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Chirality Control of a Cu(I) Complex of Boronic-acid-appended Phenanthrolines by Sugars. A Preliminary Step toward the Total Chain Helicity Control by a Chain-end Sugar-binding

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Abstract: Compound **1** which has a 1,10-phenanthroline moiety to constitute the helical structure and a boronic acid moiety to bind saccharides was synthesized. The Cu(I) complex (as $\mathbf{1}_2$·Cu(I)) gave the different CD spectra reflecting the helicity, which is regulated by the absolute configurational structure of saccharides. Thus, the P versus M helicity of the complex can be controlled by the boronic acid-saccharide interaction. The results show that the terminal boronic acid group is useful to create chiral helical structure, the helicity of which is governed by a sugar library.

Helical complexes have been of great concern as examples of self-assembled supramolecular structures in an artificial system and as a model for the DNA and RNA structures in nature.[1] Among them, one astonishing example is the chirality control of the twisting direction in the helical structure.[2-7] These systems are created by introduction of chiral substituents into "helicates". Meanwhile, Hamilton *et al.*[8] demonstrated that the self-assembled helical metal complexes with terminal hydrogen-bonding sites are useful for the recognition of dicarboxylic acids. The results imply that the host-guest-type interaction at the helix end may crucially control the twisting direction of the total chain helicity. Recently, it has been shown that boronic acid-saccharide covalent interactions which readily and reversibly form in aqueous media represent an important alternative binding force for the recognition of saccharides and related molecular species.[9] Here, it occurred to us that the chirality of the helical metal complexes produced from helicates bearing a terminal boronic acid group may be reversibly controlled by the boronic acid-saccharide interaction. If this working hypothesis is correct, it follows that a saccharide library containing abundant chirality resources is useful to create a variety of helical structures. As the first step to test this intriguing working hypothesis, we designed compound **1** which has a 1,10-phenanthroline moiety to constitute the helical metal complex and an *o*-aminomethylphenyl boronic acid moiety to bind saccharides[10] within a molecule. Interestingly, we have found that added saccharides can influence the equilibrium between plus (P) and minus (M) enantiomers, reflecting their absolute configurational structure.

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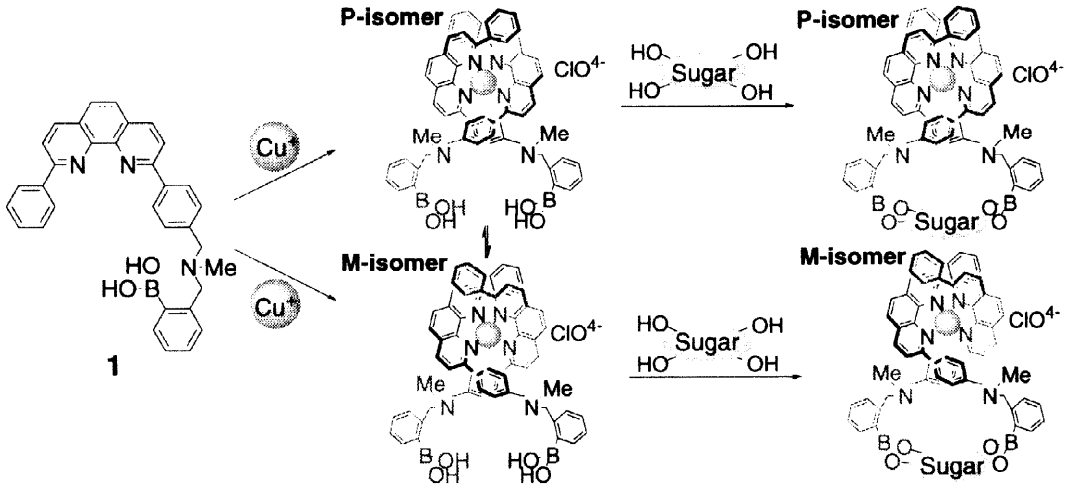
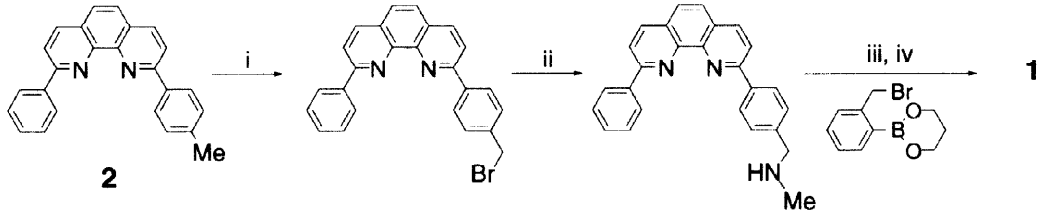


Compound **1** (mp 174-179 °C) was synthesized from 2-phenyl-9-tolyl-1,10-phenanthroline (**2**) according to Scheme 1 and identified by ^{1}H NMR and IR spectral evidence and elemental analysis.



