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Featured Article

Chiral Recognition by Flexible Coordination Polymers of Ag^+ with a Cysteine-Based Chiral Thiol Ligand That Bears a Binding Site

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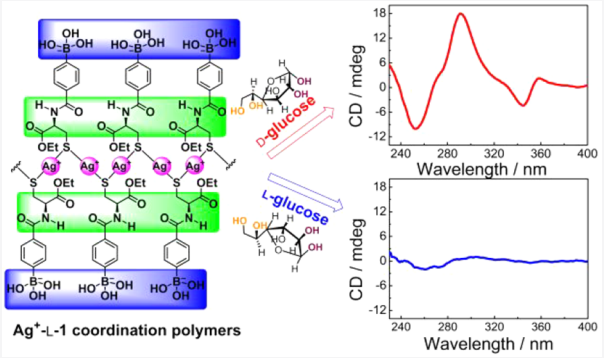
ABSTRACT: We report a new scheme for chiral recognition using coordination polymers of Ag^+ with a chiral thiol ligand that contains a binding group. *N*-Benzoyl-L-cysteine ethyl ester equipped with a boronic acid group at the para position of the phenyl ring forms coordination polymers with Ag^+ in alkaline aqueous solutions that exhibit excellent selectivity toward a D-glucose enantiomer over L-glucose, while the coordination polymers from the D-cysteine-based thiol ligand are specific for L-glucose. It is assumed that a conformation change occurs upon interaction of a saccharide molecule with the polymeric chain receptor, for which the next binding is promoted, leading to the highly effective chiral recognition, despite the flexible nature of the polymeric receptor.



INTRODUCTION

Chiral recognition is of vital importance not only in biomedical sciences but also in pharmacological research.[1] Many excellent chiral receptors hitherto reported operate in the classic mechanism of lock-and-key molecular recognition[2−5] and are thereby of a relatively rigid and, in a majority of the reported cases, a cyclic or pseudocyclic binding structure.[6−8] The most recent examples are presented by those bearing pore and cavity structures.[9−12]

In nature, however, enzyme−substrate interactions of high specificity are not due to a highly rigid binding pocket in the enzymes. Instead, enzymes provide a flexible interaction network of binding sites,[13] in which the substrate−enzyme binding takes place with an allosteric effect operative in the protein/enzyme of the polymeric structure. Crothers et al.[14] reported in 1972 that the transmission of allosteric effects in DNA alters its structural properties to exhibit a higher affinity for a drug. We therefore assumed that a well-designed supramolecular polymer of flexible structure may function under the allosteric mechanism for binding of a target molecule, affording improved affinity and selectivity.

As a proof-of-concept, we chose a coordination polymer of Ag^+ of a chiral thiol ligand that contains a binding group for monosaccharides, the phenylboronic acid derivatives of L/D-cysteine, as such polymeric receptors for chiral recognition of the saccharides. This is because the flexible $Ag^+\cdots Ag^+$ polymeric backbone holding the chiral thiol ligands makes their binding sites networked via interligand interactions, together with the $Ag^+\cdots Ag^+$ interaction (termed the argentophilic interaction[15]),[16−20] both of which can be switched on and off by tuning the solution medium pH and/or by chiral species binding, which can be probed by the characteristic spectral signals such as absorption and circular dichroism (CD). In the latter case, we would be able to observe an allosteric effect because a chiral species may require at least two ligands for interacting on the same side of the polymeric backbone, while the ligands are alternatively bound to the backbone up and down (Scheme 1). Binding of the first chiral species to two neighboring ligands on one side of the polymeric backbone would alter the steric relationship between the two neighboring ligands on the other side, better for the next binding of the chiral species. Therefore, only the very chiral species would interact with the polymeric receptor in a good manner, being both multivalent[21] and cooperative. This is expected to enhance the enantioselectivity of the molecular recognition, potentially allowing for a highly specific binding of a particular enantiomer by using the flexible receptors. We found that the flexible coordination polymers of Ag^+ with a chiral thiol ligand, *N*-benzoyl-L/D-cysteine ethyl ester, cysteine derivatives equipped with a boronic acid group (L/D-**1**; Scheme 1), exhibited highly enantioselective recognition for D- and L-glucose, respectively.

