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The effect of $\Delta\Lambda$ chirality on molecular organization in two-dimensional films of a Ru(II) complex with a mesogenic ligand

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A novel amphiphilic Ru(II) complex, [Ru(acac)$_2$L] (acac = acetylacetonato, L = 5,5′-bis(4-octylphenyloxycarbonyl)-2,2′-bipyridyl), in which L undergoes SmC, SmA and N liquid crystal phases, exhibits a remarkable chirality effect on its monolayer state: that is, a racemic mixture gives a monolayer consisting of spike-like aggregates of 1.2 nm (in height) × 50 nm (in diameter), whereas the Δ-enantiomer gives a uniform monolayer.

It is well known that chirality has a profound effect on mesomorphism.[1] The primary role of chiral centers introduced into the liquid crystal phases is to lower the symmetry of the phase, but the intricate nature of the interactions in fluid phases of chiral molecules remains largely unspecified. One approach for resolving such a problem is to study the monolayer behavior of liquid crystal molecules at an air–water interface.[2] Various spectroscopic techniques can be applied to reveal the molecular organization in floating and deposited monolayers. Use of the Δ,Λ-isomerism of 6-coordinate tris-chelate complexes would also be enlightening in studies of the effect of chirality owing to their unique steric and electronic characteristics. In this communication, we report on the monolayer behaviour of an amphiphilic metal complex in which one of the ligands is mesomorphic. As a result, a remarkable difference has been found in the molecular aggregation of the deposited films between a racemic mixture and the Δ-enantiomer.

We selected a mesogenic bpy derivative from the literature[3] and eliminated the oxo groups (dipolar components) from the attachment of alkyl tails. The mesomorphic phase sequence of the modified bpy ligand L [5,5′-bis(4-octylphenyloxycarbonyl)-2,2′-bipyridyl, Fig. 1] was determined by polarizing optical microscopy† and differential scanning calorimetry (first heating run at 10 °C min^{-1}):

$$\mathrm{K_2\ 91\ K_1\ 110\ SmJ\ 136\ SmC\ 230\ SmA\ 245\ N\ 255\ I.}$$

The phase assignment is in accordance with the literature data for the octyloxy analogue.[3]†

A Ru(II) complex, [Ru(acac)$_2$L] (acac = acetylacetonato, Fig. 1), was synthesized by reducing [Ru(acac)$_3$] with zinc powder in THF, and after adding L the solution was refluxed for 24 h under a nitrogen atmosphere. The product was purified on a silica gel column eluting with 3:1 THF:hexane. The compound thus obtained was identified with NMR, ICP and elemental analyses.‡

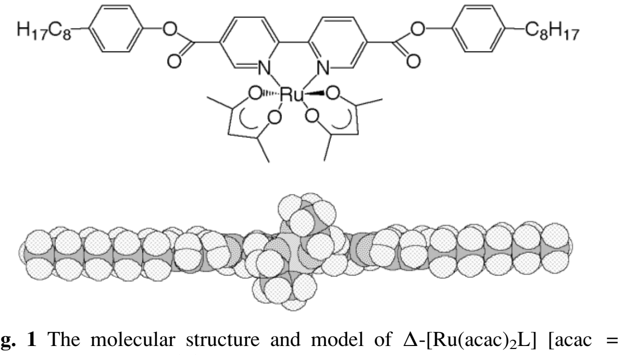

Fig. 1 The molecular structure and model of Δ-[Ru(acac)$_2$L] [acac = acetylacetonato, L = 5,5′-bis(4-octylphenyloxycarbonyl)-2,2′-bipyridyl].

Column chromatography was applied for optical resolution. A glass tube (1.0 cm i.d.) was packed with 2.0 g of an ion-exchange adduct of a clay mineral (synthetic laponite) and Δ-[Ru(phen)$_3$]$^{2+}$. This packing material is capable of resolving various kinds of tris- or bis-acetylacetonato complexes.[4] The racemic mixture of [Ru(acac)$_2$L] (*ca.* 1×10^{-5} mol) dissolved in 1.0 mL of a 1:1 chloroform:methanol mixture was mounted and eluted with 1:4 chloroform:methanol under moderate pressure. The chromatogram showed a broad single band with a shoulder. The initial and final fractions exhibited the positive and negative peaks at 400 nm in the circular dichroism spectra. By repeating recrystallization from methanol solvent at −4 °C, the optical purity of the material improved until it attained the limiting values of $\Delta\varepsilon = +2.7$ and -2.9 at 400 nm for the less and more retained isomers, respectively. Comparing these values to those of Δ- and Λ-[Ru(acac)$_3$] ($\Delta\varepsilon = +1.0$ and -1.0 at 380 nm, respectively), we assume that the material has been separated nearly fully into pure Δ- and Λ-isomers of [Ru(acac)$_2$L].

The racemic mixture did not melt until 233 °C, around which the material rapidly blackened. Samples rich in the Δ-enantiomer did not show any sign of mesomorphism either, though they exhibited seemingly lower melting temperatures. We then studied the monolayer states of [Ru(acac)$_2$L] with a purpose of obtaining information on the factors of achieving liquid crystal phases for the present type of metallomesogen. A chloroform solution of the racemic mixture or the Δ-isomer was spread onto pure water at 20 °C.

