Liquid Crystals

Metal-Ion-Induced Switch of Liquid-Crystalline Orientation of Metallomacrocycles

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Abstract: A new series of shape-persistent imine-bridged macrocycles were synthesized based on dynamic covalent chemistry. The macrocycles had an alternating sequence of dibenzothiophene and *N*,*N'*-bis(salicylidene)-ethylenediamine (salen) tethering branched alkyl chains. The macrocycles and tetranuclear metallomacrocycles bearing long and branched alkyl chains exhibited thermotropic columnar liquid-crystal-line phases over a wide temperature range and the metallomacrocycles greatly depended on the characteristics of the coordinated metal ions. The metal-free macrocycle showed

Introduction

Liquid crystals are functional anisotropic fluids and are susceptible to not only external stimuli but also their own molecular structures. In some soft materials, structural transformations at the molecular scale can change the structural and thermal properties of the liquid crystals in macroscopic domains. Under external stimuli, chiral dopants for the cholesteric mesophase,^[1] molecular motors,^[2] and photochromic molecules on the surface^[3] have been known to induce reorientation of liquid crystals. In contrast, it was recently reported that even an intramolecular structural change in topologically entangled supramolecular complexes^[4] could control liquid-crystalline (LC) properties, leading to novel designs for unconventional liquid crystals. In this regard, metal-containing liquid crystals are fascinating molecules because transition-metal ions could lead to distinctive properties involving binding of LC ligands,^[5,6a] metal-metal^[6b] and metal-ligand interactions,^[6c,d] and the luminescence of lanthanide complexes,^[6e] rendering the LC materials promising for functional materials exhibiting magnetic,^[7] electrical,^[6d, 8] and electro-optical properties.^[9] Moreover, even among the transition-metal ions with the same coordination geometry, subtle structural differences in the metal ions (hereafter called "atomic scale differences") could induce macroscopic organization of the assembly.^[10] For example, it has been reported that the phase structures and thermal properties of LCs with metallomesogens such as N,N'-bis(salicylidene)ethylenediamines (salens),^[10] porphyrins,^[8b, c, 11] phthalocyanines,^[12] and supramolecular architectures^[4a] significantly depended on the coordinated metal ions with the same coordination geometry.

Incidentally, it is a challenging problem to construct well-defined, nanometer-sized spaces in LC materials in conjunction with flowable properties and the ability to undergo phase transitions. In particular, columnar liquid crystals based on shapepersistent macrocyclic compounds have gathered increasing attention as they are expected to exhibit a nanochannel struc-

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a liquid-crystalline phase with a lamellar structure and poor birefringence. In sharp contrast, the macrocyclic Ni complex showed a columnar oblique liquid-crystalline phase, whereas the Pd and Cu complexes showed columnar liquid-crystalline phases with a lamellar structure. The macroscopic organization and thermal properties of the corresponding liquid-crystalline metallomacrocycles were significantly dependent on the subtle structural differences among the planar macrocycles, which were revealed by single-crystal X-ray crystallographic analysis of the macrocycles with shorter alkyl chains.

ture in flowable media. In pioneering works, Moore^[13] and Höger^[14] reported shape-persistent macrocycles composed of phenylacetylene units in macrocyclic frameworks, which exhibited thermotropic LC properties. However, there is a demand for utilizing heteroatoms or components other than hydrocarbons to design such columnar LC macrocycles with additional functions such as specific recognition, storage, construction of arrays, transportation, and chemical reactions of entrapped molecules.^[15-17]

Recently, we reported shape-persistent imine-based macrocycles with discrete inner pores exhibiting well-developed thermotropic columnar LC phases.^[18] The macrocycles are formed spontaneously through efficient dynamic imine formation^[19,20] so that the resultant planar macrocycle self-assembled into columnar LC phases over a wide range of temperatures. Moreover, after incorporation of transition-metal ions into the *N*,*N*'bis(salicylidene)-*o*-phenylenediamine (salphen) moieties of the macrocycle, it was found that the resultant metallomacrocycles significantly changed the thermal behavior of the columnar LC phases. The metallomacrocycles with an inner cavity as large as 1 nm in diameter showed thermotropic columnar LC phases in a reversible fashion.^[18]

Herein, we report our strategy to induce macroscopic LC organization by controlling these atomic scale differences.^[10,21] In LC metallomacrocycles, macroscopic organization of columnar LC phases could be effectively manipulated by tuning the design of the macrocyclic mesogen on the atomic scale. This design strategy would be effective to conveniently make a new series of LC metallomacrocycles to form flowable nanospaces in the LC phase (Figure 1).