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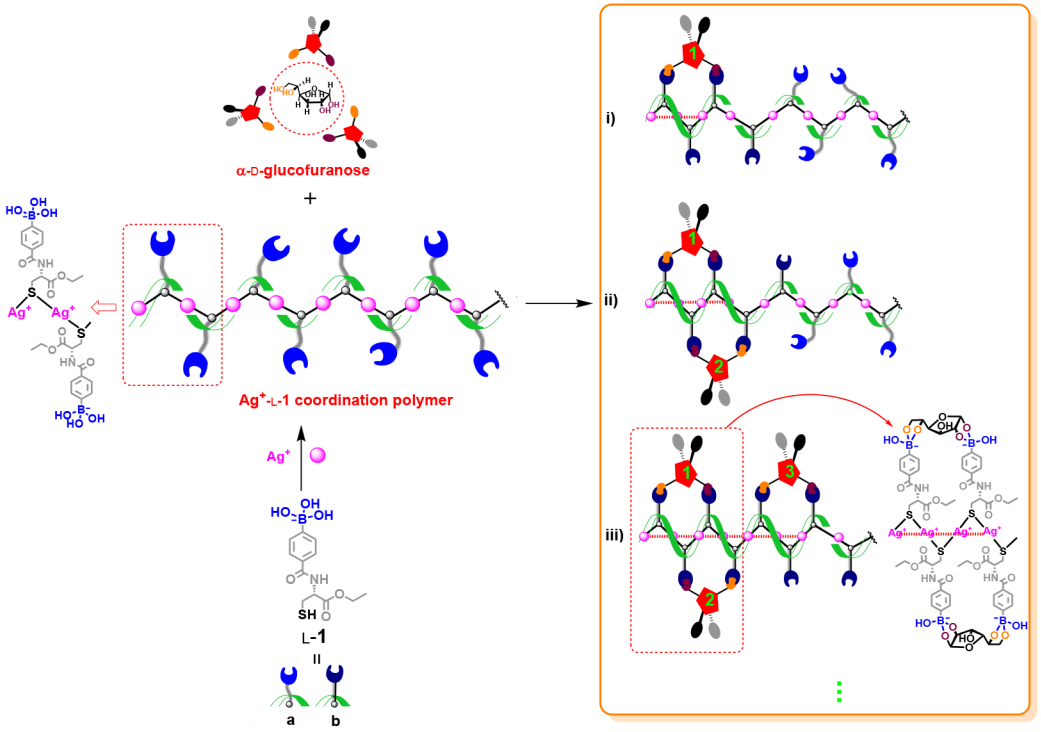
Scheme 1. Chiral Recognition of D-Glucose by a Coordination Polymer of Ag^+ with L-1 (a, Flexible Form; b, Rigid Form)[a]



[a]The first D-glucose molecule (labeled as **1**) binding to two boronic acid groups on one side of the polymeric backbone is expected to adjust the steric geometry of the two neighboring boronic acid groups on the other side, affording an enhanced binding of the next D-glucose molecule (labeled as **2**) and subsequently the enhanced binding of the third glucose molecule **3**, and so on. The red dashed lines represent the $Ag^+\cdots Ag^+$ interactions.

