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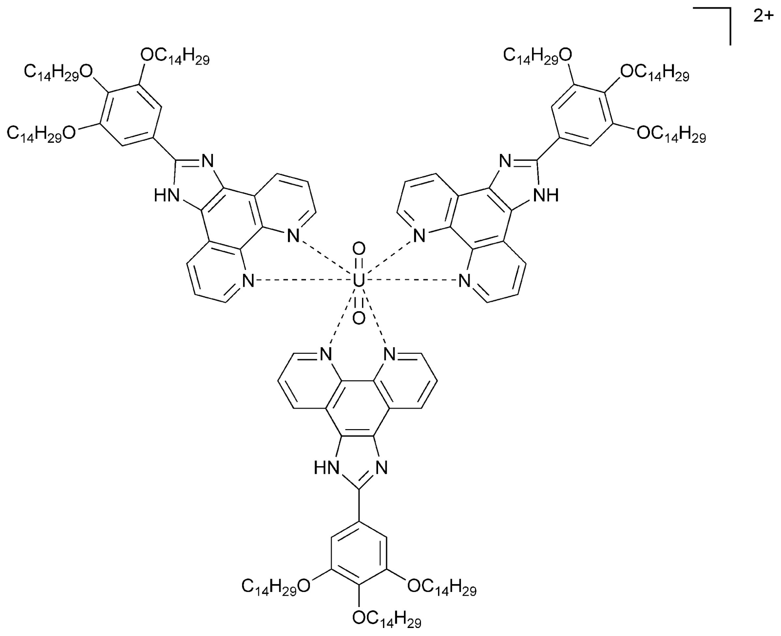

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A Propeller-like Uranyl Metallomesogen

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The attractiveness of metal-containing liquid crystals (*metallomesogens*) is that coordination of the mesogenic ligands to the metal center allows the building of molecular edifices with geometries that are impossible to achieve by all-organic liquid crystals.[1] Moreover, induction of liquid-crystalline behavior can be achieved in nonmesomorphic ligands upon coordination to metal ions. Thanks to intensive research efforts in the field of metallomesogens during the last two decades, nearly every metal of the periodic system has been incorporated into liquid crystals. Although lyotropic uranium-containing liquid crystals have been known for a long time,[2] it was not until recently that examples of thermotropic uranium-containing metallomesogens have been reported. Sinn and co-workers described calamitic uranyl complexes of β-diketonate[3] and tropolonate ligands,[3,4] whereas Sessler's mesomorphic uranium−alaskaphyrin complexes are the first examples of discotic uranium-containing metallomesogens.[5] Very recently, Aiello et al. reported on mesomorphic uranyl Schiff base complexes.[6] In all these thermotropic liquid crystals, the uranium is present in the hexavalent oxidation state as the dioxouranium(VI) or uranyl cation.

The classic design strategy to obtain columnar phases for metallomesogens is to incorporate the metal ion into the central cavity of a flat macrocyclic ligand with peripherally attached alkyl chains (e.g., liquid-crystalline metallophthalocyanines).[1] However, tris-β-diketonate complexes with an octahedral metal center and an overall propeller-like molecular shape can exhibit columnar mesophases, as well.[7,8]

Here, we present a new approach to the design of propeller-like metallomesogens, which is based on the ability of the linear uranyl cation to form complexes by coordination of ligands in the equatorial plane. The idea was to replace the 1,10-phenanthroline ligands in the previously reported[9,10] $[UO_2(phen)_3][OTf]_2$ complex (where OTf = CF_3SO_3 or triflate) by an imidazo[4,5-f]-1,10-phenanthroline moiety bearing three long alkoxy chains. This ligand was prepared by first oxidizing 1,10-phenanthroline to 1,10-phenanthroline-5,6-dione,[11] followed by reaction with 3,4,5-tris(tetradecyloxy)benzaldehyde and ammonium acetate in hot glacial acetic acid.[12] The uranyl complex was synthesized by reaction between the ligand and uranyl triflate (3:1 molar ratio) in ethanol. The structure of the uranyl complex is shown in Figure 1. Although we were not able to obtain single crystals of the uranyl complex, it is reasonable to assume that its first coordination sphere is comparable with that observed for the $[UO_2(phen)_3][OTf]_2$ complex, with an equal population of right-handed and left-handed helices.[9,10] The coordination polyhedron can be described as a bi-end-capped trigonal antiprism. The choice of the triflate ion as counterion is not arbitrary because weakly coordinating anions are required to avoid competition of the anion with the phenanthroline ligands for binding to the uranyl ion.