Results and Discussion

Synthesis of macrocycles composed of salen and dibenzothiophenes

In the present study, we designed a series of novel metallomacrocycles composed of dibenzothiophenes with tethered branched alkyl chains. Compared with rather rigid salphen moieties,^[18] we presumed that the more flexible salen in the macrocyclic mesogen would be susceptible to structural change induced by the metal coordination. The synthesis of the LC metallomacrocycles is outlined in Scheme 1. After care-

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Figure 1. Schematic illustration of the macroscopic change of thermotropic columnar liquid crystals composed of macrocycles or metallomacrocycles triggered by atomic scale differences in the flexible macrocycle.

ful choice of the molecular design, a dibenzothiophene with dialdehydes at the 2- and 7-positions, 2, and a series of ethylenediamines with branched alkyl chains 3a-c were synthesized according to the synthetic schemes shown in Schemes S1 and S2 in the Supporting Information. An imine-based cyclization reaction was utilized as the key step in the synthesis of macrocycles H₈1a-c by 4:4 condensation between 2 and 3a-c. Initially, as reported previously by the Nabeshima^[19] and MacLachlan^[20] groups as well as our group,^[18] we used o-phenylenediamine derivatives containing tethered alkyl chains instead of ethylenediamine derivatives 3a-c. The ¹H NMR spectrum of the reaction mixture indicated that the target macrocyclic compound was obtained in moderate yields (less than 37%); however, it was difficult to isolate the target macrocycle from the mixture of the intermediates owing to the strong aggregation tendency of the macrocycle. Unlike the efficient synthesis of our macrocycle composed of carbazole and salphen,^[18] the result indicates that moderate solubility was necessary to isolate the target macrocycles. In contrast, when 3c was mixed with 2, a ¹H NMR spectrum of the reaction mixture indicated that the 4:4 macrocycle was formed predominantly with only trace amounts of byproducts. After purification by gel permeation chromatography (GPC), the desired 4:4 macrocycle H_81c was isolated with a high yield of 65%. The MALDI-TOF mass spectrum showed a prominent single signal at m/z = 5985.8 $([M+H]^+)$, indicating that 4:4 condensation selectively occurred. The ¹H NMR spectrum of H_81c in CDCl₃ showed a set of proton signals for the dibenzothiophene and 1,2-substituted ethylenediamine moieties, including a new singlet signal for the imines at 8.71 ppm, suggesting that the macrocycle has a D_{4h} symmetric structure. The efficiency of the cyclization derives from two factors: the flexibility of salen and the right angle geometry of the imines connected to dibenzothiophene. Similarly, macrocycles H_81a and H_81b , with other peripheral alkyl chains, were synthesized with good yields, regardless of the side chain. Tetranuclear nickel(II), palladium(II), and copper(II) complexes derived from H₈1 were also prepared by mixing the macrocyclic ligands with the corresponding metal acetates (Scheme 1). These macrocycles and their metal complexes were soluble in halogenated solvents, toluene, and THF.

Thermotropic liquid-crystalline properties of macrocycles and metallomacrocycles

To gain insight into the macroscopic characteristics of the macrocycles, we have investigated the LC properties of the macrocycles with longer tethered alkyl chains (both metal-free and metalated 1b and 1c). The thermal properties were investigated below the decomposition temperatures, by using thermogravimetric analysis (TGA; Figures S1 and S2 in the Supporting Information). The macrocycles with shorter alkyl chains, H₈1b, and those with Ni and Pd complexes (Ni₄1b and Pd₄1b) showed solid-state characteristics below the decomposition temperatures (Figures S3, S4, and S5 in the Supporting Information). These results could be attributed to the relatively insufficient number of alkyl chains attached to the rigid macrocyclic mesogens.^[14, 18] However, H₈1 c and metal complexes Ni₄1 c, Pd₄1 c, and Cu₄1 c exhibited thermotropic LC properties owing to the presence of much longer side chains containing ether units. Although H₈1 c showed an extremely weak birefringence without texture corresponding to LC ordering under polarized



Scheme 1. Synthesis of the macrocycles and the metallomacrocycles. Reaction conditions: (a) Na₂SO₄ or NEt₃, ethanol, reflux, (b) M(OAc)₂, CHCl₃/ethanol.

