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Chiral Synthesis of a Co(III) Complex on Ammonium Bilayer Templates[1)]

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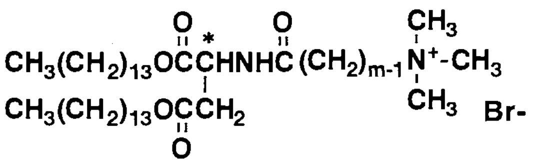
Bilayer membranes of chiral double-chain ammonium amphiphiles incorporated an anionic tridentate ligand in enantiomeric orientations, as confirmed by induced circular dichroism. Complexation of aqueous $CoSO_4$ with the bilayer-bound ligand led to formation of chiral Co(III) complexes.

Regular molecular arrangements in surface monolayers and dispersed bilayers provide specific binding sites for guest molecules and ions. For example, Landau et al. reported that monolayers of amino acid derivatives could discriminate the enantiomer of some amino acids at the air/water interface.[2)] Certain dyes are specifically bound to chiral micelles[3)] and chiral bilayers,[4,5)] as indicated by induced circular dichroism (ICD). It is clear that these chiral assemblies possess highly ordered chiral spaces that are capable of organizing guest molecules. However, these chiral bindings have not been used for synthetic purposes.



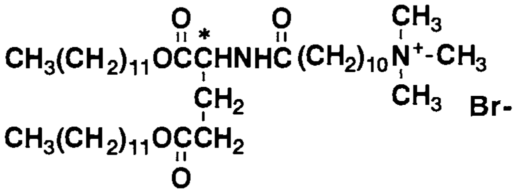
$$\begin{array}{l} CH_3(CH_2)_{13}O\overset{O}{\overset{\|}{C}}\overset{*}{C}HNH\overset{O}{\overset{\|}{C}}(CH_2)_{m-1}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_3 \quad Br^- \\ CH_3(CH_2)_{13}O\underset{O}{\underset{\|}{C}}CH_2 \end{array}$$

$2C_{14}$-L-AspC_mN^+

m = 2, $T_c = 28.5$ ℃

6, $T_c = 29.5$ ℃

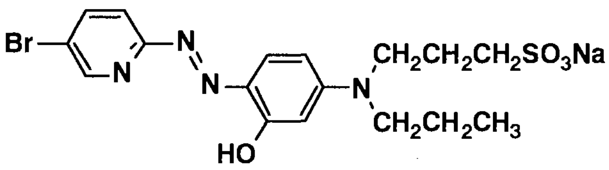
11, $T_c = 46.5$ ℃



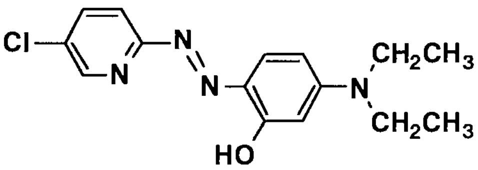
$$\begin{array}{l} CH_3(CH_2)_{11}O\overset{O}{\overset{\|}{C}}\overset{*}{C}HNH\overset{O}{\overset{\|}{C}}(CH_2)_{10}\overset{CH_3}{\underset{CH_3}{N^+}}\text{-}CH_3 \quad Br^- \\ \qquad\qquad\qquad CH_2 \\ CH_3(CH_2)_{11}O\underset{O}{\underset{\|}{C}}CH_2 \end{array}$$

$2C_{12}$-L(D)-Glu$C_{10}N^+$

$T_c = 33.0$ ℃

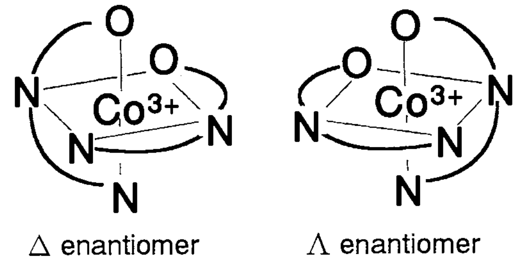


5-Br-PAPS



5-Cl-PADAP

In this paper, we describe the first example of chiral complexation using $2C_n$-L-Asp-C_mN^+ and $2C_n$-L-Glu-C_mN^+ as chiral bilayer templates. Synthesis and morphology of these bilayers were reported previously.[6] 5-Br-PAPS was selected as a ligand, because it has a structural feature common to methyl orange which was reported to bind specifically to chiral bilayers.[4,5] This ligand can form inert 2:1 complexes with transition metal ions such as Co(III), and the resulting complexes exist as Δ and Λ enantiomers.



