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NOVEL ANTHRAQUINONE BASED DISCOTIC METALLOMESOGENS

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A number of copper and palladium complexes of 1-hydroxy-2,3,5,6,7-pentaalkoxy-9,10-anthraquinones were prepared. Lower homologues of both the series are not liquid crystalline while higher homologues were found to be liquid crystalline forming columnar mesophases. The columnar phase can be induced in non liquid crystalline homologues by doping with TNF. While copper complexes were found to be thermally stable, all the palladium complexes were unstable.

Keywords: discotic liquid crystals; columnar mesophases; anthraquinone; metallomesogens

INTRODUCTION

Twenty five years ago, in 1977, Chandrasekhar and his colleagues reported that not only rod-like molecules, but also compounds with disc-like molecular shape are able to form mesophases [1]. They prepared a number of benzene-hexa-n-alkanoates and from thermodynamic, optical and X-ray studies, it was established that these materials form a new class of liquid crystals in which molecules are stacked one on top of the other in columns that constitute a hexagonal arrangement.

The introduction of metal into mesogenic molecules has brought about a considerable expansion in the field of discotic liquid crystals, because the coordination geometry of many metals (particularly square-planar) causes the molecule to adopt an approximately planar structure. The application of transition metal coordination chemistry in the design of liquid crystals has led to the discovery of a large number of novel compounds capable of exhibiting non-calamitic mesomorphism [2].

Discotic metallomesogens have recently become increasingly important due to their electronic and optoelectronic properties. The quasi-one-

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dimensional order of closely packed disks in columnar mesophase of metallomesogens makes these materials very promising candidates for charge and energy migration studies [3–10]. A number of disc-like molecules such as phthalocyanines, porphyrins, β -diketones, dithiolene, benzalimines, incorporating a variety of metals such as Ni, Cu, Pd, VO, Lu, Eu, displaying various mesophases such as columnar, discotic nematic, discotic lamellar, etc. have been synthesized and characterized [11–26].

β -Diketonate Complexes

β -Diketonates were the first disc-like complexes reported to exhibit mesomorphism in the pure state. They are amongst the most widely synthesized and studied metallomesogens [2,11–14]. They exhibit either calamitic or discotic mesomorphism depending on subtle differences in the molecular structure. A number of β -diketone derivatives are known to show nematic, smectic, columnar and lamellar mesophases [2,11–14]. β -Diketone complexes having both calamitic and discotic features are also known [27,28].

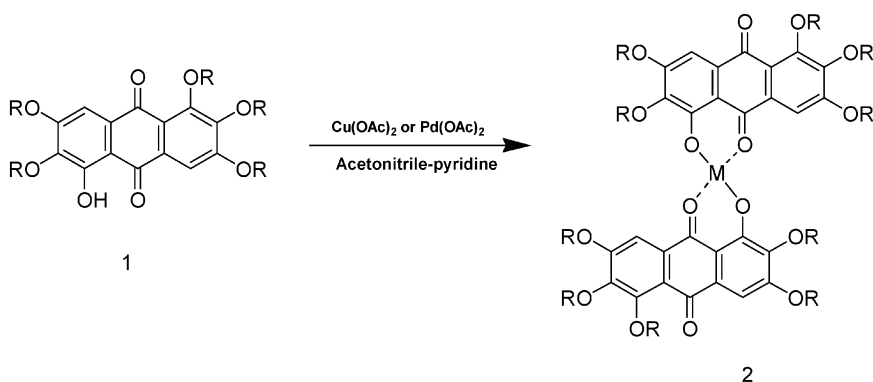
Giroud and Billard described a series of β -diketone complexes containing four aromatic rings symmetrically or unsymmetrically with various alkyl chains [15,29]. Copper complexes of the series were mesomorphic while the nickel complexes were non-liquid crystalline. On the bases of X-ray studies by Levelut, it was proposed the mesophase of Cu complexes was lamellar [30]. In the past two decades a number of β -diketone based discotic liquid crystals were prepared and studied extensively by Ohta and others [17,22,31–39].

