We report coordination polymers forming from Ag⁺ and a chiral thiol ligand that bears a β-turn structure, exhibiting supramolecular chirality showing both the majority rules effect (MRE) and the racemate rules effect (RRE).

Supramolecular chirality of assemblies arises from the non-symmetric arrangement of the chiral building blocks or of the achiral building blocks in the presence of a chiral inducer. It is of vital importance in materials chemistry, catalysis, molecular sensors, and biological processes, and in particular in the understanding of the origin of biological homochirality. The relationship between the supramolecular chirality of the assembly and the molecular chirality of the chiral building block or the chiral inducer is described by the observed CD signal of the assembly against the enantiomeric excess (ee) of the chiral species. In the majority of the reported cases, the relationship is linear, while nonlinear dependence has also been observed. In the latter cases, S- or Z-shaped dependence, termed as the majority rules effect (MRE), was first described by Green et al. in covalent polymers, and in later noncovalently bound supramolecular aggregates by Meijer et al. Another nonlinear dependence, the anti-S or anti-Z-shaped dependence, termed as the racemate rules effect (RRE), was also reported. In all those cases, the supramolecular chirality of the assembly originates from the molecular chirality of the chiral building block or the chiral inducer. We thus envisaged that if the assembly is built from a building block that itself exhibits a supramolecular chirality, there could be new features in the expressed supramolecular chirality of the assembly. We therefore chose to examine the Ag⁺-thiol coordination polymers using a chiral thiol ligand that bears a β-turn structure we recently reported in the short-peptide based amidothiourea.

The Ag⁺-cysteine coordination polymers exhibit both absorption and the corresponding CD signals around 350 nm, presumably due to the in situ formed chromophores relating to Ag⁺-···Ag⁺ interactions that support the coordination polymers, together with the interactions between the side chains of the chiral thiol ligand cysteine. We recently reported that in the N-acetylphenylalanine based amidothiourea, a β-turn structure forms via the ten-membered ring hydrogen bond and thus the molecular chirality of the phenylalanine residue transfers to the distant achiral phenylthioureia moiety (cf. the structure of TFTU, Scheme 1). We therefore designed a chiral thiol ligand N-(thioglycylphenylalanine) based amidothiourea (TFTU, Scheme 1). The thiol group in TFTU, which binds Ag⁺, links via a –CH₂ group to the carbonyl group that experiences the supramolecular chirality afforded by the β-turn structure, thus similar to the –SH group in cysteine that links via –CH₂ to the chiral α-carbon (cf. the structure of NACA, Scheme 1a). The observed splitting of the NMR signals of the –CH₂ protons in TFTU indicates the magnetic non-equivalence of these two protons as that in cysteine.

The β-turn structure in TFTU is confirmed by monitoring ¹H NMR of the –NH protons in CD₂CN/DMSO-d₆, binary solvents of increasing percentage of the hydrogen bonding component DMSO-d₆. The chemical shift of the –NH⁺ proton was found to be of low sensitivity towards the change in solvent composition (Fig. S1, ESI†), indicative of its taking part in the intramolecular hydrogen bonding. Mirrored CD spectra of L- and D-TFTUs were observed (Fig. S2, ESI†), confirming the origin of the chirality of the amino acid residue. The CD signal at 235 nm is assigned to the chiral phenylalanine residue, while that at 270 nm is assigned to the achiral phenylthioureia chromophore, by referring to the absorption spectra. The observation of CD signal from the achiral phenylthioureia chromophore thus suggests that the molecular chirality of the amino acid residue has transferred to the distant phenylthioureia moiety (Fig. S2, ESI†). It is therefore concluded that the β-turn structure forms within the TFTU...
Indeed, NMR signals of the –CH$_2$– protons are found separated from –SH in TFTU polymeric species. NMR signals of the –NHs and –SH protons already suggested by the absorption beyond 300 nm (Fig. 1a) relating to the Ag$^+$ presumably originating from the in situ formed chromophore. The CD signal at 235 nm reverses gradually, while that at 275 nm shifts slightly to the red to 275 nm and increases. Meanwhile, a new CD band appears at ca. 315 nm, presumably originating from the in situ formed chromophore relating to the Ag$^+$···Ag$^+$ interactions. Again the variation profiles of the CD spectra of the coordination polymers of Ag$^+$ with L-/D-TFTU are mirror imaged. The CD signals level off at Ag$^+$ concentration of ca. 1.5 eq. (Fig. S4, ESI†).