EXPERIMENTAL SECTION

Chemicals and Materials. All chemical reagents were of analytical grade purchased from local suppliers without further purification. ^1H and ^{13}C NMR spectra were obtained by Bruker Ascend III 500, 600, or 850 MHz spectrometers in dimethyl sulfoxide (DMSO)-d_6 using tetramethylsilane as an internal standard. Absorption spectra were recorded on a Varian Cary 300 UV spectrophotometer. CD spectra were recorded on a JASCO J-810 CD chiroptical spectrometer. High-resolution mass spectrometry (HRMS) data were acquired on a Bruker Impact II spectrometer. Dynamic light scatter (DLS) experiments were performed on a Malvern Nano S90 Mastersize. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 microscope. Transmission electron microscopy (TEM) images were obtained with a JEM 1400 microscope. All experiments were carried out at room temperature.

Synthesis of L-1. *p*-Hydroxycarbonylphenylboronic acid (0.5 mmol, 1.0 equiv), 0.06 mL of triethylamine, *N*,*N*′-dicyclohexylcarbodiimide (0.6 mmol, 1.2 equiv), and hydroxybenzotriazole (0.5 mmol, 1.0 equiv) in 20 mL of dichloromethane was stirred in an ice bath for 0.5 h, to which L-cysteine ethyl ester (L-CysOEt·HCl, 0.5 mmol, 1.0 equiv) was added and stirred for 4 h at room temperature. The mixture was filtered and washed three times by diluted HCl and saturated $NaHCO_3$. After evaporation of the organic solvent, the crude product was purified by chromatography on silica gel to obtain a white powder (38% yield). ^1H NMR (600 MHz, DMSO-d_6): δ 8.76 (d, J = 7.6 Hz, 1H), 8.22 (s, 2H), 7.86 (dd, J = 25.2 and 8.1 Hz, 4H), 4.56 (td, J = 8.4 and 4.8 Hz, 1H), 4.14 (dd, J = 7.1 and 4.2 Hz, 2H), 3.00 (ddd, J = 13.5, 8.6, and 4.8 Hz, 1H), 2.95−2.88 (m, 1H), 2.64 (t, J = 8.5 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (214 MHz, DMSO-d_6): δ 170.28, 166.66, 134.78, 133.82, 126.24, 60.71, 55.52, 24.88, 13.96 (the carbon atom next to a boron atom was not observed because of quadrupolar relaxation by a ^{11}B nucleus).[22] HRMS (FTICR MS ESI$^+$). Calcd for $C_{13}H_{17}NaBNO_5S$ ([M + CH_3OH − H_2O + Na]$^+$): m/z 334.0896. Found: m/z 334.0892.

D-**1** was similarly synthesized. ^1H NMR (500 MHz, DMSO-d_6): δ 8.73 (d, J = 7.5 Hz, 1H), 8.19 (s, 2H), 7.86 (dd, J = 21.6 and 8.2 Hz, 4H), 4.55 (td, J = 8.4 and 4.8 Hz, 1H), 4.13 (dd, J = 7.1 and 3.1 Hz, 2H), 2.99 (ddd, J = 13.4, 8.5, and 4.9 Hz, 1H), 2.95−2.86 (m, 1H), 2.66 (t, J = 8.5 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (214 MHz, DMSO-d_6): δ 170.87, 167.26, 135.37, 134.41, 126.82, 61.29, 56.11, 25.47, 14.55 (the carbon atom next to a boron atom was not observed because of quadrupolar relaxation by a ^{11}B nucleus).[22] HRMS (FTICR MS ESI$^+$). Calcd for $C_{13}H_{17}NaBNO_5S$ ([M + CH_3OH − H_2O + Na]$^+$): m/z 334.0896. Found: m/z 334.0889. Synthetic procedures are given in Scheme S1. Detailed ^1H and ^{13}C NMR and HRMS spectra of L/D-**1** are supplied in Figures S15−S20.

Buffer Solutions. Except otherwise indicated, buffer solutions of pH 6.5, 7.0, 8.0, 8.5, 8.8, and 9.0 were prepared by mixing 50 mM HEPES and 50 mM HEPES-Na at different ratios, and those of pH 9.2, 10.0, and 10.5 were similarly made by mixing 50 mM $NaHCO_3$ and 50 mM Na_2CO_3. The pH value of the buffer solution was adjusted by monitoring the pH with a pH meter (Mettler Toledo Five Easy Plus).