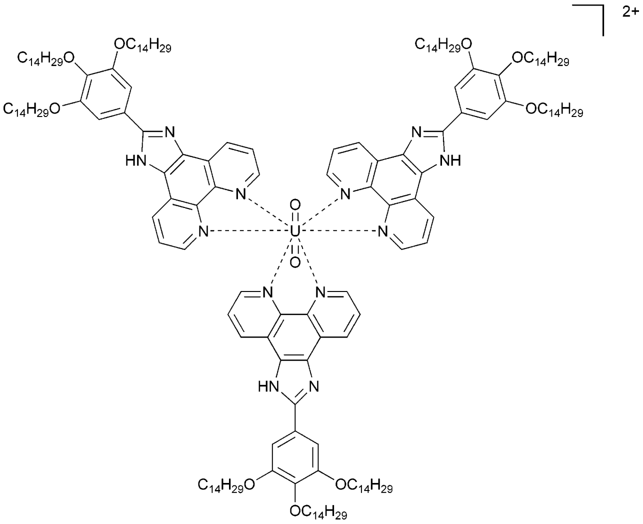

Figure 1. Structure of the uranyl complex. The two noncoordinating triflate counterions have been omitted.

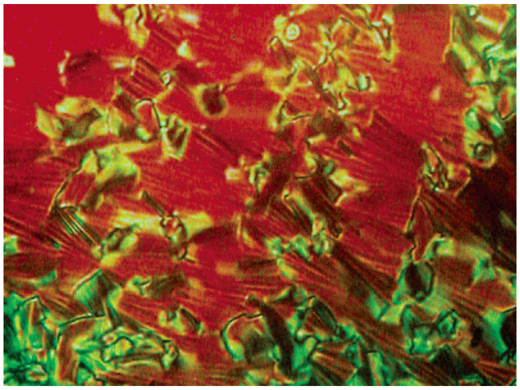

Figure 2. Natural optical texture of the uranyl complex at 170 °C (500× magnification).

The liquid-crystalline properties of the complex were examined by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction on a powder sample. The ligand is not mesomorphic, whereas the uranyl complex melts at 95 °C into a mesophase ($\Delta H = 69.5$ kJ mol^{-1}) and clears into the isotropic liquid at 181 °C ($\Delta H = 2.8$ kJ mol^{-1}). The fluid and birefringent optical texture of the uranyl metallomesogen (Figure 2, POM) confirms mesomorphism, but the mesophase could not be characterized only on this basis.

The X-ray pattern of the uranyl complex (Figure 3) is characteristic of a hexagonal columnar phase ($\mathrm{Col_h}$). Two Bragg reflections are observed in the small angle range: an intense and sharp reflection at $2\theta_1 = 2.31°$ ($d_1 = 38.2$ Å) and another small signal at $2\theta_2 = 4.012°$ ($d_2 = 22.0$ Å). The reciprocal d spacings are in the

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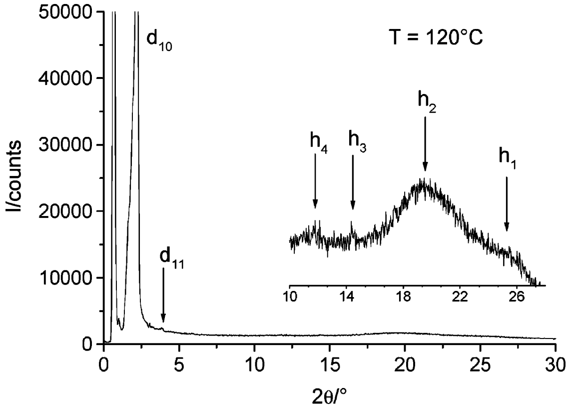

