Article

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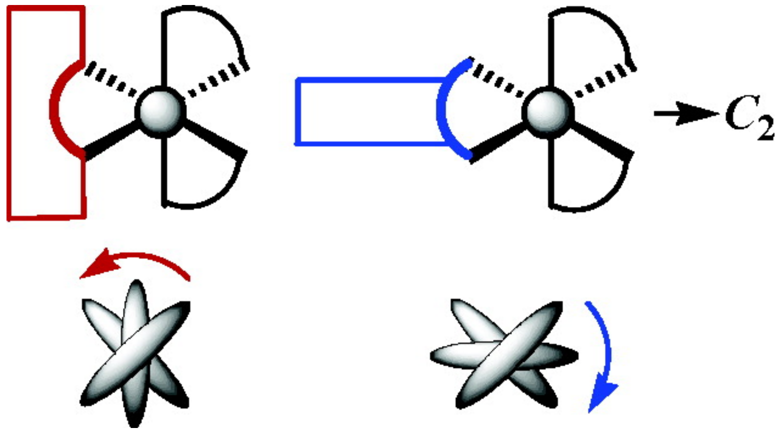

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On the Parity in Helical Twisting Power of Ru(III) 1,3-Diketonates of C_2 Symmetry in Nematic Liquid Crystals

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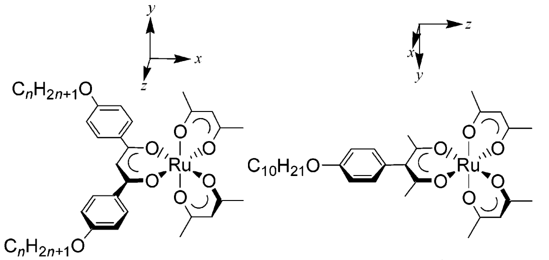
Abstract: It is demonstrated that the sign of helical twisting power (HTP) of an enantiomeric Ru(III) complex of type [Ru(acac)$_2$L] can be switched by choosing L from either L$_{per}$ or L$_{para}$, which is elongated either perpendicular or parallel to the C_2 symmetry axis, and four states become available in combination with ΔΛ-chirality of the metal center. Complexes **1**-*n*, in which 4,4′-dialkoxylated dibenzoylmethanate ligands are used as L$_{per}$, and **2** having L$_{para}$ = 3-(4′-decyloxyphenyl)pentane-2,4-dionate ligand were prepared for this purpose. They were optically resolved into the enantiomers by means of a clay column chromatography, and their performance as chiral dopants was evaluated in nematic liquid crystals including a room-temperature system, *N*-methoxybenzylidene-4-*n*-butylaniline (MBBA), which allowed facile measurements of the helical pitch lengths and CD spectra in the induced chiral nematic states. The induced CD signals have provided a clear evidence for the helical inversion between the two structure types, **1** and **2**, of the same chirality. The twisting power of these six-coordinate metal complexes and their structure versus twist sense correlations are interpreted by the shape model. Intrinsically high HTP of Δ-[Ru(acac)$_2$L$_{per}$] has also allowed for observation of the pitch band due to the selective reflection in the visible wavelength range at the doping level of 2 mol % in MBBA.

Introduction

Nematic liquid crystals are anisotropic fluids that report sensitively on the presence of a chiral substance by way of forming helical superstructures. The induction of a chiral nematic (N*) phase is thought to be thresholdless, and, when the pitch is in the UV−vis wavelength range, a bright coloration of samples due to the selective reflection can be utilized as a convenient analytical tool for stereoselective syntheses.[1] It is important to work out a theoretical framework to describe the phenomenon for device applications in prospect, and investigations into the *helical twisting powers* (HTP) of chiral dopants of various molecular types should not only merit such endeavors but also deepen our understanding of the properties of chiral liquid crystals.[2]

We wish to report herein that the sign of HTP of metal complex dopants of type [Ru(acac)$_2$L] (acac = acetylacetonate, and L = 1,3-diketonate containing phenylene groups) can be switched by a rational choice of L between L$_{per}$ and L$_{para}$, which are "elongated" perpendicular and parallel to the C_2 symmetry axis, respectively. Four states become available in combination with ΔΛ-chirality of the metal center. Chart 1 illustrates Δ-enantiomers of complexes **1**-*n* (with L$_{per}$) and **2** (with L$_{para}$) studied in this work.