Preparation of Ag^+-L-1 Coordination Polymer. A total of 10.0 μL of a L-**1** stock solution (5 mM) and 5.0 μL of a $AgNO_3$ stock solution (10 mM) were added into 2.0 mL of 1:1 (v/v) ethanol (EtOH)/0.05 M buffers to obtain a Ag^+-L-**1** coordination polymer, in which the concentrations of L-**1** and Ag^+ are both 25 μM. A Ag^+-D-**1** coordination polymer was similarly synthesized.

Recognition of D/L-Glucose. To the prepared solution of a Ag^+-L-**1** coordination polymer was added 0.5 μL of a D-glucose stock solution (0.1 M) every time, followed by recording of the absorption and CD spectra, until a final concentration of glucose of 0.5 mM. The recognition of L-glucose was similarly carried out.

Selective and Competitive Measurements. The interfering saccharide was similarly added to the buffer solution of Ag^+-L-**1**

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containing 50% EtOH by volume, in the absence or presence of D-glucose. The absorption and CD spectra of the solutions were recorded in a few minutes after mixing.

RESULTS AND DISCUSSION

Formation of Coordination Polymers of Ag^+ with L-1. The formation of the polymers in aqueous buffer solutions was confirmed by the observation of an absorption at 350 nm at pH 7.0, assigned to the ligand-to-metal−metal charge-transfer state of the in situ formed chromophore relating to extended $Ag^+\cdots Ag^+$ interaction (Figure 1a).[15] A similar observation was

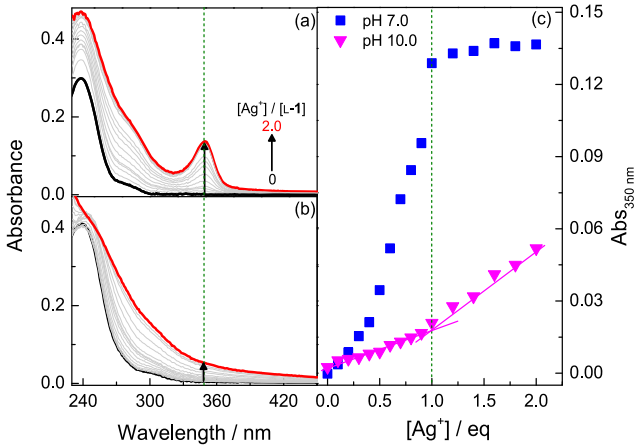

Figure 1. Absorption spectra of L-**1** in 1:1 (v/v) EtOH/0.05 M (a) pH 7.0 and (b) 10.0 buffers of Ag^+ of increasing concentration. (c) Plots of absorbance at 350 nm as a function of Ag^+. [L-**1**] = 25 μM; [Ag^+] = 0−50 μM.

made at pH 8.0, but not at higher pH such as 8.8 and 10.0. In the latter cases, a boronic acid group in the ligand exists in the anionic form, in which they repulse each other in the polymeric backbone,[16] weakening or even breaking the $Ag^+\cdots Ag^+$ interaction, where the absorption and CD at 350 nm were weakened or not observed anymore (Figures 1b and S1a). This not only supports the contribution of the interligand interaction in stabilizing the coordination polymers but also provides a means of controlling the on-and-off $Ag^+\cdots Ag^+$ interaction and related spectral signals. Absorbance at 350 nm as a function of [Ag^+] confirms the 1:1 stoichiometry (Figure 1c), confirming the $-(Ag\text{-}SR)_n-$ polymeric structure because the DLS data show that in solutions of pH 7.0 and 10.0 large species of diameters of 325 ± 29 and 447 ± 223 nm, respectively, exist (Figure S1b).

