Extraordinary Doping Effects of Chiral Helical Linear Tetrapyrrole–Zn(II) Complexes on Chiral Nematic Induction of MBBA Liquid Crystal

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The nematic liquid crystalline phase of *N*-(4-methoxybenzylidene)-4-*n*-butylaniline (MBBA) was effectively transformed into the chiral nematic phase upon addition of zinc(II) complexes of the linear tetrapyrrole bearing chiral auxiliaries at the helix terminal.

Anisotropic properties of liquid crystals (LCs) have been offering opportunities to produce various advanced materials with electric conductivity,[1] magnetism,[2] and optical properties.[3] LC phases are often controlled by external stimuli such as electric bias, thermal change, chemical doping, and so on. In particular, it is well known that nematic (N) LCs are transformed into the chiral nematic (N*) phases upon addition of chiral compounds. The produced higher-order molecular orientation with layer-by-layer helical twisting, showing selective light reflection, has been applicable to imaging technology.[4] A variety of chiral dopants with point,[5] axial,[6] and helical[7] chirality have so far been investigated. Among them, helical dopants of which chirality is based on molecular secondary structures[8] are expected to exhibit effective N* LC induction. However, there are few examples of such dopants except for helicenes[7] due to difficulties in optical resolution and asymmetric synthesis of chiral helical compounds.

We previously reported helicity induction of zinc bilinone (ZnBL), a helical linear tetrapyrrole–zinc(II) complex, by attaching a chiral auxiliary at its helix terminal.[9] Although ZnBL racemizes between the right-handed (*P*) and left-handed (*M*) helical conformers, introduction of a variety of chiral auxiliaries induced thermodynamically preferred helicity and controlled the efficiency of helicity induction (Scheme 1). In this regard, the chiral helical ZnBL is one of good candidates for dopants with helical chirality. Using the ZnBLs as dopants, here we report N* LC induction of *N*-(4-methoxybenzylidene)-4-*n*-butylaniline (MBBA), which is one of most popular nematic LCs at room temperature.

Table 1. Pitch values and helical twisting powers in the ZnBL–MBBA system obtained by the droplet method

ZnBL	Pitch/µm[a]	β_M/µm^{-1} [a,b]
1	0.54	+920
2	2.2	+210
3	2.0	+100

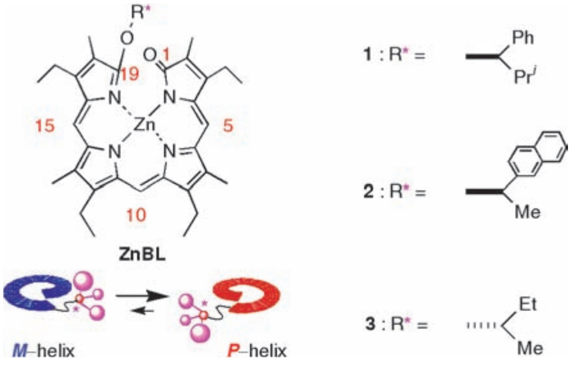
[a]Determined for the MBBA samples containing **1** (0.20 mol %), **2** (0.23 mol %), and **3** (0.51 mol %) at 35 °C. [b]A positive sign of β_M refers to the right-handed twisting of N* MBBA.

We employed ZnBLs **1**–**3** as chiral dopants, which were easily prepared by the nucleophilic ring cleavage of (oxoniaporphyrinato)zinc(II) chloride by alkoxides of the corresponding chiral alcohols **4**–**6** followed by zinc insertion, respectively.[9] ZnBLs **1**–**3** exhibited *P*-helicity with 95, 69, and 1% helicity excesses[10] (h.e.s) at 288 K in CH_2Cl_2, respectively. The LC phase changes of MBBA upon addition of **1**–**3** were investigated by polarized-light optical microscopy (POM). The addition of **1**–**3** to MBBA yielded fingerprint-type textures which were typical of N* LCs.[11] The textures for **1** and **2** were much clearer than that for **3**, indicating that the efficiency of N* LC induction of MBBA depended on the h.e. of the ZnBLs.

The efficiency of N* LC induction in MBBA by **1**–**3** was estimated by helical twisting power (HTP). The helical pitch measurements of N* LC phases were carried out according to the droplet method for the samples of MBBA containing **1**–**3** (Figure 1).[12] The results of HTP determination are listed in Table 1, and the HTP β_M was calculated by Eq 1:

$$\beta_M = (pcr)^{-1}, \tag{1}$$

where *c*, *p*, and *r* represent the mole fraction of the dopant, the helical pitch (µm), and the enantiomeric purity of the dopant, respectively. In the present case, the *r* of each ZnBL dopant



Scheme 1.