Chart 1. Complexes Studied (Illustrated for Δ-Enantiomers) and the Principal Axis Systems of Ordering Tensor Deduced from the Structures



Δ-1-*n* **Δ-2**

Results and Discussion

Synthesis and Optical Resolution. Two homologues of **1**-*n* (n = 6 and 12) and **2** were prepared following the literature procedures[3] and optically resolved into pure enantiomers by

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(1) Eelkema, R.; van Delden, R. A.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5013−5016.

(2) *Chirality in Liquid Crystals*; Kitzerow, H.-S., Bahr, C., Eds.; Springer-Verlag: New York, 2001.

(3) For the L$_{per}$-type diketones in **1**, see: (a) Serrette, A. G.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1994**, *6*, 2252−2268. (b) Zheng, H.; Lai, C. K.; Swager, T. M. *Chem. Mater.* **1995**, *7*, 2067−2077. Synthesis of the L$_{para}$ ligand in **2** was after: (c) Cativiela, C.; Serrano, J. L.; Zurbano, M. M. *J. Org. Chem.* **1995**, *60*, 3074−3083. (d) Okuro, K.; Furuune, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1993**, *58*, 7606−7607. (e) Thiruvikraman, S. V.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1597−1598. Complexes were prepared following: (f) Kasahara, Y.; Hoshino, Y.; Shimizu, K.; Satô, G. P. *Chem. Lett.* **1990**, 381−384.

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Table 1. Values for the HTP (β_M)[a] Evaluated for the Enantiomeric Samples of Ru(III) Complexes and the ICD Spectral Data (θ/deg)[b] for Doped N* Phases

	β_M/μm^{-1}				θ/deg			
dopant	Δ	Λ	host[c]	T/°C	Δ	Λ	λ/nm	p/μm
1-6	−146	130	MBBA	30	−0.83	1.05	420	5.1
1-12	−127	120	MBBA	30	−0.78	0.59	420	8.3
	−66	72	EBBA	60	−0.69	0.88	420	7.5
	−55	58	ZLI-1132	35	−1.00	1.07	330	17
	−63[d]	39[d]	PAA	120	−1.34	1.33	480	7.2
2	24	−25	MBBA	30	0.13	−0.16	420	14
	16	−13	EBBA	60	0.55	−0.41	420	13
	24	−22	ZLI-1132	35	0.22	−0.28	330	24
	17	−13[d]	PAA	120	0.25	−0.37	480	15

[a] The signs + and − indicate that P- and M-helical superstructures are induced, respectively. [b] Ellipticity readings taken at band edges of the ICD spectra, which are exemplified in Figure 2. Concentrations of the listed samples with Δ- and Λ-eantiomers are not exactly matched, and the mean helical pitch length is given for each pair, for comparison to the specified wavelength (λ/nm). [c] Abbreviations and experimental nematic ranges: N-(4-methoxybenzylidene)-4-n-butylaniline (MBBA, 21−47 °C), N-(4-ethoxybenzylidene)-4-n-butylaniline (EBBA, 36−73 °C), and 4,4′-azoxydianisole (PAA, 118−135 °C). ZLI-1132 is a mixture of 4-(4-alkylcyclohexyl)benzonitrile and 4-(4-alkylcyclohexyl)-4′-cyanobiphenyl derivatives (Merck Japan, T_{NI} = 72.3 °C, average mw = 263.2). [d] Rough estimates from finite concentrations within a range of x = 0.14−0.18 mol %.

means of a clay column chromatography.[4] This method involves a column material modified with Δ-[Ru(phen)$_3$]$^{2+}$ and has proven to be useful for neutral metal complexes. Once the complexes had been purified chemically by a usual silica-based column (while racemic), the optical resolution was accomplished with further separation of impurities. Two major peaks off this chiral column were well-separated from each other to the “baseline” level in the very first run of elution with methanol. Identification of the stereoisomers has been established in the case of [Ru(acac)$_3$]. An intense positive band at 275 nm, followed by a negative and a positive band, in the CD spectrum was ascribed basically to the ligand $\pi-\pi^*$ exciton band of the Δ-form,[5a] which was corroborated later by the single crystal determination of this absolute configuration.[5b] Accordingly, more retained fractions in all cases of **1**-n and **2** exhibiting the same CD spectral pattern were assigned to the Δ-enantiomers, and the less retained to their antipodes, in this study (Supporting Information).[6]

