are assumed to exist in individual polymeric chains. However, the helical assemblies of the Ag⁺−1 coordination polymers show heights ca. 32 nm (Fig. 2e and f), which is 10-times that of a single Ag⁺−1 chain (3.2 nm, Fig. S21, ESI†), suggesting that packing of individual Ag⁺−1 polymeric chains occurs. This is ascribed to the fluorophobic effect or the solvophobic effect of the perfluorinated alkyl group that drives the assembly of individual Ag⁺−1 polymeric chains. Compared with the Ag⁺−2 coordination polymers, Ag⁺−1 polymers are of a larger size (Fig. S2 and S3, ESI†) and greater thermostability (Fig. 3), which can also be attributed to the packing of the Ag⁺−1 polymeric chains.

Concentration-dependent DLS measurements (Fig. S22, ESI†) showed that the diameters of the Ag⁺−2 coordination polymers change little with increasing concentration, whereas those of the Ag⁺−1 polymers increase dramatically. This supports the existence of individual polymeric chains of Ag⁺−2, in contrast to further packing of Ag⁺−1 polymeric chains.

It was therefore proposed that the perhydrogenated ligands 2 form individual Ag⁺−thiol polymeric chains in EtOH, allowing extended Ag⁺···Ag⁺ interactions along the polymeric chain (Fig. S20, ESI†), showing absorption and CD signals at 350 nm of ligand-to-metal–metal charge transfer (LMMCT) nature (Fig. 1c and d).²⁷ In contrast, for the perfluorinated ligands 1, once the Ag⁺−thiol polymeric chains are formed, they intercalate with each other to form helical nanofibers. The extended Ag⁺···Ag⁺ interaction existing in a single polymeric chain is disrupted because of intercalation, and consequently only the binuclear Ag⁺···Ag⁺ interaction exists (Fig. S21, ESI†), such that a short-wavelength absorption was observed at 280 nm.²⁶

The hierarchical assembly of Ag⁺−1 coordination polymers leads to an opposite supramolecular chirality from that of the Ag⁺−2 coordination polymers (Fig. 1), and different CD-ee profiles (Fig. 4). While the individual Ag⁺−thiol polymeric chain prefers homochiral ligands, giving rise to positive nonlinear CD-ee dependence for the Ag⁺−2 coordination polymers, the inter-chain intercalation between Ag⁺−1 polymeric chains likely leads to a heterochiral preference, resulting in a negative CD-ee dependence.³³ The latter was supported by the different CD profiles of Ag⁺−1 polymers at different ees of 1 (Fig. 4a), such that at high ees of ±100% or ±80%, inter-chain homochiral interactions dominate, while heterochiral interactions become dominant at lower ees from ±60% to 0%.²⁰

Co-assembling perfluorinated compounds and their hydrocarbon counterparts is meaningful to the construction of...
diverse structures from the limited perfluorinated species. The poor affinity of perfluorinated moieties towards hydrocarbon counterparts, however, makes it hard to achieve. Mixed coordination polymers were attempted using ligands of \( \text{L-1} \) or \( \text{r-1} \) and \( \text{r-2} \). CD profiles suggest that in the case of \( \text{L-1} \) and \( \text{r-2} \), mixed coordination polymers formed, as evident from the dramatically different profile at a \( \text{r-1} \) to \( \text{r-2} \) molar ratio of 3 : 7 (Fig. S23, ESI†) and the difference in the observed and calculated CD profiles of the coordination polymers at a ligand molar ratio of 5 : 5 (Fig. S24, ESI†). An SEM image of the coordination polymers with a 5 : 5 ligand molar ratio shows a right-handed helical ribbon structure with a 207 nm pitch (Fig. S25 and S26, ESI†), close to that observed for pure Ag\(^{+}\)-\( \text{L-1} \). In contrast, mixed ligands of \( \text{r-1} \) and \( \text{r-2} \) appear not to form mixed coordination polymers with Ag\(^{+}\), and the CD profiles are the sum of those of individual polymers of Ag\(^{+}\)-\( \text{r-1} \) and Ag\(^{+}\)-\( \text{r-2} \) (Fig. S27 and S28, ESI†). The SEM image shows a left-handed helical ribbon with a pitch of 263 nm (Fig. S29, ESI†), a value close to that of the pure Ag\(^{+}\)-\( \text{r-1} \) system. It was confirmed that forming an Ag\(^{+}\)-thiol coordination polymer is a powerful means to co-assembly the perfluorinated compound and its hydrocarbon counterpart, during which the homochiral selectivity of the chiral ligands holds.

In summary, we formed coordination polymers of the derived thiol ligand of a perfluorinated compound with Ag\(^{+}\), to create supramolecular aggregates that allowed differences from the hydrocarbon counterpart to be observed. N-(Perfluorooctanoyl)cysteine ethyl esters thus created form in EtOH from the hydrocarbon counterpart to be observed. Differences between the hydrocarbon and their hydrocarbon counterparts can be seen. The absence of absorption at 350 nm, with only the short-wavelength absorption at 280 nm assigned to the binuclear Ag\(^{+} \cdots \text{Ag}^{+}\) interaction, is particularly worthy of note.

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**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**