The solid and dotted curves in Fig. 2 show the surface pressure *versus* molecular area isotherms for the racemic mixture and the Δ-isomer, respectively. In both cases, the surface pressure rose from zero at the molecular area of 0.35 nm^2 molecule^{-1}. This lift-off area is close to the cross-sectional area of the complex when the molecular rigid cores lie flat on the water surface. Thus the metal complex forms a monolayer at the air–water interface. The surface pressure rises more steeply for the racemic mixture than for the Δ-isomer. It implies that the racemic mixture forms a more rigid monolayer than the enantiomer, while the molecular packing is less dense. The isotherm for the Δ-isomer exhibits an inflection point around 0.15 nm^2 molecule^{-1}, suggesting that some structural change occurs at this molecular area. Passing through this point, the surface pressure increases as steeply as for the racemic mixture. We assume that the molecules in both of the monolayers orient initially flat on the water surface around 0.35 nm^2 molecule^{-1} and that they change to vertical orientation upon compression. The drawings within Fig. 2 show the possible molecular packing of the racemic mixture and the Δ-enantiomer in the highly condensed states below 0.20 and 0.12 nm^2 molecule^{-1}, respectively.

The floating films were transferred onto mica at a surface pressure of 15 mN m^{-1} and the surface structures studied with

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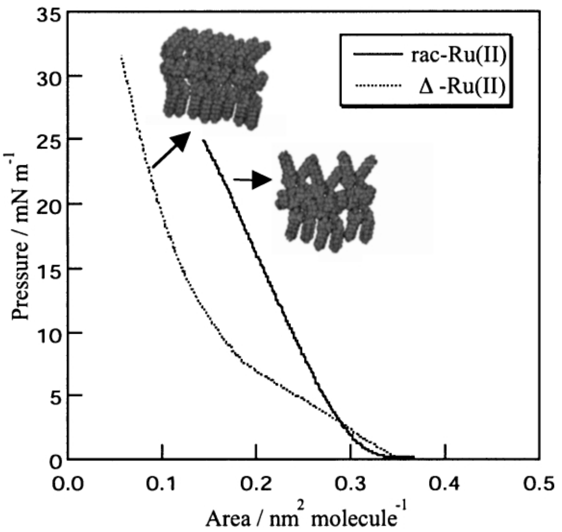

Fig. 2 Surface pressure *versus* molecular area isotherms for the racemic mixture (solid line) and the Δ-isomer (dotted line). The sub-phase was pure water at 20 °C.

an atomic force microscope (AFM) in a tapping mode. Fig. 3(A) is the 2 μm × 2 μm AFM image of the deposited film of the racemic mixture. The film consists of an aggregate of spikes whose height and diameter are estimated to be 1.2 and 50 nm, respectively, and one spike contains *ca.* 10^3 molecules. The height is nearly equal to the length of the octyl moieties. Thus the vertical molecular arrays may either become tilted or change their structure during deposition. The strong lateral adhesion between metal centers in the ΔΛ pairs as suggested in the packing model (Fig. 2) would probably be related to such transformations. Fig. 3(B) is the 2 μm × 2 μm AFM image of the deposited film of the Δ-isomer. The surface is very flat over the observed region. There were only a small number of dotted regions. Since the thickness of the film is difficult to estimate, the orientation of molecules in the film is uncertain. Nevertheless, it can be concluded that the enantiomers are oriented vertically, considering a very small molecular area at deposition (0.12 nm^2 molecule^{-1}).

As a concluding remark, close contact of Δ- and Λ-isomers of metal complexes may well lead to three-dimensional ordering, which should be controlled if one wishes to obtain liquid crystals of either two- (columnar)[5] or one-dimensional (smectic) order. The enantiomers of the present type appear to form rather compressible monolayers, and their packing characteristics are to be fully scrutinized. In this light, our test for their performance as a chiral dopant has proven highly promising.[6]

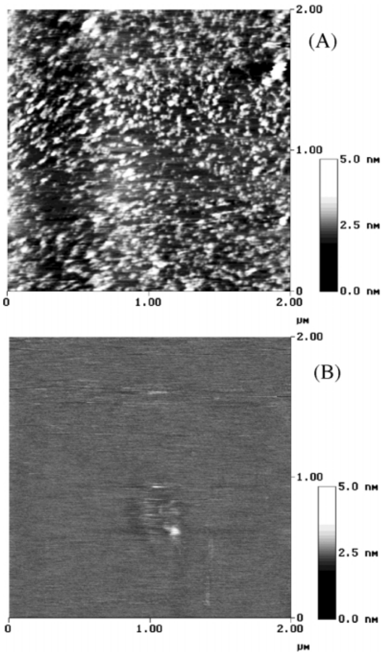

Fig. 3 The 2 μm × 2 μm AFM image of the deposited film of the racemic mixture (A) and the Δ-isomer (B). The films were transferred onto mica at a surface pressure of 15 mN m^{-1}.

Notes and references

† The SmC→SmA transition was of second order and, intriguingly, the SmA→N transition was also of weakly first order. The reported transition temperatures were therefore determined by polarizing optical microscopy alone. The optical textures for the N and SmA phases commonly involved homeotropic areas, and the temperature ranges for each of these phases was estimated from the duration of coexisting marble or fan-shaped textures. The SmA/C transition was in turn recognized by a change of the homeotropic area to birefringent pattern of a blurred Schliren type. The rest of the transitions were associated with the enthalpy changes of 11.7 (K_2→K_1), 8.0 (K_1→SmJ), 31.0 (SmJ→SmC), and 1.6 kJ mol^{-1} (N→I); all of these values are in accordance with the literature.[3]

‡ Calculated for $C_{50}H_{62}N_2O_8Ru$: C, 65.27; H, 6.79; N, 3.04. Found: C, 65.43; H, 6.97; N, 3.18%.

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