Figure 3. X-ray pattern of the uranyl complex in the hexagonal columnar phase at 120 °C.

ratio of 1:$\sqrt{3}$, which allows their indexation (*hk*) in the hexagonal 2D symmetry as (10) and (11), respectively, the corresponding lattice parameter of the Col_h phase being $a = 44.05$ Å. A broad scattering band, reflecting the liquid-like organization of the paraffinic chains ($h_2 = 4.6$ Å), and three other weak signals ascribed to various intermolecular interactions were also seen. The signal observed at 3.5−3.6 Å, h_1, broad and weak, corresponds to the average distance between successive stacking molecular cores (taken hereafter as the stacking periodicity, h_1). The broadness of this signal indicates that such a regular stacking is simply short-range correlated and also confirms that the bonded ligands are slightly tilted with respect to the hexagonal lattice plane (expected to be due to the propeller-like shape of the complex). The Bragg reflection at 6.0−6.2 Å, h_3, is likely due to the strongly scattering uranyl cation $[UO_2]^{2+}$. Comparison with the crystalline structure of a homologous compound[9,10] leads us to propose that this signal may reflect reticular planes rich in uranium. Finally, the broad signal at 7.2−7.4 Å ($h_4 \approx 2 \times h_1$) seems to indicate that the stacking is also alternated (staggered): starting from one molecule, the next one is rotated by 60° in order to partially "fill" the space left unoccupied by the first molecule. The next molecule is also rotated by 60°, therefore, totally superposed with the first one, and so on. The volume and the dimensions of the complex are in good agreement with a portion of column defined by $h_1 \times S$ (the columnar cross-section $S = 1680$ Å^2). For one mesogen per such a slice, a density of ca. 1 is deduced for the complex (i.e., a molecular volume of ca. 5600 Å^3 at 120 °C), reasonable in the present case due the presence of the heavy metal atom.

The complex, which approximates a D_3 symmetry, exists as two optical isomers, Δ and Λ, present in a 50:50 ratio (Figure 4). Thus, packing frustrations can be explained by steric constraints and polar order within the columns.[7,8,13] To accommodate an antiferroelectric order in a ternary symmetry lattice (Col_h phase), the columnar phase can result from the random piling of these propeller-like mesogens, however, with important stacking faults all along the columns. For a more efficient packing, complexes of identical absolute configuration about the metal center may stack on top of each other into polar aggregates. However, to escape from the polar ordering, such molecular bundles made of a few consecutive stacking enantiomers are necessarily randomized within the columns.

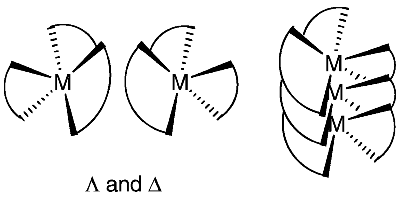

Figure 4. Schematic of the two isomers and stacking of one pure enantiomer into a polar column.

Experiments to observe photoluminescence for the complex in the solid state or in solution were unsuccessful. The absence of photoluminescence in this type of complex is not surprising because it is known that, for instance, in uranyl complexes of macrocyclic Schiff base ligands, the luminescence is quenched, as well.[14]

In conclusion, we presented the first example of a propeller-like uranyl-containing metallomesogen. The uranyl ion acts as a template to bring the ligand into the correct position, so that the supramolecular assembly approximates a propeller-like repeating unit of a hexagonal columnar phase. These metallomesogens stack in such a way that the polar order is annihilated.

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Supporting Information Available: Experimental procedures and characterization for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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