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Figure 2. POM images of the macrocycle (a) H_81c at 30 °C, metallomacrocycles, (b) Ni_41c at 25 °C, (c) Pd_41c at 170 °C, and (d) Cu_41c at 150 °C.

optical microscopy (POM, Figure 2a), the POM observation and differential scanning calorimetry (DSC, Figure S6 in the Supporting Information) revealed that H_81c forms a LC phase from -4 °C to 84 °C. Grazing incidence X-ray diffraction (GIXRD) analysis of H_81c showed diffraction peaks indexed as (001), (002), and (003), indicating a lamellar structure in the LC phase (Figure 3a). The *d*-spacing of 33.7 Å can be modeled as a layered structure of the macrocycles with interdigitation of the side chains between the layers, and the layered structure fits in the space filling model. On the basis of the relatively weak birefringence in the POM images and the GIXRD results, it was suggested that the orientation of the macrocycle was obscure in the layered mesophase.^[22]

In contrast to H₈1c, Ni₄1c exhibited strong birefringence and a clear fan-shaped texture in the POM image upon cooling from the clearing point between the LC phase and the isotropic liquid of 161°C (Figure 2b). Although the POM texture did not exhibit a chiral LC phase, which was expected from association of the chiral macrocycles, the fan-shape texture suggesting formation of a columnar association of the macrocycle. As Ni₄1 c was shearable, the phase between the two transitions at -17°C and 161°C in the DSC (Figure S6 in the Supporting Information) was assigned as the LC phase. As shown in Figure 3 b, GIXRD analysis of Ni₄1 c showed several diffraction peaks in the small-angle region and they were indexed by retrostructural analysis. The analysis indicated that Ni₄1 c takes on an oblique columnar phase (Col_{ob}) in which the columns are organized into monoclinic packing, with the following estimated unit cell parameters: a = 67.6 Å, b = 65.2 Å, and $\gamma = 85.2^{\circ}$ (Figure 2b and 3b).^[22a, b, 23] The columnar structure of Ni₄1 c has higher order that that of H_81c , probably owing to the planar macrocyclic structure induced by coordination of nickel(II) ions with square-planar geometry. The temperature at which the isotropic point was reached was also significantly higher for Ni_4 **1 c** than for H_8 **1 c**.

Similarly, thermal and structural characterizations of the LC phases of Pd_41c and Cu_41c were performed. These metal cen-



Figure 3. GIXRD patterns for (a) $H_81\,c$ at 60 $^\circ C$, (b) $Ni_41\,c$ at 100 $^\circ C$, and (c) $Pd_41\,c$ at 180 $^\circ C$ on glass substrates.

ters also take square-planar configurations similar to the Ni complex. DSC analysis of Pd_41c showed a higher clearing point of 235 °C. Below the clearing point, LC phases of Pd₄1 c were observed between 153 °C and 235 °C (Figure 2 c). The higher transition temperatures to the LC phase of Pd₄1 c suggest stronger association forces for Pd₄1c compared with those of Ni₄1 c. This may be related to the lower solubility of Pd₄1 a in CDCl₃ than Ni₄1 a. Furthermore, compared with the less ordered lamellar LC phase of H₈1c (Figure 2a), a distinguished broken fan-shaped texture indicating a columnar arrangement was observed in the POM image of Pd₄1c (Figure 2 c). GIXRD patterns of Pd₄1 c suggested that the complex adopted a lamellar structure in the LC phases (Figure 3c). The spacing of 30.4 Å was comparable with the column diameter estimated from space filling molecular modeling of Pd₄1 c. Interestingly, a broad but significant diffraction with a spacing of 11.1 Å was observed in the in-plane direction to the substrate (see the Supporting Information, Figures S8 and S9), indicating that there was a repetitive stacking distance of the macrocycle within the layer in the LC phase. Therefore, we assigned the LC phase as the lamellar-columnar mesophase, Col_L, which is consistent with the POM observation. $^{[22a,b,24]}$ When $\mathsf{Pd}_4\mathbf{1\,c}$ was further cooled from 153 $^{\circ}$ C to $-10 \,^{\circ}$ C, it showed a harder crystalline phase without fluid properties. The GIXRD results indicated that the lamellar structure was retained in this phase, implying that the fluid columnar structure appeared frozen (Figure S8 in the Supporting Information).^[25,26b] Cu₄1 c exhibited bright bire-