Chiral Recognition of Glucose. Given the pH dependence of the interaction of boronic acid with *cis*-1,2- or 1,3-diol,[23] we optimized the solution pH for the interaction of a coordination polymer with monosaccharides (Figure S2a,b). This leads to an optimal pH 8.8 at which the addition of D-glucose results in the largest change in the CD signal (Figure S2c).

Note that at pH 8.8 $Ag^+\cdots Ag^+$ interaction does not happen in the Ag^+-L-**1** coordination polymers, for which the absorption and CD signal at 350 nm are not observed. Upon the introduction of D-glucose, absorption (Figure S3a) and CD (Figure 2a) spectra of the coordination polymers undergo substantial changes, showing increasing CD signal and absorbance at 350 nm, which means that the $Ag^+\cdots Ag^+$ interaction is turned on by the interaction of D-glucose.

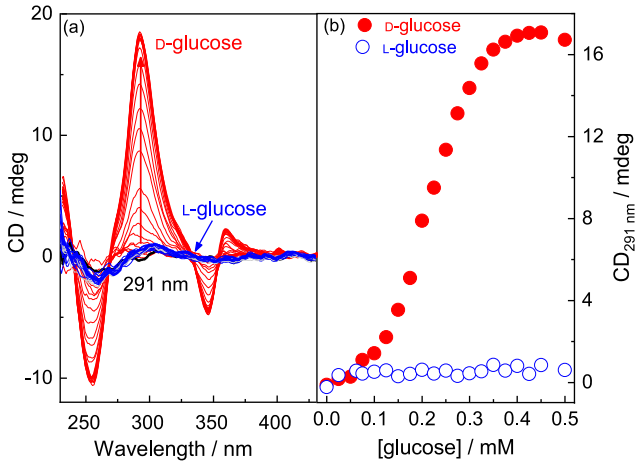

Figure 2. (a) CD spectra of Ag^+-L-**1** in the presence of D-glucose (red lines) and L-glucose (blue lines) of increasing concentration. (b) Plots of the CD signals at 291 nm against the concentration of D/L-glucose in 1:1 (v/v) EtOH/0.05 M pH 8.8 buffer. [L-**1**] = [Ag^+] = 25 μM; [glucose] = 0−0.5 mM.

However, in the presence of L-glucose, not much change was found in the absorption (Figure S3b) and CD (Figure 2a) spectra, with the CD signal at 291 nm being $^1/_{17}$ of that in the presence of D-glucose (Figure 2b). The flexible Ag^+-L-**1** coordination polymers, therefore, exhibit a distinct chiral recognition toward the D-glucose enantiomer over the L counterpart. The limit of detection of Ag^+-L-**1** for D-glucose was evaluated to be 4.1×10^{-5} M (Figure S4). When Ag^+-D-**1** coordination polymers were employed, chiral recognition for L-glucose over D-enantiomer was observed (Figure S5). A Hill coefficient[24] of n = 3.9 was obtained for the binding of D-glucose with a Ag^+-L-**1** polymeric receptor (Figure S6), which is much higher than 1, indicating the cooperative nature of the interaction of the flexible coordination polymers with D-glucose. The fact that the CD signal varies in a sigmoidal manner with the concentration of D-glucose (Figure 2b) does support the cooperative characteristic or allosteric effect of the glucose interaction (Scheme 1), for which the binding of one D-glucose molecule preorganizes the vacant boronic acid binding sites on the other side of the polymeric backbone, which become more favorable for binding of the next D-glucose molecule. Other metal cations such as Ca^{2+}, Cd^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and Al^{3+} were also taken to form complexes with L-**1** for chiral recognition of D-glucose, but no significant spectral response was observed (Figure S7). Therefore, Ag^+ is necessary for chiral recognition, in the way of forming Ag^+-L-**1** coordination polymer that undergoes off−on switching of the $Ag^+\cdots Ag^+$ interaction upon glucose binding.