Structure−HTP Relations. The molecular HTP, β_M defined by eq 1, has been evaluated by the Cano method,[7] plotting the inverse pitch (p^{-1}) against mole fraction (x) of the dopant in four kinds of nematic liquid crystals including a room-temperature system, N-methoxybenzylidene-4-n-butylaniline (MBBA). Induced CD (ICD) spectra were also recorded for each of the induced N* phases at appropriate concentrations. Table 1 summarizes the β_M values thus evaluated and the ICD spectral data relevant to their signs. The pitch data collected by the polarizing optical microscopy are also compiled in Figure 1 for representative cases.

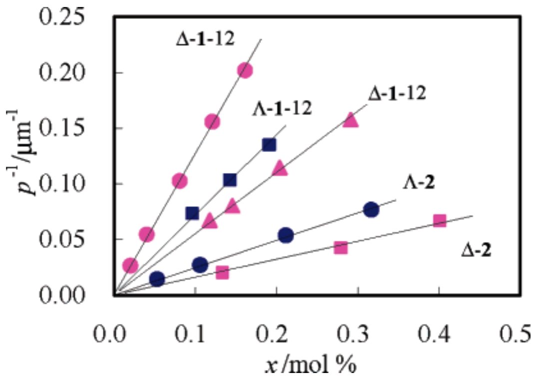

Figure 1. Selected plots of the inverse helical pitch (p^{-1}) versus mole fraction of the dopant (x, in mol %) for doped N* phases obtained with either Δ- or Λ-enantiomer of **1**-12 and **2**. Symbols for the base liquid crystals are ● for MBBA (30 °C), ■ for EBBA (60 °C), and ▲ for ZLI-1132 (35 °C).

$$\beta_M = \left(\frac{\partial p^{-1}}{\partial x}\right)_{x \to 0} \tag{1}$$

The most notable feature at a glance here is that the HTPs differ in sign between Δ-**1** and Δ-**2**, while *both* of them are Δ-enantiomers. For example, complex Δ-**1** has proven to be a remarkably powerful dopant (β_M = -1.4×10^2 and -1.2×10^2 μm^{-1} for n = 6 and 12, respectively, in MBBA), and the performance of complex Δ-**2** is also pretty good (+24 μm^{-1}). Λ-Enantiomers were also studied and, of course, resulted in the same β_M values within experimental errors but with opposite signs. The + and − signs of β_M indicate P- and M-helical twists of the host nematic director, respectively, which was verified by measuring the ICD spectra due to the helical arrangement of conjugated imine chromophores of MBBA molecules.[8] Figure 2 exemplifies such intense ICD spectra, which are positive for Λ-**1**-12 and Δ-**2** and negative for Δ-**1**-12 and Λ-**2**. In other words, the chirality versus twist sense correlation for complex **1** is Δ-M and Λ-P, and for complex **2** Δ-P and Λ-M. The intensities for the latter are relatively weak despite their higher concentrations, reflecting a smaller magnitude of HTP. Essentially the same correlations were observed in other nematics, for which longitudinal chromophoric components are recognizable (Table 1).

Theoretical Interpretations. Thus, the complexes prepared in this work have proven not only to contain a structural element necessary for powerful twisters particularly for MBBA, but also to provide a set of parity relations. The opposite handedness of induced helices arises naturally from the ΔΛ-isomerism, but the effect has its origin also in the distinction between L$_{per}$ and L$_{para}$. To interpret the observed behaviors in the induction of N* phases, a shape model proposed by Nordio, Ferrarini and co-workers is quoted.[9] Equation 2[9d] describes the “chirality parameter” Q, to which the HTP is proportional ($\beta \propto Q$), and this is given in turn by the elements of “surface chirality tensor” $\boldsymbol{Q}$ and of the orientational ordering tensor $\boldsymbol{S}$. Both of the tensors

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(4) Kashiwara, S.; Takahashi, M.; Nakata, M.; Taniguchi, M.; Yamagishi, A. *J. Mater. Chem.* **1998**, *8*, 2253−2257.