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fringence and a clear texture consisting of small domains of the LC phase (Figure 2d). Cu₄1 c formed an LC phase between 125 °C and 189 °C and a frozen crystalline phase below 125 °C (Figure 4, Figure S4 in the Supporting Information). The GIXRD patterns of Cu₄1 c suggested that the LC phase was comprised of a lamellar structure (Figure S8 in the Supporting Information). From the results above, we concluded that Pd_41c and Cu₄1 c exhibit thermotropic columnar LC phases in which the columnar assemblies were arranged into lamellar structures. These assembled structures could be ascribed to the presence of columnar structures composed of rigid macrocyclic mesogens. It is noteworthy that the LC phases and the self-assembled structures were strongly influenced by the coordination of square-planar metal ions with the square-planar geometry to the macrocyclic host. Unlike the related compounds previously reported,^[18] ordering of both the columns and the thermal properties of the metallomacrocycles were drastically influenced by the atomic scale differences in the macrocyclic mesogens (Figure 4). The metallomacrocycles showed bright birefringence with clear fan-shaped textures, which represent the formation of columnar LC phases with large domain sizes, whereas H₈1c forms a less-ordered LC phase with weak birefringence. It should be noted that the macrocyclic nickel(II) complex formed a well-developed columnar oblique LC phase, whereas the palladium(II) and copper(II) complexes formed lamellar-columnar structures in the mesophase. These thermal and structural variations among the metallomacrocycles occur as a result of the difference in the flowability of the nickel(II) complex and the palladium(II) and copper(II) complexes. The palladium(II) and copper(II) complexes solidified at higher temperatures owing to their higher association ability, and the lamellar-columnar structures froze before transitioning to more ordered structures upon cooling from the clearing points. Thus, we presumed that the subtle structural differences between the complexes, such as enhanced planarity and/or the size of the metal ions in the macrocyclic mesogens induced by square-planar metal complexation, lead to drastic differences in the macroscopic order of their LC phases. Therefore, in the subsequent sections, we discuss the structural analyses of the metallomacrocycles to reveal the switching of the macroscopic assembled structure.

Solid-state NMR spectroscopy of macrocycles and metallomacrocycles

To gain further insight into the structural and dynamic properties of the macrocycles, solid-state NMR experiments were carried out by using the magic angle spinning technique.^[26, 14d] The cross-polarization magic angle spinning (CPMAS) ¹³C NMR experiments were performed at room temperature, at which metal-free macrocycles H_81a and H_81b are in the solid state, whereas H₈1c forms an LC phase. As shown in Figure S10 in the Supporting Information, crystalline H₈1a forms well-resolved crystallographic split signals in the aromatic region (100–180 ppm). The spin-lattice relaxation time (T_{1C}) of H₈1 a was estimated to be more than 17 s for the aromatic carbons and 1-3 s for the alkyl chains (Table S5 in the Supporting Information). As investigated in polyethylenes, the T_{1C} of the crystalline and noncrystalline components are on the order of 10³ s and 10⁻¹ s, respectively.^[27] These characteristics indicate that the aromatic core has nonequivalent and static environments in the solid state on the NMR timescale. In contrast, the aromatic carbon spectra of crystalline H_81b with branched N,N-dioctylamide chains became broader, indicating less ordered packing of the macrocycle. Other than the assignment of each signal, however, the number and chemical shifts of the carbon signals were similar to those in CHCl₃ solution. These results suggest that the macrocyclic framework of H₈1 b did not expe-



Figure 4. 2D packing structures of (a) H_81c , (b) Ni_41c , and (c) Pd_41c in LC phases. (d) Phase diagrams of macrocycles H_81c , Ni_41c , Ni_41c , and Cu_41c traced on the second heating cycle of DSC with a heating rate of $10 \,^{\circ}Cmin^{-1}$. Phase notation: Cr, crystal; L, LC phase with lamellar structure; Col_{ob} , oblique columnar LC phase; Col_{LFP} frozen glassy phase with lamellar structure; Iso, isotropic liquid.