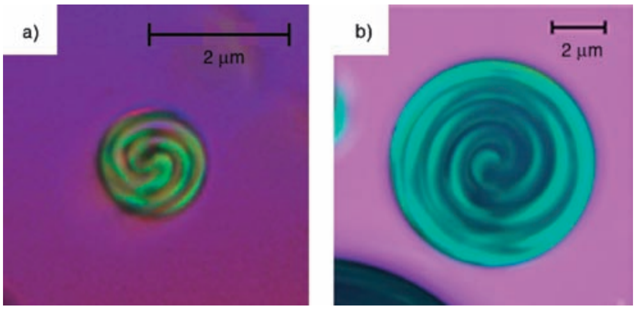


Figure 1. Droplets of MBBA containing ZnBL suspended in glycerol at 35 °C; (a) **1** (0.20 mol %) and (b) **2** (0.23 mol %).

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in MBBA was unknown,[13] and therefore, the r value was tentatively represented by 1.0. That is, the obtained HTPs for **1**–**3** can be regarded as the minimum values. From the circular dichroism (CD) spectra as discussed below, the helical sense of each sample was determined to be right-handed,[14] and thus, the value of β_M was positive. The HTP increased in the order of **3** < **2** < **1**. Especially, the β_M value of **1** reached +920 μm^{-1}, which was larger than HTPs of any other chiral dopants for MBBA so far reported.[15]

In order to verify the β_M values based on Eq 1, the pitch measurements were carried out in the presence of varying concentrations of **1**–**3** in MBBA. The inverse of the N* LC pitch (p^{-1}) proportionally increased with increase in the mole fraction of the dopant (c). The HTP β_M is also defined by Eq 2:

$$\beta_M = \left(\frac{\partial p^{-1}}{\partial c}\right)_{c\to 0}. \qquad (2)$$

The values of β_M were determined by the linear least-squares fitting of the plots to be +900, +250, and +99 μm^{-1} for the **1**-, **2**-, and **3**-MBBA systems, respectively ($R > 0.99$).[16] These values are in reasonable agreement with those calculated by Eq 1. Therefore, it was concluded that the β_M values calculated by Eq 1 were valid in the concentration ranges of 0.03–0.2 mol % for **1**, 0.2–0.5 mol % for **2**, and 0.5–0.9 mol % for **3**.

Further investigation of the N* LC induction of MBBA was examined by CD spectroscopy. In Figure 2a are shown the CD spectra of MBBA doped with **1**–**3**. The positive Cotton effect in the near-UV region was observed for each ZnBL–MBBA system, indicating that the right-handed helical alignment of MBBA chromophores was induced.[14] The CD signal increased in the order of **3**-MBBA < **2**-MBBA < **1**-MBBA. Therefore, the N* LC induction efficiency unambiguously increases with increase of h.e. of ZnBL. One can see that two chiral sources contribute to the N* LC induction; the chiral auxiliary appended at the 19-position of ZnBL and the *pseudo*-intrinsic chiral helical framework of ZnBL. In order to confirm the contribution of the chiral auxiliary, CD spectra of MBBA doped with the alcohols **4**–**6** were measured (Figure 2b). Contrary to the ZnBL–MBBA system, the negative Cotton effect, showing left-handed helical twisting of N* MBBA, was observed for each alcohol, and no relationship in N* LC induction efficiency was observed between the alcohol and the ZnBL dopant with the corresponding chiral auxiliary. The HTPs of **4**–**6** were much smaller than those of **1**–**3** ($\beta_M < 62$ μm^{-1}).[16] From these results, the N* phase of MBBA was mainly induced by helicity of ZnBL, rather than point chirality of the appended chiral auxiliary.

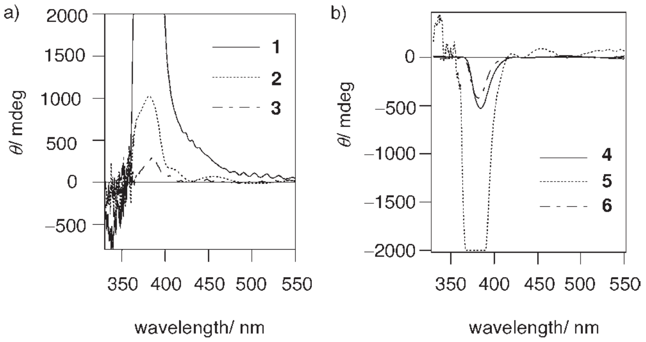

Figure 2. Induced CD spectra of MBBA doped with (a) ZnBLs **1**–**3** (0.23–0.26 mol %) and (b) alcohols **4**–**6** (0.93–1.0 mol %); cell gap 5 μm, recorded at ambient temperature.

In conclusion, we demonstrated extraordinarily effective N* LC induction of MBBA by addition of ZnBLs bearing chiral auxiliaries. As the h.e. of the ZnBL framework increased, the N* LC induction was enhanced. Especially, the HTP β_M of ZnBL **1** reached up to +920 μm^{-1}. Thus, it is clear that the present chiral ZnBLs are quite effective in the N* LC induction of MBBA. The key essence is the hierarchical chiral transmission from the point chirality, via the chiral helical secondary structure of ZnBL, to the MBBA assembly.

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16 See Supporting Information.

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