(5) (a) Kobayashi, H.; Matsuzawa, H.; Kaizu, Y.; Ichida, A. *Inorg. Chem.* **1987**, *26*, 4318−4323. (b) Matsuzawa, H.; Ohashi, Y.; Kaizu, Y.; Kobayashi, H. *Inorg. Chem.* **1988**, *27*, 2981−2985.

(6) Although it might seem intuitive that the Λ-isomers would be more strongly adsorbed to the Δ-modified clay, it has been shown previously that the situation is reverse for certain tris- and mixed 1,3-diketonates of Ru(III) (ref 4).

(7) (a) Matsumura, K.; Iwayanagi, S. *Oyo Butsuri* (*J. Appl. Phys., Jpn.*) **1974**, *43*, 126−131. (b) Hoshino, N.; Matsuoka, Y.; Okamoto, K.; Yamagishi, A. *J. Am. Chem. Soc.* **2003**, *125*, 1718−1719.

(8) (a) Pirkle, W. H.; Rinaldi, P. L. *J. Org. Chem.* **1980**, *45*, 1379−1382. (b) Rinaldi, P. L.; Naidu, M. S. R.; Conaway, W. E. *J. Org. Chem.* **1982**, *47*, 3987−3991. (c) Rinaldi, P. L.; Wilk, M. *J. Org. Chem.* **1983**, *48*, 2141−2146.

(9) (a) Ferrarini, A.; Moro, G. J.; Nordio, P. L. *Liq. Cryst.* **1995**, *19*, 397−399. (b) Ferrarini, A.; Moro, G. J.; Nordio, P. L. *Mol. Phys.* **1996**, *87*, 485−499. (c) Ferrarini, A.; Moro, G. J.; Nordio, P. L. *Phys. Rev. E* **1996**, *53*, 681−688. (d) di Matteo, A.; Todd, S. M.; Gottarelli, G.; Solladié, G.; Williams, V. E.; Lemieux, R. P.; Ferrarini, A.; Spada, G. P. *J. Am. Chem. Soc.* **2001**, *123*, 7842−7851.

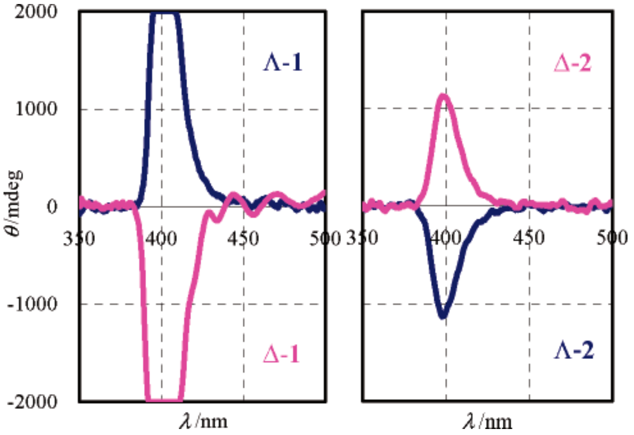

Figure 2. ICD spectra for MBBA* materials doped with Δ- and Λ-enantiomers of **1**-12 (0.1 mol %, left) and **2** (0.3 mol %, right). Each spectrum was recorded at 30 °C in a glass cell of 25-μm gap at normal incidence.

are traceless,[10] and the principal axis system of the latter is usually chosen for eq 2. Most plausible axis systems are included in Chart 1 for our complexes Δ-**1**-*n* and Δ-**2**. Of primary importance is that the direction along which the ligand L_{per} in **1** or L_{para} in **2** has been elongated by design should be designated as the *z* axis, as it should have the highest propensity of alignment.

$$Q = -\sqrt{\frac{2}{3}}(Q_{xx}S_{xx} + Q_{yy}S_{yy} + Q_{zz}S_{zz}) \tag{2}$$

In short, the HTP depends not only on how chiral the dopant's surface is seen along each axis *x*, *y*, or *z*, but also on how well these axes are aligned to the local nematic director. The surface elements are defined by eq 3:[9d]

$$Q_{ij} = \sqrt{\frac{3}{8}}\int_S [s_i(\hat{s} \times \vec{r})_j + (\hat{s} \times \vec{r})_i s_j] d\vec{r} \tag{3}$$

where $\vec{r}$ is a vector giving the position of a point on the molecular surface, $\hat{s}$ is the surface normal outward at the same point, and the integral covers the whole molecular surface.