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rience any deformation of the mesogen, but retained the symmetric environment to some extent through the packing.^[26] LC H_81c showed a similar tendency as that shown by H_81b in the aromatic region; however, significantly sharp signals appeared in the aliphatic region (10-40 ppm). It was also observed that the T_{1C} of H₈1 c was 21–23 s for the aromatic carbons, whereas that of the aliphatic carbons was much shorter at 0.61-0.70 s. Moreover, the aromatic signals of H₈1c at 100-180 ppm appeared more pronounced in the cross-polarization spectrum than in the direct-excitation spectrum (see the Supporting Information, Figure S11).^[26] Such characteristics of the spectrum reflect a rather dynamic and liquid-like environment around the alkyl chains, as found in other discotic LC molecules, whereas the macrocyclic mesogen remains less mobile.[14d, 28, 29] The ¹³C NMR spectra and relaxation behavior of the columnar LC nickel complex Ni₄1 c were similar to those of the lamellar LC H₈1c. The T_{1C} of Ni₄1c was 12–13 s for the aromatic carbons, whereas that of the aliphatic carbons was much shorter at 0.61-0.70 s. These results indicate that the molecular-level structures as well as the dynamic properties of LC Ni₄1 c on the NMR timescale are similar to those of the lamellar LC H₈1c (Figure S10 in the Supporting Information). Notably, all the solid-state NMR signals of these nickel(II) complexes showed diamagnetic properties, indicating that the Ni center retains the square-planar configuration without any axial coordination by neighboring macrocycles even in the condensed solid or LC phases.

¹H NMR spectroscopy of macrocycles and metallomacrocycles

To understand the molecular structure in detail, we performed structural analysis of the macrocycles in solution. All signals of these compounds were assigned by using ${}^{1}H{}^{-1}H$ COSY, NOESY, and HMQC techniques. Similar to macrocycle H₈1c, the ${}^{1}H$ NMR spectra of metal complexes Ni₄1c and Pd₄1c in CDCl₃ supported the *D*_{4h} symmetric structures of the metallomacrocycles (Figure 5). Intriguingly, chemical shifts of the proton signals in the aromatic region were significantly affected by the coordination of the metal ions to the macrocyclic ligands. The imine signals at 7.69 ppm for Ni₄1c and at 7.98 ppm for Pd₄1c appeared upfield compared with that of H₈1c, which were consistent with those of other salen complexes.^[30,31]

Furthermore, it is noteworthy that several signals at around 3.50–4.50 ppm, which were assigned to the protons in proximity to the metallosalen, were more affected compared with H₈1c. In particular, signals of the geminal protons, H_e and H_{e'} in H₈1c were significantly split ($\Delta \delta = 137$ Hz, Figure 5 a), indicating that these protons might be under different magnetic environments owing to the distorted chiral salen moiety on the NMR timescale. In contrast, the differences in the chemical shift between the two sets of the signals, H_e and H_{e'}, of the metallomacrocycles Ni₄1c ($\Delta \delta = 86$ Hz) and Pd₄1c ($\Delta \delta = 28$ Hz) were smaller than that of the metal-free H₈1c. This result may indicate that the magnetic environments of the geminal protons are similar to each other owing to the restricted configuration of the metallosalen moieties through coordination.

Indeed, this tendency was also observed in other metallosalen complexes with a similar configuration, as reported by Saalfrank et al., who found the following differences in the chemical shifts of the geminal protons: $\Delta \delta = 64$ Hz for metal-free salen and $\Delta \delta = 32$ Hz for the Ni–salen complex.^[31] Following Saalfrank et al., we investigated the vicinal coupling constant of H_d . However, the H_d signals for H_81c and Ni_41c were hidden by other proton signals owing to the side chains. Fortunately, for Pd_41c , the H_d signal was isolated and the vicinal coupling constant of $J_{dd'}$ was found to be 0 Hz, indicating that the methylene groups showing the ${\sf H}_{{\scriptscriptstyle e}}$ signal were oriented in the axial direction.^[31] This prediction is in good agreement with the single-crystal structures (Figure 7 and Figure 8). The phenomena may imply a change in the flexibility of the macrocyclic mesogens through metal coordination, which is discussed in the next section.



Figure 5. Partial 1H NMR spectra of (a) $H_81\,c,$ (b) $Ni_41\,c,$ and (b) $Pd_41\,c$ (600 MHz, CDCl3, 298 K).

UV/Vis absorption and circular dichroism of macrocycles and metallomacrocycles

The optical properties of H₈1c and the Ni, Pd, and Cu complexes were investigated by UV/Vis absorption and circular dichroism (CD) spectroscopies in CHCl₃ (3.0×10^{-6} M). H₈1c exhibited absorption maxima at 257, 316, and 359 nm in the UV/Vis absorption spectrum (Figure 6a). The latter two absorptions were accompanied by shoulder bands of shorter wavelengths. A broad absorption band at 420 nm in the visible region was also observed, probably owing to the n- π^* transition associated with the azomethine group.^[32a] In contrast, metal complexes Ni₄1c, Pd₄1c, and Cu₄1c showed strong bands in the 400–500 nm region with absorption coefficients of 6.5×10^4 – 1.2×10^5 m⁻¹ cm⁻¹, followed by weak and broad absorption bands at around 500–580 nm. The characteristics and absorption coefficients were consistent with those of other metallosalen complexes.^[32]