Comparison between β -Diketone and 1-hydroxyanthraquinone Systems

Anthraquinone derivatives are one of the earliest systems reported to form columnar mesophases. A number of alkoxy and alkanoyloxy derivatives are known to show different columnar mesophases. If we compare the structure of a 1-hydroxyanthraquinone derivative with that of a β -diketone molecule, it can be clearly seen that there is a similarity between the two systems. Therefore, the rich chemistry that has been developed for the β -diketone system can also be applied to the anthraquinone molecule and thus, a variety of novel metallomesogens can be prepared [40–41].

Synthesis and Characterization of Anthraquinone based Metallomesogens

We have previously reported the synthesis of various 1-hydroxy-2,3,5,6,7 pentaalkoxyanthraquinones [42]. These ligands were easily converted to metal complexes by refluxing with metal acetate in acetonitrile-pyridine as shown in Scheme 1. Two series of complexes; one with copper and other with Pd were prepared in this way. All the compounds were purified by microfiltering the dichloromethane solution followed by crystallization in dichloromethane-ethanol mixture.



	R	M		R	M
2a	C ₄ H ₉	Cu	2f	C ₄ H ₉	Pd
2b	C ₅ H ₁₁	Cu	2g	C ₆ H ₁₃	Pd
2c	C ₆ H ₁₃	Cu	2h	C ₇ H ₁₅	Pd
2d	C ₈ H ₁₇	Cu	2i	C ₈ H ₁₇	Pd
2e	C ₁₂ H ₂₅	Cu	2j	C ₉ H ₁₉	Pd
			2k	C ₁₀ H ₂₁	Pd
			2l	C ₁₂ H ₂₅	Pd

SCHEME 1 Synthesis of anthraquinone metal complexes.

All the Pd complexes **2f-1** were characterized from their ^1H NMR, ^{13}C NMR, IR, UV-Vis and elemental analysis while the Cu complexes **2a-e** were characterized from their elemental analysis (the paramagnetic nature of copper(II) hampered their characterization by NMR spectroscopy).

CONCLUSION

Several novel discotic liquid crystalline anthraquinone based metal complexes in which a Cu or Pd metal was co-ordinated into the mono-functionalized anthraquinone ligand were prepared and characterized. While the Pd complexes of 1-hydroxy-2,3,5,6,7-pentaalkoxyanthra-9,10-quinone were found to be thermally unstable at higher temperature, the Cu complexes of the same ligand were stable. The synthesis of new anthraquinone ligand and the incorporation of metal in it opens many exciting possibilities. A variety of novel symmetrical and unsymmetrical (e.g. a combination of anthraquinone and β -diketone ligands) metallomesogens incorporating various metals such as, Cu, Ni, Pd, VO, Tl, etc., can be realized. Metal bridged novel symmetrical and unsymmetrical trimers and polymers can also be prepared.

EXPERIMENTAL

General Information

Chemicals and solvents (AR quality) were used without any purification. All reactions were monitored by employing TLC technique using appropriate solvent system for development. All solvent extracts were washed successively with water, brine and dried over anhydrous Na_2SO_4 and concentrated at reduced pressure on a Buchi E1 rotary evaporator. Chromatographic separations were performed on silica gel (230–400 mesh) and neutral aluminum oxide. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (merck, Kieselgel 60, F254). Visualisation of the spots on TLC plates was achieved by exposure to UV light. Thermal behaviour was checked using a Mettler FP82HT hot stage and central processor in conjunction with a Leitz DMRXP polarizing microscope as well as by differential scanning calorimetry (DSC7 perkin-Elmer). Ultraviolet Spectra recorded on UV-Vis spectrometer (Perkin-Elmer Lambda 20). IR Spectra were recorded on Perkin-Elmer FT-IR spectrometer Spectrum 1000 NMR Spectra were recorded on a 200 or 400 MHz machine (Bruker). All chemical Shifts were recorded in δ units downfield from Me_4Si , and J values are given in Hz.

^{13}C NMR Spectra were recorded on Bruker AC 200 (50 MHz) or 400 (100 MHz) Spectrometer. Elemental analysis were performed on Carlo Erba Strum Entazione Elemental Analyzer-MOD. 1106 or on an Euro Vector Elemental Analyzer.