While the theory has been applied with much success to the structure−performance relations for organic chiral dopants,[9,11] it involves extensive calculation of each of the tensor elements. In contrast, the rigid and *orthogonal* coordination geometry of metal chelates allows one to estimate principal elements Q_{ij}'s with little computational efforts and with reasonable accuracy. Our reasoning is explained for the Δ-enantiomers first. As a crude but useful approximation, the acac ligand can be regarded as a rectangular blade of side length r_0 and the backbone ligand L_{per} constrained in the *xz* plane. The elements can then be analytically estimated as follows for Δ-[Ru(acac)$_2$L$_{per}$].

$$Q_{xx} = -\sqrt{\frac{3}{8}}{r_0}^3, \quad Q_{yy} = 0, \quad Q_{zz} = +\sqrt{\frac{3}{8}}{r_0}^3 \tag{4}$$

It is safely concluded that $Q_{xx} < 0$ and Q_{zz} ($\sim -Q_{xx}$) > 0 for Δ-**1**, and this yields $Q < 0$ (hence $\beta < 0$) from eq 2 in a uniaxial ordering potential (S_{zz} is positive and the largest element).[12]

The signs of Q_{xx} and Q_{zz} flip upon transforming the axis system from (*x*, *y*, *z*) to (*z*, −*y*, *x*) for Δ-[Ru(acac)$_2$L$_{para}$], and therefore a positive *Q* should result (hence $\beta > 0$). This is exactly as reported above for Δ-**2**. In fact, this complex carries bis-chelate group at its terminus, and this must be a disadvantage in achieving a large S_{zz}. Just one 1,4-phenylene group in L_{para} ligand may not be sufficient either, and this very group may also be in hindered rotational state, possibly making a nonnegligible contribution to Q_{yy}. At any rate, not only the sign but also the magnitude of HTP can thus be interpreted consistently.[12]

Table 1 shows that the shortening of two tails in **1** (from $n = 12$ to 6) has only a small enhancing effect on the HTP, which seems to justify the approach based on the rigid part of a dopant. A more quantitative analysis of the magnitude of HTP requires knowledge of the proportionality constant relating *Q* to β, which include such temperature-dependent properties as "orienting strength"[9d] ξ, twist elastic constant K_{22}, and molar volume for the nematic medium v_m, within the above theoretical framework. Although we evaluated the β_M values over only a small range of reduced temperatures ($T/T_{N^*I} = 0.95{-}0.96$, except for the ZLI formulation), the nature in the interactions between the dopant and liquid crystal molecules can vary from one host to another. In fact, it came to our surprise that *N*-(4-ethoxybenzylidene)-4-*n*-butylaniline (EBBA), which is a higher homologue of MBBA by only one methylene unit, experiences the HTP of **1**-12 nearly half that of MBBA. It is suggested by a literature report[13a] that the solvent elastic constant K_{22} for EBBA amounts to roughly twice that for MBBA at temperatures of the experiments, and this could account for the large gap observed, since β is inversely proportional to K_{22}. Effects of other parameters cannot be excluded, however, and weakening in the solute−solvent interactions (lowering ξ/v_m) and the solute orientational disordering (lowering S_{zz}) in EBBA at a higher temperature may also contribute to the decrease in β. The ZLI formulation has also reported on generally lower HTP for the dopants studied here, but this we previously observed for a similar complex of Ru(II).[7b] Higher temperature ranges of some

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(10) The definition of ***Q*** being traceless, and consequently eqs 2 and 3, involves an approximation in which the isotropic contribution of a dopant is left out of consideration. In reality, effects of chirality are not necessarily canceled by the isotropic distribution, and ***Q*** is better regarded as anisotropic content of the surface chirality. For a full tensorial approach, see: Kuball, H.-G.; Höfer, T. In *Chirality in Liquid Crystals*; Kitzerow, H.-S., Bahr, C., Eds.; Springer-Verlag: New York, 2001; Chapter 3, pp 67−100.

