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Preliminary communication

The first columnar discotic liquid crystalline anthraquinone metal complexes

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In this communication we present the synthesis and characterization of the first two members of a new class of metallomesogen. The Pd and Cu complexes of 1-hydroxy-2,3,5,6,7-pentakis-(dodecyloxy)anthra-9,10-quinone were prepared by reacting the respective metal(II) acetate with the ligand. Preliminary mesophase characterization by DSC and polarizing optical microscopy indicates the formation of columnar mesophases in both the complexes.

A variety of metallomesogens with unique geometries and molecular shapes has previously been created by incorporation of a metal centre into organic ligands. These metal-containing liquid crystalline materials are of great interest because they are expected to have properties associated with metal atoms such as magnetism, electron-rich nature, colour, etc., in conjunction with liquid crystalline properties such as fluidity, processability, supramolecular order, etc. In the last two decades a large number of metallomesogens has been prepared. Their synthesis, characterization and applications have been described in several review articles [1–6].

Discotic metallomesogens have recently become increasingly important due to their electronic and opto-electronic properties. The quasi-one-dimensional order of closely packed disks in columnar mesophase of metallomesogens makes these materials very promising candidates for charge and energy migration studies [7]. Many disc-like molecules such as phthalocyanines, porphyrins, β-diketones, dithiolenes, benzalimines, etc. incorporating a variety of metals such as Ni, Cu, Pd, VO, Lu, Eu, etc., and displaying various mesophases such as columnar, discotic nematic, discotic lamellar, etc., have been synthesized and characterized [1–6, 8].

β-Diketonates, figure 1 (*a*), are among the most widely synthesized and studied metallomesogens [1–6]. They exhibit either calamitic or discotic mesmorphism depending on subtle differences in the molecular structure. A number of β-diketone derivatives are known to show nematic, smectic, columnar and lamellar mesophases [1–6]. β-Diketone complexes having both calamitic and discotic features are also known [9]. Recently, during the synthesis of monofunctionalized rufigallol-based discotic liquid crystals, we realized that the 1-hydroxyanthraquinone structure, figure 1 (*b*), is analogous to the well-known β-diketone system. Therefore, the rich chemistry that has been developed for the β-diketone system can also be applied to the anthraquinone molecule and a variety of novel metallomesogens can be prepared.

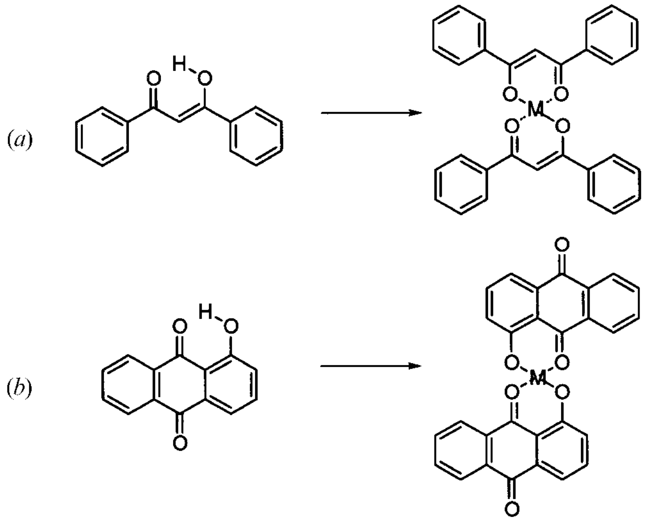

Figure 1. Molecular structures of (*a*) a β-diketone and a complex and (*b*) anthraquinone systems.

The ligand 1-hydroxy-2,3,5,6,7-pentakis (dodecyloxy)-anthra-9,10-quinone **5** was prepared by partial alkylation of 1,5-dihydroxy-2,3,6,7-tetradodecyloxyanthra-9,10-quinone [10] as shown in the scheme. It was purified

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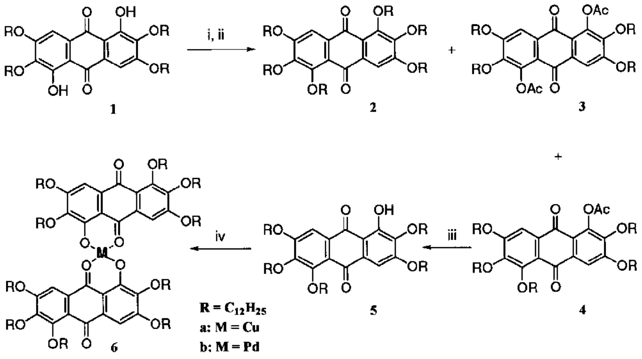