This alternative interaction of D-glucose molecules along the polymeric chain would lead to the rigidizing of the polymeric chain (Scheme 1, right). This was supported by the DLS data in that the size distribution of the Ag^+-L-**1** polymers became narrower when D-glucose was introduced and that the polydispersity index also decreased from 0.395 to 0.310, whereas that L-glucose, not recognized by the polymeric receptor, leads to a broader size distribution (Figure S8a). This difference in the size distribution was also reflected in the morphologies of the coordination polymers, being of a rodlike structure when binding to L-glucose, identical with the structure of free Ag^+-L-**1** polymers, but a fibril structure with D-glucose (Figure S8b). The broadened proton resonance

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signals of L-**1** in the presence of Ag^+ suggest the formation of a Ag^+-L-**1** coordination polymer (Figure S9). Through DOSY experiments, M_w of a Ag^+-L-**1** coordination polymer is evaluated to be 5987 (diffusion coefficient $D = 1.04 \times 10^{-10}$ m^2/s), suggesting a polymerization degree of $n = 15$. In the presence of D-glucose, the diffusion coefficient decreased to $D = 9.48 \times 10^{-11}$ m^2/s, indicating a higher M_w of 7904, but the polymerization degree cannot be evaluated because it is not clear whether all of the boronic acids on the polymeric chain are involved in binding with D-glucose (Table S1).

CD-ee (ee = enatiomeric excess) dependence serves as another support. CD signals of the Ag^+-**1** coordination polymer vary in a negative nonlinear way with ee of the chiral thiol ligand **1** in 1:1 (v/v) EtOH/buffer of pH 8.5 (Figures 3 and S10c), which was previously termed as the racemate rules effect.[25−28] This means that D-**1** and L-**1** prefer to appear in pairs to bind on the Ag^+-**1** polymeric backbone, likely with all D-**1** ligands on one side and all L-**1** ligands on the other side of the backbone. A Ag^+-**1** coordination polymer shows the same CD profiles at different ee of **1** (Figure S10), whereas in some of the previous reports that also exhibit negative nonlinear CD-ee dependence, the CD profiles were ee-dependent.[18,19,27] Interestingly, when a racemic mixture of glucose was added, the CD-ee dependence turns out to be linear (Figures 3 and S10d). It is assumed that D- and L-glucose selectively bind to the L-**1** and D-**1** ligands on two sides of the polymeric backbone, respectively, in agreement of the chiral recognition of D-glucose by Ag^+-L-**1** and of L-glucose by Ag^+-D-**1**.

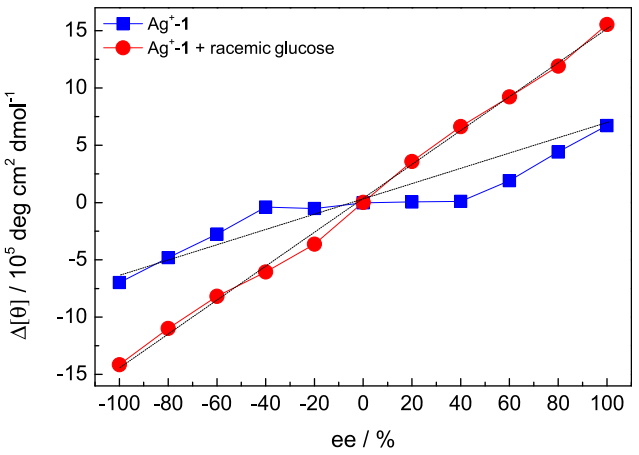

Figure 3. Plots of the CD signals of Ag^+-**1** as a function of ee of **1** in the absence (blue squares) and presence (red circles) of racemic glucose in 1:1 (v/v) EtOH/0.05 M pH 8.5 buffer. $\Delta[\theta] = [\theta]_{291\ nm} - [\theta]_{254(1)\ nm}$. [**1**] = [$Ag^+$] = 40 μM; [D-glucose] = [L-glucose] = 0.8 mM. The straight dashed black lines are auxiliary lines that help with the discrimination of linear or nonlinear CD-ee dependence.