(11) (a) Ferrarini, A.; Gottarelli, G.; Nordio, P. L.; Spada, G. P. *J. Chem. Soc., Perkin Trans. 2* **1999**, 411−417. (b) Pieraccini, S.; Donnoli, M. I.; Ferrarini, A.; Gottarelli, G.; Licini, G.; Rosini, C.; Superchi, S.; Spada, G. P. *J. Org. Chem.* **2003**, *68*, 519−526.

(12) Input in eq 2 of a test parameter set, $Q_{xx} = -Q_{zz} = -77$ Å^3 ($r_0 = 5$ Å), for the Δ-(acac)$_2$ moiety of **1** together with plausible order parameters for uniaxial rodlike behavior, $S_{xx} = -0.3$ and $S_{zz} = 0.6$, leads to $\beta = -1.2 \times 10^2$ μm^{-1}, reproducing the HTP of Δ-**1**-12 (the proportionality constant between β and *Q*, which is appropriate for MBBA at 300 K, has been taken from ref 9c). If $Q_{xx} = -Q_{zz} = 77$ Å^3 is assumed instead for Δ-**2**, with the constant unchanged, an order parameter set such as $S_{xx} = -0.1$ and $S_{zz} = 0.2$ yields $\beta = 39$ μm^{-1}. This means a far less ordered state, while rodlike behavior is still assumed. Further disordering towards $S_{xx} = 0$ (while $S_{zz} = 0.2$) would yield β diminishing toward 26 μm^{-1}.

(13) (a) Tolmachev, A.; Ferdoryako, A.; Lisetski, L. *Mol. Cryst. Liq. Cryst.* **1990**, *191*, 395−399. From the plots reported therein of temperature dependences of the elastic constants for a homologous series of *N*-(4-alkoxybenzylidene)-4-*n*-butylanilines, the "K_{22}" readings for EBBA and MBBA at $T_{NI} - T = 13$ °C compare at about 2:1 ratio, although the axis labeling for these plots is not clear. (b) Karat, P. P.; Madhusudana, N. V. *Mol. Cryst. Liq. Cryst.* **1977**, *40*, 239−245. The odd−even effect is also seen in the K_{22} values of 4′-*n*-alkyl-4-cyanobiphenyls (*n*CB). The values interpolated at $T_{NI} - T = 15$ °C compare roughly at 8:5 (in pN) for 6CB to 7CB, for instance. (c) Bualek, S.; Patumtevapibal, S.; Siripitayananon, J. *Chem. Phys. Lett.* **1981**, *79*, 389−391. The odd−even alternation in the HTP values of certain chiral dopants has been observed in the presence (at 20 mol %) of 4,4′-dialkoxyazoxyzenzenes in a nematic host, although the effect upon elongation from methoxy to ethoxy terminal groups is much weaker (2−5% diminution) in this case.

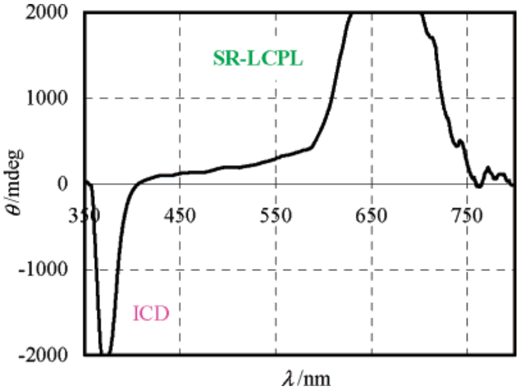

Figure 3. CD spectrum for an MBBA* material doped with Δ-**1**-12 (2.1 mol %, nominal), recorded at 22 °C in a glass cell of 2-μm gap at normal incidence.

hosts have allowed observations on the thermal effect(s). The pitch lengths of the EBBA* specimens traced from 60 to 30 °C showed little temperature dependence (slight concavity by 2% at most), evidencing for the inert nature of the helix induction of **1**-12. Use of PAA at elevated temperatures resulted in rather unstable textural signatures, though we managed to run the Cano experiments. It appeared after standing at 120 °C overnight that racemization had occurred to some extent. Despite these variations, it is stressed again that the sign of HTP could be controlled regardless of its magnitude, and the chirality versus twist sense correlation, which is reversed between **1**-12 and **2**, has been confirmed in four different systems.[14]