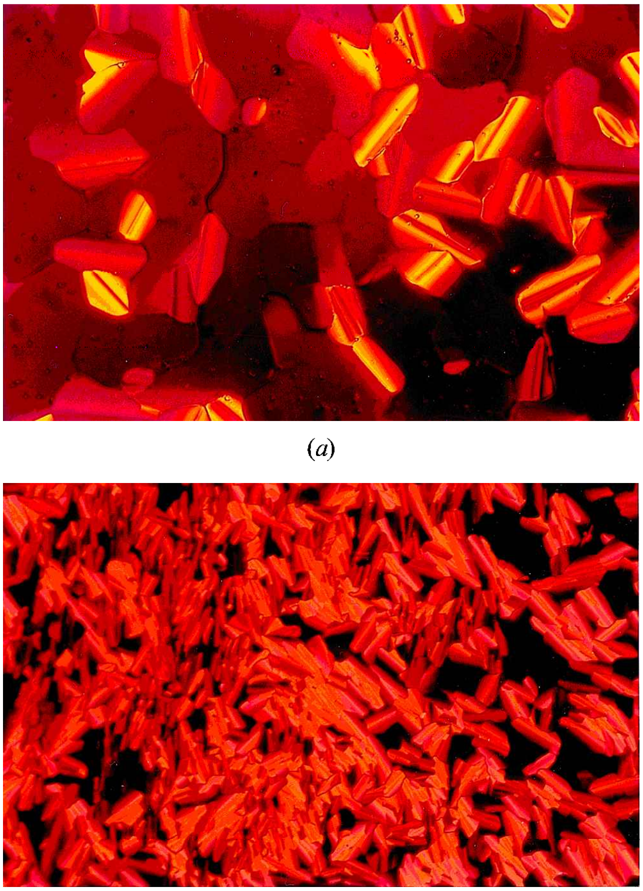
Scheme. Synthesis of metal complexes of 1-hydroxy-2,3,5,6,7-pentakis(dodecyloxy)anthra-9,10-quinone. Reagents and conditions: (i) $CsCO_3$, DMF, RBr, 100°C, 20 h; (ii) Ac_2O, pyridine, reflux, 27%; (iii) aq. NaOH, EtOH, reflux, 80%; (iv) $Cu(OAc)_2$ or $Pd(OAc)_2$, acetonitrile–pyridine, 20%.

as its acetate and the free phenol was regenerated by hydrolysis of the acetate. Treatment of the ligand **5** with copper(II) acetate or palladium(II) acetate in boiling acetonitrile–pyridine yielded the metal complexes. They were further purified by microfiltering their dichloromethane solutions followed by crystallization from a dichloromethane–ethanol mixture. The Pd complex **6b** was characterized by ^{1}H NMR and elemental analysis, while the Cu complex **6a** was characterized by elemental analysis (the paramagnetic nature of copper(II) hampered its characterization by NMR spectroscopy). The relevant analytical data are given below:

^{1}H NMR (400 MHz, $CDCl_3$): compound **5**, δ 12.65 (s, 1H), 7.63 (s, 1H), 7.38 (s, 1H), 4.11 (m, 10H), 2.0–1.26 (m, 100H), 0.88 (t, 15H); compound **6b**, δ 7.72 (s, 2H), 7.42 (s, 2H), 4.17 (m, 12H), 4.04 (m, 8H), 1.9–1.2 (m, 200H), 0.86 (m, 30H). Elemental analysis: **6a**, calc for $C_{148}H_{254}O_{16}Cu$ C 75.52, H 10.89; found C 75.33, H 11.03%. **6b**, calc for $C_{148}H_{254}O_{16}Pd$ C 74.19, H 10.69; found C 74.50, H 10.82%.

Both compounds were found to be liquid crystalline. Their mesophase behaviour was checked by polarizing optical microscopy as well as by differential scanning calorimetry (DSC). The thermograms recorded for the copper complex **6a** on heating showed three endothermic peaks. The first, located at 71.9°C, corresponds to an enthalpy of 42 J g^{-1}, related to the transition from the crystal into a columnar mesophase. The second weak peak at 121°C corresponds to an enthalpy of only 1.5 J g^{-1} and is associated with a columnar to columnar phase transition. The third peak at 146.2°C with an enthalpy of 4.7 J g^{-1} indicates the columnar to isotropic phase transition. The thermal behaviour was found to be reversible: on cooling from the isotropic liquid, the thermograms showed three exothermic peaks at 144.2, 118.0 and 67.1°C with roughly the same enthalpy values as in the heating run. A Leitz DMRXP polarizing microscope with a Mettler FP82HT heating stage was used to observe the optical textures of the phases. On cooling from the isotropic liquid, the copper complex **6a** shows a mosaic texture, figure 2(*a*). The texture closely resembles the normal texture of columnar phases. The texture becomes striated at about 122°C and finally crystallizes at around 67°C. These transformations are reversible.

The palladium complex **6b** behaves similarly in the microscope. A classical texture of a columnar phase appears at about 168°C upon cooling the isotropic liquid, figure 2(*b*). A fingerprint texture appeared at about 138°C. The texture is very similar to that reported for the D_{rd} mesophase of hexa-alkanoyloxytriphenylenes [11]. The compound crystallizes at about 68°. The DSC thermograms of this compound on heating and cooling showed only two endothermic peaks. The columnar to columnar phase transition at about 138°C could not be


(*a*)

(*b*)

Figure 2. (*a*) Optical texture of copper complex **6a** obtained on cooling from the isotropic liquid at 144°C (crossed polarizers, magnification ×200); (*b*) photomicrograph of the texture of Pd complex **6b** obtained on cooling from the isotropic liquid at 165°C (crossed polarizers, magnification ×200).

detected by DSC. Similar behaviour has previously been reported for some phthalocyanine [12] and triphenylene [11] discotic liquid crystals. While the copper complex was found to be thermally stable, the palladium complex starts to decompose on heating above the isotropization temperature. The second heating run of the DSC showed about a 4°C decrease in the melting and isotropization temperatures. ^{1}H NMR analysis of the material after three heating cycles indicated about 20% decomposition of the pure product. Efforts are now in progress to reduce the isotropization temperature, by replacing the normal alkyl chains by branched alkyl chains, to overcome the decomposition problem.

In conclusion, we have reported the first two examples of discotic liquid crystalline anthraquinone-based metal complexes in which a Cu or Pd metal was coordinated into the monofunctionalized anthraquinone ligand. Both complexes form two types of columnar mesophases. While the Pd complex of 1-hydroxy-2,3,5,6,7-pentakis-(dodecyloxy)anthra-9,10-quinone was found to be thermally unstable at higher temperatures, the Cu complex of the same ligand was stable. Synthesis of a variety of metal complexes of monofunctionalized anthraquinone ligand and their full characterization by X-ray diffraction are in progress.

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