The CD spectra of the macrocycles provided significant details about the chiral salen moieties (Figure 6). For $H_8 \mathbf{1} \mathbf{c}$, posi-

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tive CD bands were observed in the π - π^* transition region. Furthermore, all the metallomacrocycles exhibited positive CD intensities in the 400–500 nm region. Both properties are consistent with the *R*,*R* configuration of the metallosalen moieties.^[32] Although the metallomacrocycles investigated in the present study showed similar tendencies as H₈1c, Ni₄1c showed a weaker Cotton effect than those of the other macrocycles. These results show that the Ni complex possessed a certain planarity with a square-planar configuration, as observed in the simple model complexes,^[32] and are consistent with the structural investigation unveiled by the single-crystal analysis of the model compounds (Figure 7 and Figure 8).

X-ray crystallographic analyses of the macrocycles and metallomacrocycles

Single-crystal X-ray analyses of the model macrocycles with short alkyl chains showed the detailed structures of the macrocycles. The crystals were grown by slow evaporation of solvents from a $CHCl_3$ and hexane solution for H_81a and Pd_41a or from a CHCl₃, hexane, and toluene solution for Ni₄1a and Cu₄1 a. As expected, Ni₄1 a adopts a flat macrocyclic structure, in which all the sulfur atoms were arranged on the outside fringe of the macrocycle and the Ni ions were embedded in the salen ligands on the corners of the macrocycle, leading to an electronically neutral tetranuclear metallomacrocycle. The diameter of the vacant inner cavity of the macrocycle was elucidated to be 10.1 Å, which is comparable to that of a related macrocycle reported previously.^[18] In the packing structure of Ni₄1 a, the metallomacrocycles are aligned in an alternating and overlapping pattern and the cavities are filled by the side chains of the neighboring macrocycles (Figure 7a). The conformations of the carbon atoms connected peripherally to the ethylenediamine moieties were consistent with the ¹H NMR results discussed in Figure 5. The molecular packing in the crystal is completely different from the one-dimensional stacked columnar assembly in the liquid-crystalline phases owing to the shorter alkyl chains. The square-planar geometry of the metal complexes affects the planar configuration of the macrocyclic mesogen. In fact, the average dihedral angle between the π planes of the neighboring dibenzothiophenes was 8.85° (Figure 8a, shown in blue, Table 1) and the dihedral angle of the mean planes of O–C=C–C=N atoms was only 7.48° (Figure 8a, shown in red, Table 1), whereas the corresponding parameters for H_8 **1 a** were 10.3° (Figure 8b, shown in blue, Table 1) and 13.0° (Figure 8b, shown in red, Table 1). These differences in the parameters reflect the planarity of the macrocycles (Figure 8c and d). Standard vertical deviations of all the sp² atoms in the macrocycles from the mean planes were calculated as σ =0.32 for Ni₄1 a and σ =0.88 for H₈1 a (Table 1). These parameters were sufficiently consistent with the experimental results of the UV/Vis and CD data recorded in solution. Therefore, metallomacrocycle Ni₄1 a is more planar than metal-free H₈1 a. Furthermore, the packing structures of the metallomacrocycles significantly differ from that of H₈1a (Figure 7c and d). In fact, the metallomacrocycles self-assembled with each other, where the metallosalen moieties gathered in anti-parallel fashion, whereas H₈1 a stacked dibenzothiophenes rather than the distorted salen moieties (see the Supporting Information). It seems reasonable to assume that the differences in the planarity among the macrocycles directly affected the differences in the liquid-crystalline phases. Such an enhanced planarity of the macrocycle was also observed in the other metallomacrocycles, that is, Pd₄1 a and Cu₄1 a (see Table 1, and the Supporting Information). Although it was somehow unexpected that the single-crystal X-ray structures of Pd₄1a and Cu₄1a were almost similar to that of Ni₄1 a, we presumed that the subtle structural difference at the submolecular scale involving size and intermolecular interactions of the square-planar metal ions might induce macroscopic differences among the self-assembled LC macrocycles (see the Supporting Information, Figure S17, Table S7).



Figure 6. CD (top) and UV/Vis (bottom) spectra of the macrocycle (a) H_81c , and metallomacrocycles (b) Ni_41c , (c) Pd_41c , and (d) Cu_41c recorded at 293 K in $CHCI_3$ (3.0×10⁻⁶ M).

