

Δ -[Ru(acac)₂L] (L = a Mesogenic Derivative of bpy) as a Novel Chiral Dopant for Nematic Liquid Crystals with Large Helical Twisting Power

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Liquid crystals, particularly nematics, are a fascinating system in terms of their ability to transfer and magnify the *molecular chirality* into the *form chirality*, most notably the helical superstructure. Doping nematics with enantiomeric organic compounds is a common practice both in today's LCD industry and in chirality research,^{1,2} but little attention has been paid to the potential of Δ -isomerism of transition metal complexes as a source of chirality in liquid crystals. We now wish to report on our evaluation of the helical twisting power (HTP) of Δ -[Ru(acac)₂L], in which L and acac denote a mesogenic derivative of bpy, 5,5'-(4-octylphenyl-oxycarbonyl)-2,2'-bipyridyl, and acetylacetonate, respectively (Figure 1).

The synthesis, optical resolution, and monolayer behavior at the air–water interface of this amphiphilic complex have been recently reported.³ It can be seen from the space-filling model in Figure 1 that the Ru complex has an overall rodlike shape, although not mesomorphic itself, with two acac moieties acting as chiral “blades” at the center. This lowered symmetry of point group C_2 , which is conformationally rigid, is expected to serve as a novel “twister” for calamitic liquid crystals. Several nematics including ZLI-1132 (Merck Japan), *N*-(4-methoxybenzylidene)-4-*n*-butylaniline (MBBA), *p*-azoxyanisole (PAA), and two-ring *N*-salicylideneaniline derivatives⁴ (SA) were tested for the induction of the chiral phase(s) by doping with Δ -[Ru(acac)₂L]. Focal conic textures were observed by polarizing microscopy in all cases, and some preparations of up to 1 mol % doping level (nominal, in PAA and SA) showed iridescence like cholesterics, suggesting the formation of chiral nematic (N*) phases with helical pitches (p) approaching the visible spectral range.

The pitch measurements were then performed with dilute solutions in the ambient temperature systems, ZLI-1132 and MBBA, by the Cano wedge method.⁵ The results are shown in Figure 2, which compiles data of the inverse pitch (p^{-1}) versus wt % of the dopant (x') at temperatures of 19–23 °C. The molecular HTP β_M is defined by eq 1, based on the mole fraction (x) of a pure enantiomer. The helical sense was determined to be left-handed, and the sign of β_M should be negative for both of the hosts (vide infra). The estimates of HTP (based on the weight fraction) were then obtained by the linear least-squares fitting in Figure 2 to be -20 and $-52 \mu\text{m}^{-1}$ in ZLI-1132 and MBBA, respectively. The values of β_M on the mole fraction basis⁶ were determined to be

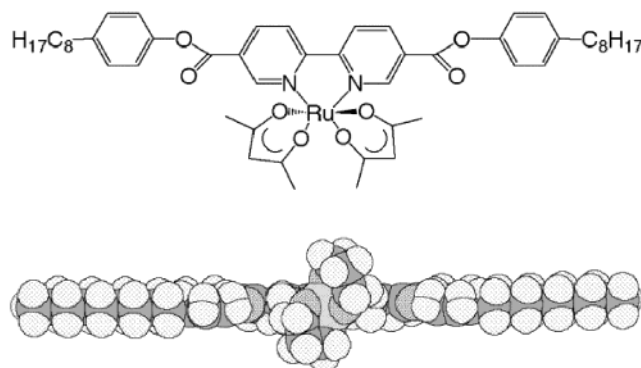


Figure 1. The molecular structure of and a space-filling model for Δ -[Ru(acac)₂L].

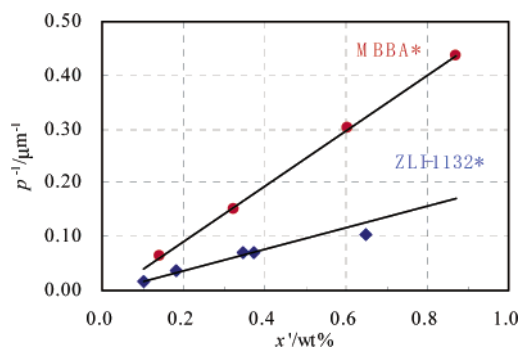


Figure 2. Plots of the inverse helical pitch (p^{-1}) versus weight percentage of the dopant (x') for solutions of Δ -[Ru(acac)₂L] in ZLI-1132 and MBBA.

-71 and $-1.8 \times 10^2 \mu\text{m}^{-1}$, correspondingly.

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

The experiments were repeated with two or three wedge cells of different tangencies (E.H.C., Japan), and several spots of Grandjean–Cano steps were measured and averaged. The variances in p^{-1} are no greater than the cell specifications ($\pm 5\%$). Small amounts of the dopant were added in aliquots of a chloroform solution of known concentration, which was thoroughly evaporated before the host liquid crystal was weighed in, and therefore the uncertainty in the concentration parameter may be a little greater. Still, the plots in Figure 2 are rather conservative ones in that the material is assumed to be enantiomerically pure. With all of these aspects considered, we conclude that our chiral dopant is quite powerful indeed in the helix formation.