Selective Reflections. It is worth mentioning that the complex **1**-12 has gained increased solubility possibly owing to the full optical resolution as well as to the peripheral alkyl appendage, and that a general immiscibility of metal complexes with liquid crystal solvents may be amended. As we managed to dissolve Δ-**1**-12 up to 2 mol % in MBBA, the material stayed in the N* phase barely at room temperature and exhibited greenish coloration when a planar preparation was viewed upright. Figure 3 shows its CD spectrum, recorded at normal incidence under cooling. It contains a huge positive band around 660 nm in addition to the negative ICD below ca. 400 nm. The former signal indicates selective reflection of the left-handed circularly polarized light (SR-LCPL) and is consistent with the relationship for the pitch band,[15] $\lambda_0 = n_{av}p = n_{av}/(\beta_M x)$, in which n_{av} and λ_0 are the average of refractive indices (~1.6 for MBBA)[16] and the corresponding wavelength of reflection, respectively. It is rarely possible to obtain such a spectrum on the same UV−vis scale with *doped* N* samples, while literature examples exist for cholesteryl materials.[17]

We measured the visible spectra of MBBA* specimens of different concentrations in Δ-**1**-12, and Figure 4 displays two examples, one in concentration lower than and the other in concentration higher than the one displayed in Figure 3. The spectral lines have been corrected for absorption effects by subtracting the transmittance baseline recorded in the isotropic liquid state for each sample, and the remaining dips are characteristic of the N* state, as the intensity of transmitting light passing along the helical axis should be halved for the pitch band. It is shown here that the band shifts from around 690 to 610 nm with increasing the doping level from 1.9 to 2.2 mol %, and thus the nature of the observed coloring phenomenon is actually the selective reflection associated with the optical structure that is helical. The present findings will encourage further studies on CPL related applications.

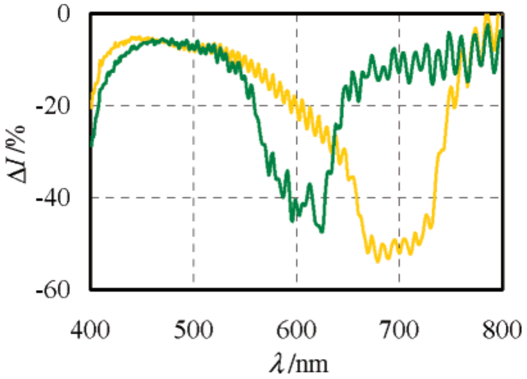

Figure 4. "Difference" transmittance (Δ*I*) spectra for MBBA* materials doped with Δ-**1**-12 (1.9 and 2.2 mol % for yellow and green spectra, respectively), showing dips due to the selective reflection in the N* state. The original spectra were measured at 20 °C in glass cells of 25-μm gap at normal incidence.

In summary, the metal complex dopants of a composition [M(blade)$_2$(backbone)] have acquired another degree of freedom to manipulate their HTP in addition to their ΔΛ-chirality. This is an important asset in view of the fact that the symmetry axis in chiral mesophases (helical axis generated) is perpendicular to the director for nematics, but parallel to the layer normal for smectics.[18] Coordination space in metal complexes seems to offer a variety of new opportunities for designing chiral dopants with versatile and practical uses in liquid crystals.

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Supporting Information Available: The Experimental Section and the associated analytical and solution CD spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

JA042549U

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(14) We thank the reviewer for directing our attention to nematics other than MBBA.

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(16) Mitra, M.; Majumdar, B.; Paul, R.; Paul, S. *Mol. Cryst. Liq. Cryst.* **1990**, *180B*, 187.

(17) Saeva, F. D.; Wysocki, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 5928−5929.

(18) For doping of smectic hosts, see: Hegmann, T.; Meadows, M. R.; Wand, M. D.; Lemieux, R. P. *J. Mater. Chem.* **2004**, *14*, 185−190 and references therein.