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Figure 7. X-ray crystal structures of (a) the metallomacrocycle Ni₄1 **a** and (c) the macrocycle H₈1 **a**. ORTEP diagrams with thermal ellipsoids at the 50% probability level. The packing structures of (b) Ni₄1 **a** and (d) H₈1 **a** shown as space filling models.



Figure 8. Comparison of macrocyclic mesogen structures of (a) Ni₄1 **a** and (b) H₈1 **a** determined by X-ray crystallography. Hydrogen atoms and side chains were omitted for clarity. The mean planes formed by the O–C=C–C= N atoms in the salen moieties are shown in red, whereas the π planes of the dibenzothiophenes are shown in blue. The dihedral angles between these adjacent planes are summarized in Table 1. The structures of each salen moiety in the macrocyclic mesogens of Ni₄1 **a** and H₈1 **a** are highlighted in (c) and (d), respectively.

Conclusion

We have demonstrated the orientation switch of the LC phase of a macrocyclic compound induced by metal complexation. The macrocyclic framework, consisting of dibenzothiophenes and salens, forms tetranuclear metal complexes with squareplanar metal ions to afford planar mesogens, the structures of which are similar to that of the metal-free macrocycle. However, the atomic scale differences among 2H⁺, Ni^{II}, Cu^{II}, and Pd^{II} when bound to the salen ligands induced a significant variability in the macroscopic LC organization on the phase structure and transition behavior. Single-crystal X-ray structural analyses of model macrocycles with shorter alkyl chains revealed that the mesogen moieties of the metallomacrocycle formed more rigid and planar conformations than those of the metal-free macrocycle owing to the square-planar configurations of the transition-metal ions. This showed that the metallomacrocycles had highly ordered LC phases and higher transition temperatures. In particular, the macrocyclic nickel(II) complex formed a well-developed columnar oblique LC phase, which reversibly underwent a phase transition, whereas the palladium(II) and copper(II) complexes formed the lamella-columnar structure in the mesophase. This difference is derived from the difference in the flowability among the metallomacrocycles. The palladium(II) and copper(II) complexes solidified at higher temperatures owing to the higher association ability and the lamellarcolumnar structures froze before transition to more ordered structures. As the nanospace in a liquid crystal would be influenced by the assembly of the macrocycles based on the structure and fluidity, the metal-ion-induced switch of LC orientation at the atomic scale differences could produce functional diversity and generate much higher order nanospaces in flowable media.

Experimental Section

Materials

Synthetic procedures were carried out under an atmosphere of dry nitrogen unless otherwise specified. All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. Detailed syn-

Table 1. Crystallographic data for the macrocycles.				
	H ₈ 1 a-CHCl ₃	Ni ₄ 1 a·CHCl ₃ ·hexane·toluene	Pd ₄ 1 a	Cu ₄ 1 a-CHCl ₃ -hexane-toluene
Moiety formula	$C_{108}H_{132}CI_{12}N_8O_{16}S_4$	C ₁₂₈ H ₁₆₁ Cl ₁₅ N ₈ Ni ₄ O ₁₆ S ₄	$C_{104}H_{120}Pd_4N_8O_{16}S_4$	$C_{127}H_{160}CI_{12}Cu_4N_8O_{16}S_4$
Space group	P2 ₁	P212121	P212121	P212121
Ζ	2	4	4	4
Dihedral angle [°] ^[a]	10.3	8.85	11.0	9.52
Dihedral angle [[°]] ^[b]	13.0	7.48	6.64	7.12
$\sigma^{[c]}$	0.88	0.32	0.32	_[d]
Inner diameter [Å]	10.1	9.22	9.63	9.61
R_1, R_W	0.1346, 0.3514	0.1434, 0.3861	0.1085, 0.2868	0.2181, 0.4767
GOF	1.345	1.616	1.039	1.475

[a] The average dihedral angles between the π planes of two adjacent dibenzothiophenes in the macrocycles. [b] The average dihedral angles between the mean planes composed of N=C-C=C-O atoms in the salen moieties. [c] The standard deviation of the distance from the mean plane composed of the sp² atoms (C, N, O) in the macrocycles. [d] This characterization was not performed owing to the moderate quality of the crystal.