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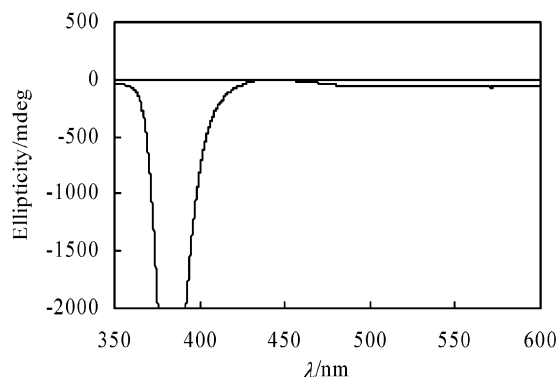


Figure 3. The ICD spectrum of an MBBA solution of Δ -[Ru(acac)₂]L (0.30 wt %, cell gap 5 μm , normal incidence, i.e., along the helical axis, recorded at 22 °C).

The CD spectroscopy is very useful in determining the helical sense of a chiral liquid crystal phase. Our measurement for MBBA solutions revealed a strong, negative induced CD (ICD) signal toward UV range, indicating that left-handed helical alignment of the host imine chromophores had been induced.⁷ This ICD spectrum is exemplified in Figure 3.⁸ It was in turn found by microscopic examination of contact preparations, showing no discontinuity at all, that the helical sense of the N* phase of doped ZLI-1132 is also left-handed.

Chiral dopants of binaphthyl type and substituted aminoanthraquinones have been reported to possess large (absolute) values of HTP. Some examples are about +80 and +60 μm^{-1} for alkylendioxy-bridged derivatives of the former (with *P* helicity)⁹ in 4'-*n*-pentyl-4-biphenylcarbonitrile (5CB) and MBBA, respectively. The values reach -130 μm^{-1} (with *M* helicity, in a ZLI formulation) upon further modification of the bridging group.² Among the highest examples is +115 μm^{-1} for 1,5-bis(1-(*R*)-phenylethylamino)-9,10-anthraquinone¹⁰ with two chiral centers also in ZLI. Two lessons could be learned from these precedents with regard to the efficiency of intermolecular chirality transfer: (1) conformationally rigid substituent(s) at the chiral center(s) or even an explicitly helical conformation like binaphthyl compounds would constitute better "chiral parts," and (2) it is important to arrange these "chiral areas" appropriately relative to the molecular orientational axis (principal axis of the ordering tensor). The Ru complex used in this study contains a rodlike ligand L, which is an excellent mesogen itself,³ and it must assist the orientational matching of the complex with host molecules. The chiral acac groups might then exert on neighbors the left-handed orientational twist about an axis perpendicular to the long molecular axis. Temperature dependence of the HTP of Δ -[Ru(acac)₂]L was found to be rather weak, although preliminary, with slight convexity between ambient and clearing temperatures. Inversion of the Δ - to Λ -enantiomer is unlikely at the temperatures of our experiments, while the orientational ordering would be perturbed on heating.

It is well known that the helical induction in liquid crystals depends on the nature of the solvent molecules. It has been proposed

for the above case of axially chiral biaryl systems that a specific interaction with the solvent of the cyanobiphenyl type such as 5CB stabilizes its conformation of the same helicity, thereby amplifying the number of chiral species.¹¹ Structural matching of molecular details would be necessary for such a mechanism to operate, and in fact ZLI yielded smaller (absolute) values of HTP than MBBA for our Ru complex.

We might point out that the solubility of this Ru complex in ZLI-1132 is not desirably high. It is seen in Figure 2 that the data point at 0.65 wt % already starts to deviate from the linear relation of p^{-1} versus x' . It was observed over 1–8 days that some dark particles had separated out of ZLI-1132 mixtures of the two highest compositions plotted. Perhaps metastable (supersaturated) solutions were employed in our measurements, and its influence may be reflected in the above nonlinearity. The dopant is also highly colored, which may be considered unfavorable for certain applications. The complex is yet highly versatile in terms of synthesis and well suited to the investigation of structure/response relation² for the helical induction in the anisotropic fluids. Besides, the polar nature of metal complexes may be useful in the investigation of induced ferroelectric liquid crystals.¹² We are also pursuing possibilities of doping smectic materials with metal complexes with $\Delta\Lambda$ -chirality.

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- (8) The spectrum is too intense to be recorded on scale; for example, the observed ellipticity at 402 nm (band edge) was -638 and -1760 mdeg for samples of 0.30 and 0.87 wt % solution, respectively. The CD induction is thus reasonably reproducible. Note that the CD spectrum of Δ -[Ru(acac)₂]L in methanol exhibits a positive band in this spectral region ($\Delta\epsilon = +2.7$ at 400 nm, ref 3) and a negative band around 450 nm tailing over the rest of visible wavelength range.
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