DLS data of the CH$_3$CN solutions of Ag$^+$–TFTU show the existence of large species, being 21 nm and 87 nm in diameter at the concentrations of L-TFTU of 20 μM and 100 μM, respectively, both in the presence of 1.5 eq. Ag$^+$ (Fig. S5, ESI†). This supports the formation of the coordination polymers that is already suggested by the absorption beyond 300 nm (Fig. 1a) and shows that increasing the concentration leads to longer polymeric species. NMR signals of the –NHs and –SH protons in TFTU disappear upon the introduction of Ag$^+$, while those of the phenyl protons broadened (Fig. S6, ESI†), both in agreement with the formation of coordination polymers. The diffusion coefficient of TFTU in the presence of 1.0 eq. Ag$^+$ in CH$_3$CN, measured from DOSY spectra, 8.95 × 10$^{-10}$ m$^2$ s$^{-1}$, is lower than that of TFTU (2.16 × 10$^{-9}$ m$^2$ s$^{-1}$), suggesting a larger species formed in the Ag$^+$–TFTU solution in CH$_3$CN, calculated to be in the form of (Ag$^+$–TFTU)$_{11}$ (Table S1, ESI†). Those data therefore confirm the formation of coordination polymers of TFTU with Ag$^+$ in CH$_3$CN (Scheme 1b(i)). AFM images of the coordination polymers prepared from Ag$^+$ and TFTU of varying ee (Fig. S7, ESI†) show similar fibrillar assemblies at ee of TFTU of 100%, 50% and 0%. According to the AFM height profiles, the heights of those fibres are determined to be 2.17–2.48 nm, agreeing with the height of the Ag$^+$–TFTU coordination polymer, 2.1 nm, calculated from the structural model shown in Scheme 1b.

CD spectra of TFTU of varying ee in the presence of 1.5 eq. Ag$^+$ were recorded (Fig. 2a). Plot of the CD signal at 235 nm against ee appears in a slightly Z-shaped curve (Fig. 2b), showing the occurrence of the majority rules effect (MRE). In contrast, the corresponding plots of the CD signals at 275 nm and 340 nm both appear anti-Z-shaped (Fig. 2b), suggesting a racemate rules effect, the RRE. The CD signal at 235 nm relates to the chiral phenylalanine residue in the thiol ligand TFTU, being thus a reflection of the molecular chirality of the amino acid residue. The CD signal at 275 nm, however, is due to the achiral phenylthiourea chromophore that is included within the Ag$^+$–TFTU coordination polymer, 2.1 nm, calculated from the structural model shown in Scheme 1b.
varying ee of TFTU confirm that the contribution of LD to CD spectra is negligible (Fig. S8 and S9, ESI†). It is noted that the CD profiles between 300 nm and 360 nm for the ±100% and ±80% ee samples are different from those of the other ee%, while their absorption spectra are the same (Fig. 2a and Fig. S10, ESI†).

In those coordination polymers, the ligand side chains exist in different chirality. In the case where the polymers were prepared from Ag⁺ with the pure enantiomer form of the ligand (Scheme 1b(i)), the side chains would be of uniform chirality. While in the polymers built from Ag⁺ and enantiomeric mixtures of the chiral ligand, the side chains of the ligands may exist in differing chirality (Scheme 1b(ii)). Alternatively, the coordination polymers were obtained by mixing two coordination polymers respectively prepared from Ag⁺ with pure enantiomers (Scheme 1b(iii)). In the latter case, CD spectra measured immediately upon mixing lead to a CD-ee plot showing a much weaker nonlinear character (Fig. S11, ESI†). The CD profiles are the same over ee of −100% to +100% (Fig. S12, ESI†). After standing for 1 h, the CD spectra of the samples lead to a CD-ee dependence practically the same as those shown in Fig. 2 (Fig. S13 and S14, ESI†). This is understood in that the ligand exchange takes place when the two coordination polymers are mixed, reaching equilibrium in 1 h. It appears that the heterochiral interactions of the side chains within the same coordination polymer backbone are critical for the RRE to be observed together with the MRE.

DLS profiles of the coordination polymers show a larger size of the sample of higher ligand ee, the diameters being 16 nm (ee 0%), 35 nm (50%) and 87 nm (100%), respectively (Fig. S15, ESI†). This means that the ligand of higher ee favours to form longer coordination polymers, as the AFM images show that the height of the polymeric species does not change (Fig. S7, ESI†). Concentration-dependent absorption data of the Ag⁺–TFTU solutions indicate that the polymerization can be described by the isodesmic model (Fig. S16, ESI†). Upon increasing ee of TFTU from 0% to 50% and 100%, the association constant increases in that $K_{0\%} = (2.25 \pm 0.14) \times 10^3$ M⁻¹, $K_{50\%} = (8.72 \pm 0.87) \times 10^5$ M⁻¹ and $K_{100\%} = (1.84 \pm 0.29) \times 10^6$ M⁻², consistent with the observation made in the DLS profiles of the Ag⁺–TFTU solutions (Fig. S15, ESI†). This suggests that the homochiral pairing of the ligands in the coordination polymeric backbone is favoured. It is therefore assumed that in the coordination polymers built from 1/2–TFTU mixture with Ag⁺, heterochiral ligands likely attach at different sides of the backbone to ensure the maximal homochiral interactions. This leads to a structural model of the coordination polymers of Ag⁺ with TFTU of ee 0% (Fig. S17, ESI†). This may help to understand the co-existence of the homochiral and heterochiral pairing in one coordination polymeric backbone that relates to the MRE and RRE in the same supramolecular system, since MRE is related to the homochiral preference during the polymerization, while the RRE to the favoured heterochiral pairing.