Selectivity. Selectivity was next examined in terms of the response to individual saccharide and under competitive conditions. The CD spectrum of Ag^+-L-**1** in 1:1 EtOH/pH 8.8 buffer practically does not change when monosaccharides other than D-glucose are introduced, indicating an excellent selectivity for D-glucose (Figure S11a,b). Disaccharides and even polymeric sugars also did not cause spectral change of the Ag^+-L-**1** coordination polymers (Figure S12). In competitive experiments, however, D-fructose interferes with the recognition of D-glucose at pH 8.8 (Figure S11c). This is understandable because fructose interacts with monoboronic acid much more strongly.[29] It is known that the optimal pH for the interaction of boronic acid with an individual saccharide exhibits subtle differences. We expected that the multivalent interactions of the boronic acid groups on the polymeric backbone with a monosaccharide molecule may magnify the differences, affording different optimal pH values for an individual monosaccharide. We therefore explored to further improve the binding selectivity for glucose under competitive conditions. The CD spectral responses of Ag^+-L-**1** to various saccharides at different pH values (Figure S13) do indicate that the response of Ag^+-L-**1** toward saccharide is pH-dependent, for which a better selectivity for glucose can be achieved in buffers of pH 8.8, 9.2, and 9.5. In the competitive experiments performed at pH 9.2 (Figure 4) and 9.5 (Figure S14), we found that a much better selectivity toward D-glucose can be obtained in a pH 9.2 buffer (Figure 4a−c).

The size distribution of the Ag^+-L-**1** coordinate polymers at this pH, broad over 217−535 nm, remains unchanged in the presence of D-fructose; it however becomes much narrower in the presence of D-glucose even with the coexistence of D-fructose (Figure 4d). Moreover, SEM images show that the Ag^+-L-**1** coordination polymers in the presence of D-fructose are rodlike (Figure 4f), similar to the Ag^+-L-**1** coordination polymers themselves (Figure 4e), whereas they turn out to be fibril-like when binding to D-glucose (Figure 4g). It appears that the multivalent nature of the interaction of boronic acid groups on this polymeric backbone affords an enlarged difference in the optimal pH values for interactions with glucose and fructose, for which a pH can be chosen for a better selectivity for glucose under the competitive conditions.

CONCLUSIONS

We developed a new strategy for highly efficient chiral recognition using flexible a Ag^+-L-**1** or a Ag^+-D-**1** coordination polymer from a chiral thiol ligand. In the chosen examples of recognition of D- or L-glucose, boronic acid-containing cysteine-based chiral ligands L- or D-**1** were organized into a Ag^+-L-**1** or a Ag^+-D-**1** coordination polymer to function as a highly enantioselective multivalent receptor for D- or L-glucose, respectively. Only for both sets of the two neighboring boronic acid groups on the Ag^+-L-**1** polymeric backbone, for example, matching well with the requirement of interacting with two consecutive D-glucose molecules, can an effective interaction occur with optimal $Ag^+\cdots Ag^+$ interactions in the coordination polymers, leading to characteristic CD and absorption signals. The system demonstrates an extremely high enantioselectivity with binding to one enantiomer but practically no binding with the other enantiomer. This polymeric allosteric receptor is also distinctive in that the signaling $Ag^+\cdots Ag^+$ interaction can be made on-and-off via solution pH tuning and/or guest binding and the optimal binding pH could be obtained because of enlarged differences in the optimal pH values among a set of monosaccharides between the polymeric receptor and the small ligand containing the same binding group. Our work opens up a new avenue to enantioselective chiral recognition by using dynamic coordination polymers of a flexible chiral ligand that contains binding sites for the chiral species, easing dramatically the synthetic challenges to classic receptors of rigid structure operating under the lock-and-key mechanism. The strategy proposed here can, in principle, be applied to other chiral target molecules via ligand design using a suitable binding site.