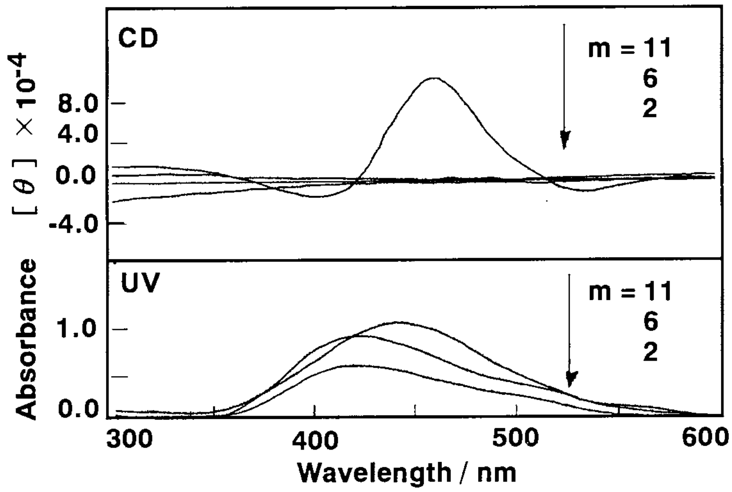


Fig. 1. UV-vis and ICD spectra of 5-Br-PAPS bound to aqueous bilayers of $2C_{14}$-L-Asp-C_mN^+(m=2, 6, 11). 5 °C, 5-Br-PAPS 25 μM(1 M = 1 mol dm^{-3}), Bilayer 50 μM.

Figure 1 shows UV-vis and CD spectra of 0.5 equivalent of 5-Br-PAPS bound to $2C_{14}$-L-Asp-C_mN^+ (m = 2, 6, 11). The matrix bilayers do not display CD peaks in the 300-to-600 nm region. A moderately large CD peak was found in the case of m = 11, but it was not detectable for shorter spacers (m = 2 and 6). Conceivably 5-Br-PAPS is bound in the spacer region and the binding site must be large enough to specifically accommodate guest molecules. On the other hand, the tail length (C_n part) was not influential, because ICD spectra were almost unchanged for a series of host bilayers of $2C_n$-L-Asp-$C_{11}N^+$ (n = 12, 14, 18)(data not shown). Mirror-image CD spectra were observed for 5-Br-PAPS (0.25 equiv.) bound to $2C_{12}$-L-Glu-$C_{11}N^+$ and $2C_{12}$-D-Glu-$C_{11}N^+$(Fig. 2). This clearly indicates that the ICD spectra correspond to the chirality of the amino acid residue. The chiral environment also depended on the kind of the amino acid, since the L-aspartate

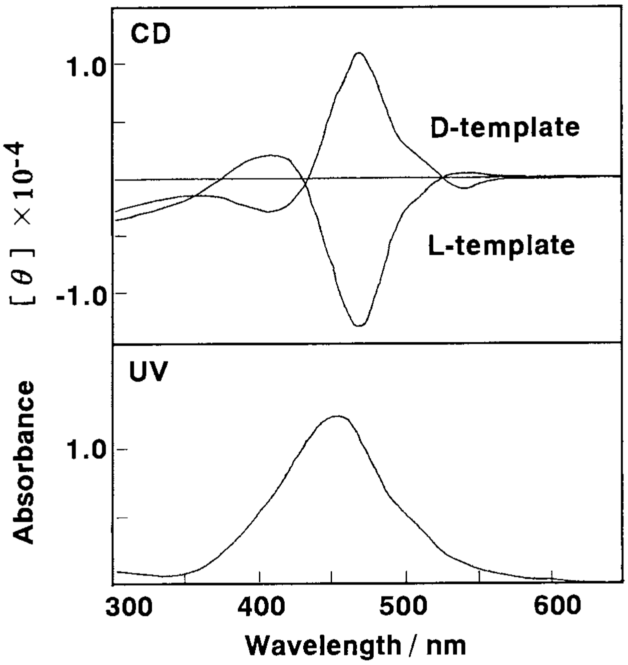


Fig. 2. UV-vis and ICD spectra of 5-Br-PAPS bound to aqueous bilayers of $2C_{12}$-L-Glu-$C_{11}N^+$ and $2C_{12}$-D-Glu-$C_{11}N^+$ at 5 °C. 5-Br-PAPS 25 μM, $2C_{12}$-L(D)-Glu-$C_{11}N^+$ 100 μM. UV spectra are identical in both systems.

residue in $2C_{14}$-L-Asp-$C_{11}N^+$ and the D-glutamate residue in $2C_{12}$-L-Glu-$C_{11}N^+$ gave analogous Cotton effects.

The organized 5-Br-PAPS was subsequently subjected to metal complexation. Half equivalent of $CoSO_4$ was allowed to react with 5-Br-PAPS/bilayer dispersions at 5 ℃ for one week. After solvent removal, the residue taken up in methanol was applied to a cation exchange column (Whatman CM-52, Na^+ type) to separate the product metal complex. IR and UV-vis spectra of the isolated complexes were identical with the reported data for Na[Co(III)(5-Br-PAPS)$_2$].7) This indicates that the initially formed Co(II) complex must have been oxidized by air during the chelation process, and that the chiral bilayer matrix was completely removed. This Co(III) complex is enantiomeric(Δ and Λ forms). They are in the d^6 electronic configuration and are substitution inert.8) Thus, the product complexes would possess the same stereochemistry as those of their unoxidized intermediates.