Fig. 2a shows that the CD signal around 320 nm is monosignate at TFTU ee of ±100% or ±80% when there is only (ee ±100%) or dominantly (±80%) the homochiral interactions of the chiral ligands. The CD signal however turns to be bisignate, i.e. the excitation-coupled, at ee ±60% or lower to 0% when heterochiral interactions become increasingly more important. This suggests that the RRE shown in the CD at 340 nm against the ee of TFTU (Fig. 2b) relates to the heterochiral interactions of the ligands. The MRE linked to the monosignate CD signal at 235 nm (Fig. 2b) would thus be linked likewise to the homochiral interactions. In agreement with this assumption is that the CD signal at 275 nm exhibiting the RRE (Fig. 2b) starts to be coupled to that at longer wavelength at ee ±60% or lower. The structural model of the Ag⁺–TFTU coordination polymer of TFTU ee 0% given in Fig. S17 (ESI†) would help understand the observation of MRE and RRE in the same coordination polymer that reflects respectively the homochiral and heterochiral interactions of the chiral ligands.

AcO⁻ is known to bind the thiourea moiety, breaking the β-turn structure to form an extended binding complex.21 CD signals of the polymers of TFTU with 1.5 eq. Ag⁺ change dramatically upon the addition of AcO⁻, exhibiting an enhanced CD at 300 nm and a new band at 250 nm of opposite sign (Fig. S18, ESI†). The diffusion coefficient changes little in the presence of 1.5 eq. AcO⁻, from 8.95 × 10⁻¹⁰ to 8.26 × 10⁻¹⁰ m² s⁻¹ (Table S1, ESI†), suggesting that the basic polymeric structure remains. Therefore, the resultant coupled Cotton effect implies the efficient communication of chirality within the three-component polymers (Scheme 2). In the presence of AcO⁻, the CD profiles over ee...
Fig. 3  (a) CD spectra of Ag⁺–TFTU of varying TFTU ee in CH₂CN in the presence of 1.5 equivalent AcO⁻ and (b) CD signals at 250 nm and 300 nm as a function of ee. [TFTU] = 100 μM, [AgNO₃] = [AcO⁻] = 150 μM. AcO⁻ exists as its (n-Bu)₄N⁺ salt.

−100% to +100% of TFTU are the same (Fig. 3a) and the CD-ee relationships are linear (Fig. 3b). The CD-ee plots are also linear from the samples by the other way of mixing two coordination polymers (Scheme 1b(ii)), in the presence of AcO⁻ (Fig. S19, ESI†). CD spectra and character of CD-ee plots remain unchanged after standing for 1 h (Fig. S20, ESI†). In the three-component polymers the side-chains bearing bound AcO⁻ will interact much weaker, if any, because of the electrostatic repulsions. Again this suggests that the interactions between heterochiral ligands are responsible for both MRE and RRE occurring in the same supramolecular polymer. With TFTU or the TFTU–anion complex, the CD-ee relationships are both linear (Fig. S21 and S22, ESI†).

In summary, we observed both MRE and RRE in the same Ag⁺–thiol coordination polymer in which the thiol ligand contains a β-turn structure and thus exhibits both the molecular and supramolecular chirality. Weakening in general the interactions between the ligands by introducing an AcO⁻ anion or minimizing the interactions between the heterochiral ligands in the coordination polymers leads to the disappearance of the nonlinear CD-ee relationship. This suggests that the interactions between heterochiral ligands are critical for the observation of RRE together with MRE. It is identified that the supramolecular chirality of the coordination polymers exhibit MRE when the CD signal (235 nm) is of molecular chirality origin of the amino acid residue in the ligand, while they exhibit RRE when the signals are of the supramolecular chirality origin of the ligand (275 nm) or of the Ag⁺–Ag⁺ chain in the coordination polymers (320 nm). Work is underway to clarify the mechanism for the interesting observation of both MRE and RRE in the same coordination polymers.

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Conflicts of interest
There are no conflicts to declare.

Notes and references