Scheme 1 *Reagents and conditions* [yields] : i, NBS, AIBN, CCl_4, reflux ; ii, $MeNH_2$, CCl_4 [62 %, calculated from *2*] ; iii, K_2CO_3, MeCN, reflux ; iv, H_2O [53 %]

The measurements of absorption and CD spectroscopies were carried out in MeOH : MeCN = 1 : 1 (v/v) at 25 °C. Figure 1 shows the absorption spectral change induced by the Cu(I) (added as $[Cu(MeCN)_4]ClO_4$) addition. The plots of the absorbance against [Cu(I)] / [**1**] (Fig. 2) afford a clear break-point at 0.5, indicating that the complex consists of one Cu(I) and two **1** ligands (as illustrated above). In the subsequent CD measurements which are not so sensitive as the absorption spectral measurements, we enhance the concentrations up to [**1**] = 0.200 mmol dm^{-3} and [Cu(I)] = 0.100 mmol dm^{-3}. Judging from the sharp break-point in Fig. 2, they should be fully converted to the $\mathbf{1}_2$·Cu (I) complex.

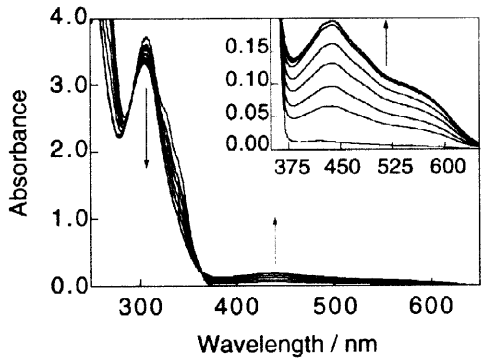


Fig. 1. Absorption spectral change of **1** (0.100 mmol dm^{-3}) with increasing Cu(I) concentration

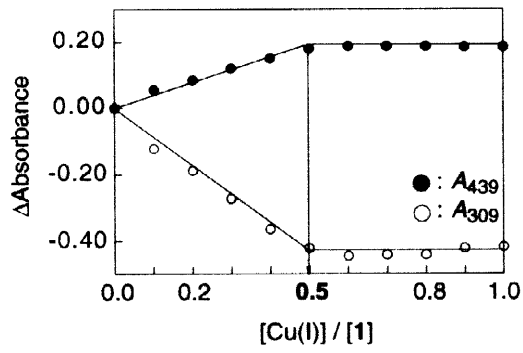


Fig. 2. Plots of absorbance versus [Cu(I)] / [**1**]

When D-glucose was added to the $\mathbf{1}_2$·Cu(I) complex, the CD bands appeared at 290-360 nm region and 400-600 nm region (MLCT region) gradually (Fig. 3). This CD appearance reflects the slow D-glucose binding to the boronic acid groups in the organic medium and means that one enantiomer of the ternary complex has become excess over the other. In the following experiments, therefore, we measured the CD spectra after 12 h. The continuous variation plots of CD intensity versus [$\mathbf{1}_2$·Cu(I)] / ([$\mathbf{1}_2$·Cu(I)] + [D-glucose]) provided a maximum at 0.5, indicating that the ternary complex consists of 1 : 1 stoichiometric $\mathbf{1}_2$·Cu(I) and D-glucose (Fig. 4). These spectroscopic data consistently support the complexation mode as illustrated above: that is, the $\mathbf{1}_2$·Cu(I) complex binds D-glucose with two boronic acid-diol interactions to form a macrocyclic structure. Thus, the chirality in the D-glucose moiety is transmitted to the helicity in the metal complex moiety. In D-glucose the CD sign at the MLCT region is positive. This means that the ternary complex is classified into the P isomer[2, 3]: that is, D-glucose has induced the clockwise twisting motif in the 1,10-phenanthroline-based helicates.