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thesis and analytic data are described in the Supporting Information. ¹H and ¹³C NMR spectra were recorded with a JEOL JNM-ECS400 or JNM-ECS600 spectrometer at a constant temperature of 298 K. Tetramethylsilane (TMS) was used as an internal reference for ¹H and ¹³C NMR measurements in CDCl₃. MALDI-TOF-MS was performed with an ultraflex III, Bruker Daltonics, and dithranol or α -cyano-4-hydroxycinnamic acid (CHCA) was used as the matrix. Elemental analyses were performed with a Yanaco MT-6 analyzer. Silica gel column chromatography and thin-layer (TLC) chromatography were performed by using Merck silica gel 60 and Merck silica gel 60 (F254) TLC plates, respectively. GPC was performed by using a JAI LC-9204 equipped with JAIGEL columns.

Methods

DSC measurements were carried out under a N₂ atmosphere with a TA Instruments Q2000 DSC equipped with a RCS 90 cooling accessory and the transition temperatures were determined from the second heating run at a rate of 10°Cmin⁻¹ by using Universal Analysis 2000 software. TGA analysis was performed under a N₂ atmosphere with a TA Instruments TGAQ50 with the temperature raised from 30 °C to 600 °C at a rate of 10 °C min⁻¹. Polarized optical microscopy (POM) observations were performed with an OLYMPUS BX51 microscope with crossed polarizers, Linkam LTS 350 heating stage under $N_{\rm 2}$ atmosphere, and an OLYMPUS DP20 camera. XRD and GIXRD analyses were measured by using a Rigaku R-AXIS IV Xray diffractometer ($Cu_{\kappa\alpha}$) equipped with a temperature-controlled heating stage and an imaging plate for collection of the diffracted patterns. GIXRD analysis of the samples placed on glass plates was measured with the temperature-controlled heating stage at various temperatures. The incidence angle was set to $\sim 0.4^{\circ}$. The diffracted radiation was recorded by an imaging plate that had a sample-todetector distance of 30 cm, with exposure time of 3 min. The solidstate NMR experiments were performed with a JNM-ECA 600 spectrometer at 600 MHz (JEOL), by using a 3.2 mm MAS probe with a spinning frequency of 12 kHz. Hexamethylbenzene was used for the external reference. The temperature was calibrated by a correction relationship that was determined in a separate study by using $Pb(NO_3)_2$. The ¹³C{¹H} CP MAS measurements were carried out at 12 kHz MAS, with a contact time of 2 ms and a relaxation delay of 2 s, using two-pulse phase-modulated (TPPM) decoupling. Several CP contact times of 50 µs to approximately 2 ms were examined to distinguish the carbons directly bound to protons for the assignment. The ¹³C MAS measurements using the direct-excitation method were measured at 10 kHz MAS, with a relaxation delay of 15 s. The absorption spectra were recorded with a Hitachi U-4100 spectrophotometer in CHCl₃ solutions at 20 ± 0.1 °C in 1.0 cm quartz cells. CD spectra were recorded in a 1.0 cm quartz cell by using a JASCO J-720WN spectrophotometer. Single-crystal X-ray diffraction measurements were performed with a Rigaku X-ray diffractometer equipped with a molybdenum MicroMax-007 and Saturn70 CCD detector. Further experimental details are described in the Supporting Information.

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FULL PAPER

Atomic scale difference induces macroscopic organization: The macroscopic organization and thermal properties of liquid-crystalline metallomacrocycles are significantly dependent on the coordinated metal ions. The subtle structural differences among the planar macrocycles play a role in the macroscopic organization as revealed by single-crystal X-ray crystallographic analyses of the macrocycles with shorter alkyl chains.



Liquid Crystals

S.-i. Kawano, T. Hamazaki, A. Suzuki, K. Kurahashi, K. Tanaka*



Metal-Ion-Induced Switch of Liquid-Crystalline Orientation of Metallomacrocycles



Metallomacrocycles

Tetranuclear metal complex formation of the macrocyclic ligand induced the orientation switch and phase transition of the liquid-crystalline macrocycle depending on the metal ions. Even though Ni²⁺, Pd²⁺, and Cu²⁺ ions form square-planar complexes with a salen ligand (*N*,*N'*-bis(salicylidene)-ethylenediamine) and difference of the ionic sizes among these metal ions are much smaller than the size of the macrocycle, the "atomic-scale differences" among 2H⁺, Ni²⁺, Cu²⁺, and Pd²⁺ when bound to the salen ligands induced a significant variability in the macroscopic liquid crystalline organization on the phase structure and transition behavior. For more details, see the Full Paper by K. Tanaka et al. on page **I f**.