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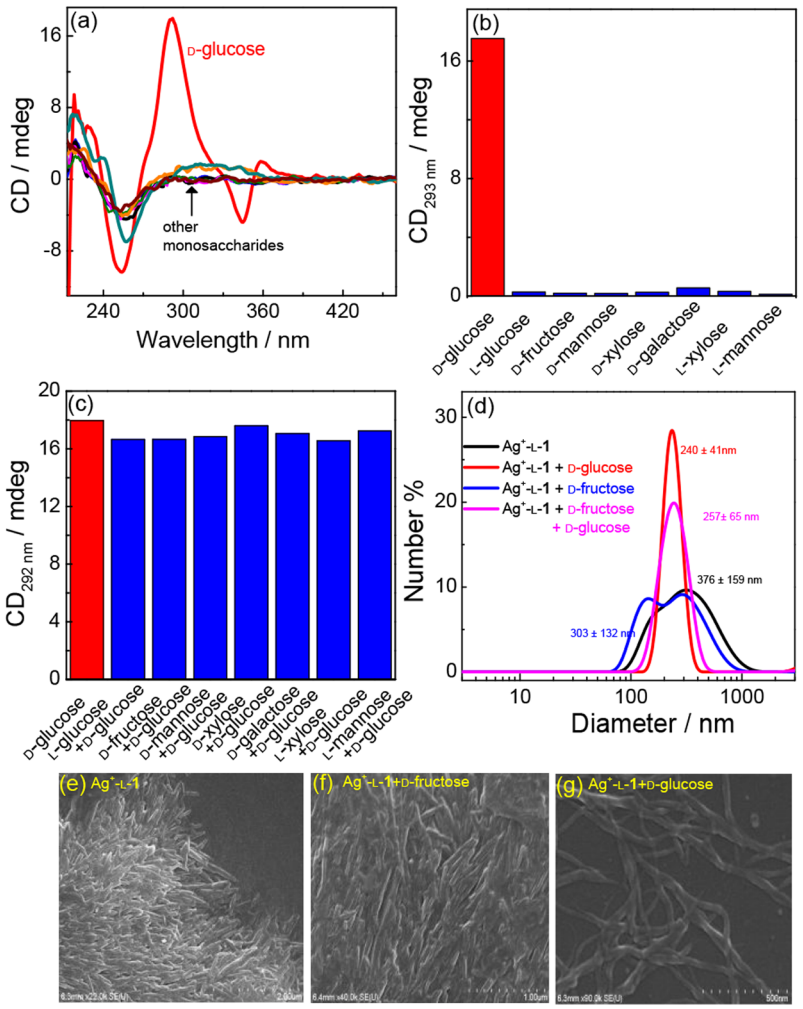

Figure 4. (a) CD spectra of Ag^+-L-**1** in a 1:1 (v/v) EtOH/0.05 M pH 9.2 buffer in the presence of monosaccharides: D-glucose, L-glucose, D-fructose, D-mannose, D-xylose, D-galactose, L-xylose, and L-mannose. (b) Histogram graph of the CD signal at 293 nm versus saccharide identity and (c) histogram graph of the CD signal in the presence of D-glucose together with other monosaccharides. (d) DLS size distributions of Ag^+-L-**1** coordination polymers in the absence and presence of 0.4 mM D-glucose or 0.5 mM D-fructose or both of them. SEM images of Ag^+-L-**1** (e) in the presence of D-fructose (f) or D-glucose (g). [L-**1**] = [Ag^+] = 25 μM; [D-glucose] = 0.4 mM; [other monosaccharides] = 0.5 mM.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00104.

Synthesis procedures, absorption and CD spectra, DLS data, TEM images, and ^{1}H and ^{13}C NMR and HRMS spectra of L/D-**1** (PDF)

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Notes

The authors declare no competing financial interest.

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