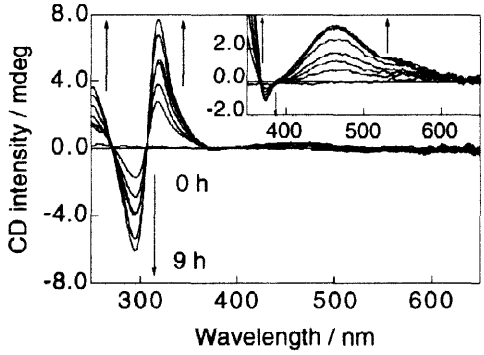


Fig. 3. Time dependence of the CD appearance after the addition of D-glucose (0.100 mmol dm^{-3}): cell length 0.1 cm; (inserted) cell length 1.0 cm

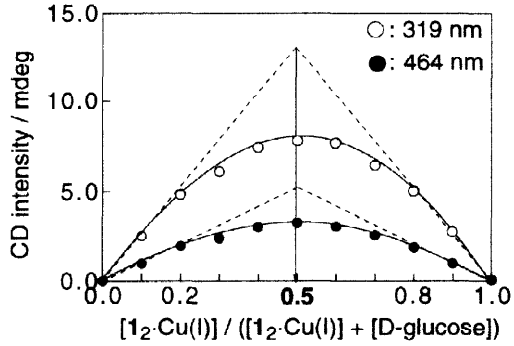


Fig. 4. Continuous variation plots: the [$\mathbf{1}_2$·Cu(I)] + [D-glucose] concentration was maintained constant (0.200 mmol dm^{-3})

The CD spectroscopic data obtained in the presence of various monosaccharides are summarized in Table 1. Examination of Table 1 raises an intriguing coincidence between the CD sign of MLCT region (*i.e.*, the complex helicity) and the absolute configuration of 3-OH: that is, when 3-OH is the (S)-configuration ("up" to the pyranose ring: D-glucose, D-fucose, D-galactose, D-xylose, and D-mannose), the ternary complex tends to adopt the P-helicity, whereas when 3-OH is the (R) configuration ("down" to the pyranose ring: D-arabinose and D-allose), it tends to adopt the M-helicity. Conceivably, when two **1** molecules wind themselves around Cu(I), the 3-OH group regulates the twisting direction.

In conclusion, the present study has evidenced that the saccharide-binding to the edge of the metal complex is effective enough to control the complex helicity. This is a preliminary step toward the total chain helicity control by a chain-end saccharide-binding. One strong advantage of the present system is to use a saccharide library with natural, abundant resources as a chiral trigger through a reversible binding process. We believe that the chirality of high molecular-weight with the terminal boronic acid group can be also controlled by the reversible complexation with saccharides.

Table 1. The CD spectroscopic data obtained in the presence of various monosaccharides[a)]

Monosaccharides	π–π* band[b)]			MLCT band[c)]		Structure of monosaccharides	
	$\lambda_{max\ or\ min}$ / nm (CD max or min intensity / mdeg)		λ_0 /nm		$\lambda_{max\ or\ min}$ / nm (CD max or min intensity / mdeg)	1, 2-diol	3-OH
D-Glucose	319.0 (25.61)	295.0 (-20.34)	307.0	P	463.5 (10.23)	down	up
D-Fucose	322.0 (5.25)	299.5 (-3.38)	308.0	P	480.5 (2.31)	down	up
D-Galactose	321.5 (3.06)	290.0 (-1.97)	308.0	P	498.0 (1.38)	down	up
D-Xylose	318.0 (1.85)	297.5 (-0.51)	302.0	P	458.0 (0.64)	down	up
D-Mannose	319.0 (0.89)	296.0 (-0.86)	309.0	P	463.5 (0.50)	up	up
D-Arabinose	319.5 (-2.12)	295.0 (1.51)	308.0	M	490.5 (-1.03)	up	down
D-Allose	319.5 (-1.00)	290.0 (0.56)	307.0	M	491.0 (-0.47)	down	down

a) [$\mathbf{1}_2$·Cu(I)]=0.100 mmol dm^{-3}, [monosaccharide]=7.50 mmol dm^{-3} ([D-galactose]=1.50 mmol dm^{-3} [D-mannose]=3.00 mmol dm^{-3}), MeOH:MeCN=1:1(v/v), 25 °C. b) cell length : 0.1 cm. c) cell length : 1.0 cm

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10. The *o*-aminomethyl group interacts intramolecularly with the boronic acid group and stabilizes the saccharide complex.[9]