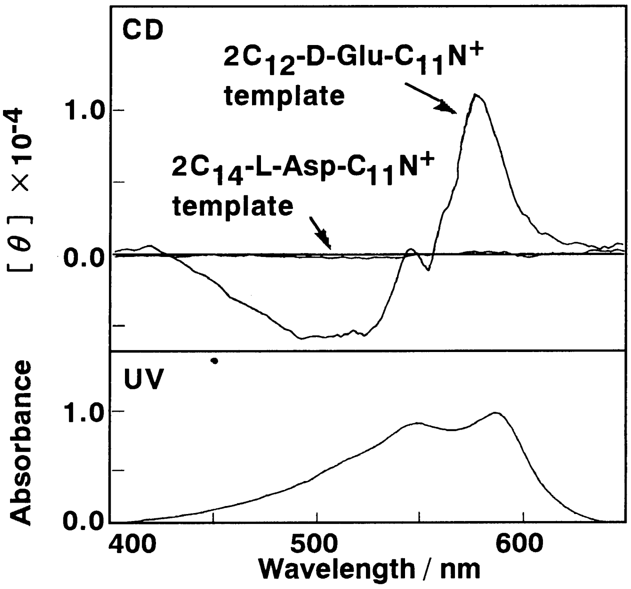


Fig. 3. UV-vis and CD spectra of Na[Co(III)(5-Br-PAPS)$_2$] in water, 12 μM. Bilayer template, $2C_{14}$-L-Asp-$C_{11}N^+$ and $2C_{12}$-D-Glu-$C_{11}N^+$.

As shown in Fig. 3, the complex prepared on the $2C_{14}$-L-Asp-$C_{11}N^+$ template did not show any Cotton effect, whereas the complex isolated from the $2C_{12}$-D-Glu-$C_{11}N^+$ matrix gave $[\theta]_{max}$ of 12000 deg · cm^2 · $dmol^{-1}$ at 580 nm. This is a direct proof of chiral synthesis of Na[Co(III)(5-Br-PAPS)$_2$] on a chiral bilayer template. Unfortunately, we could not determine the optical purity of the chiral product.9) If we assume that optically pure [Co(III)(5-Cl-PADAP)$_2$]Cl possess a $[\theta]$ value similar to that of Na[Co(III)(5-Br-PAPS)$_2$], the Co(III) complex synthesized on the $2C_{12}$-D-Glu-$C_{11}N^+$ template would have an optical yield of ca. 20% e.e.

The contrasting template effects of $2C_{14}$-L-Asp-$C_{11}N^+$ and $2C_{12}$-D-Glu-$C_{11}N^+$ are intriguing. We can conceive at least two explanations. One is the spatial difference of the ligand binding site due to the structural difference of connectors; glutamate vs. aspartate residues. It is possible that the bilayer of $2C_{14}$-L-Asp-$C_{11}N^+$ gives a limited binding space that allows specific ligand binding but not chiral complexation. Then the ligand molecule removed from the specific site alone would undergo complexation with Co(II) ion, or the chiral binding site would have to be extensively perturbed to allow the less specific complexation process. The second possibility may be related to bilayer morphologies. Formation of helical superstructures from $2C_{12}$-L(D)-Glu-$C_{11}N^+$ has been confirmed by optical microscopy,11) and by transmission and scanning electron microscopies.[6,12] In contrast, the chiral $2C_{14}$-L-Asp-$C_{11}N^+$ bilayer forms fibrous aggregates, but not helical superstructures. In fact, we confirmed by optical microscopy that $2C_{12}$-D-Glu-$C_{11}N^+$ with 0.25 equiv. of 5-Br-PAPS formed helical superstructures, but that $2C_{12}$-D-Glu-$C_{11}N^+$ with 0.5 equiv. of 5-Br-PAPS did not. The former system acted as chiral template, but not the latter. Therefore, the formation of a helical superstructure from bilayer/ligand composites appears to be directly related to enantiomeric complexation.

Toda et. al. reported topochemical reactions in co-crystals made of chiral hosts and photoactive guests.[13] The dye/bilayer composite possesses features common to these co-crystals. Most importantly, exaggerated chiralities of bilayers are observed in the crystalline state, and guest molecules are bound in highly specific manners. The concept described in this paper will be applicable to other metal complexation reactions.

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9) Yamagishi reported enantiomeric separation of a related complex, [Co(III)(5-Cl-PADAP)$_2$]Cl on a Λ-Ru(1,10-phenanthrolin)$_3^{2+}$-montmorillonite column.[10] Enantiomeric separation of the present product was performed without success by using the following columns of Daicell Co.: CHIRALCEL OR-D(solvent; CH_3CN/H_2O=60/40 and 80/20, aq $HClO_4$(pH 2.0)/CH_3CN = 40/60), CHIRALCEL OD(solvent; CH_3OH), CHIRALCEL OJ(solvent; CH_3OH), CHIRALPAK AD(solvent; CH_3OH).
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