Preparation of Metal Complexes of 1-hydroxy-2,3,5,6,7-pentaalkoxy-9,10-anthraquinones: General Procedure

A solution of 1-hydroxy-2,3,5,6,7-pentaalkoxy-9,10-anthraquinone (0.25 mmol), copper(II) acetate or palladium(II) acetate (0.25 mmol) in acetonitrile-pyridine (~15 ml) was refluxed for about 24 hours in nitrogen atmosphere. The solid obtained was filtered and washed with methanol. The crude product was purified by microfiltering the dichloromethane solution followed by crystallization in dichloromethane-ethanol mixture. All the metal complexes were obtained as brown solids in about 50% yield.

2a-e (Copper Complexes)

IR data: Similar spectrum is obtained for all the compounds **2a-e**: $\nu_{\text{max}}/\text{cm}^{-1}$ 2955, 2921, 2852, 1660, 1630, 1582, 1510, 1467, 1349, 1284, 1140. UV-Vis data: all samples were measured in dichloromethane and similar spectrum is observed for all the compounds. $\lambda_{\text{max}}/\text{nm}$ 500 (sh), 420 (sh), 336, 289.

Elemental analysis: All the compounds give satisfactory elemental analysis.

2f-l (Palladium Complexes)

^1H NMR (200 MHz, CDCl_3): All the compounds give similar spectra differing in only the number of alkyl chain CH_2 protons. δ 7.7 (s, 2H), 7.4 (s, 2H), 4.1 (m, 20H), 1.8–1.3 (m, alkyl chain CH_2), 1.0–0.8 (m, 30H). ^{13}C NMR (100 MHz, CDCl_3): All the compounds give similar spectra differing in only the number of alkyl chain C signals. δ 180.7, 178.1, 163, 157, 156, 147, 142, 131, 130, 120, 114, 108.8, 74.6, 69.7, 32.3–14.4 (alkyl chain carbons). IR data: Similar spectrum is obtained for all the compounds **2f-l**: $\nu_{\text{max}}/\text{cm}^{-1}$ 2956, 2856, 2363, 1660, 1630, 1582, 1561, 1511, 1461, 1352, 1320, 1283, 1262, 1147. UV-vis data: all samples were measured in dichloromethane and similar spectrum is observed for all the compounds. $\lambda_{\text{max}}/\text{nm}$ 550 (sh), 420 (sh), 365. Elemental analysis: All the compounds give satisfactory elemental analysis.

Thermal Behaviour

The mesophase behaviour of all the complexes was checked by polarized optical microscopy as well as by differential scanning calorimetry (DSC). In both the series, lower homologues were found to be non-liquid

crystalline but all the higher homologues were mesogenic. The crystalline copper complexes 2a-c, melt at 184, 175, 170°C respectively. The thermograms recorded for copper complex **2d** on heating showed three endothermic peaks. The first one, located at 151.7°C, corresponds to an enthalpy of 12.1 J/g, related to the transition from the crystal into a columnar mesophase. The second weak peak at 156°C corresponds to an enthalpy of only 0.43 J/g, is associated with a columnar phase to columnar phase transition. The third peak at 165.8°C with enthalpy of 6.3 J/g is for the columnar phase to isotropic phase transition. The thermal behaviour was found to be reversible. Upon cooling from the isotropic liquid, the thermograms showed three exothermic peaks at 164°C, 155°C and 148°C with roughly the same enthalpy values. 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 **2d** shows usual texture of columnar phase. Fingerprints texture appeared at about 155°C. The texture is very similar to the texture reported for the Col_{rd} mesophase of hexaalkanoxy triphenylenes [43,45]. The compound crystallizes at about 148°C. Compound **2e** shows similar behaviour [41]. All the palladium complexes start decomposing on heating and therefore, their thermal behaviour is not reproducible. As mentioned above, lower homologues of both the series are not liquid crystalline but the columnar phase can be induced by doping them with electron acceptor such as trinitrofluorenone (TNF) [40]. Mesophase induction and stabilization due to charge-transfer interactions in metallomesogens as well as in classical liquid crystals is well documented [46].

TABLE 1 Phase Transition Temperatures (Peak Temp.) and Enthalpies of New Anthraquinone Copper Complexes. Cr = Crystal, Col = Columnar Liquid Crystalline phase, I = isotropic

Compound	Thermal transitions/°C and enthalpy changes (J/g in parentheses)	
	Heating scan	Cooling scan
2a	Cr 184 I	I 155 Cr
2b	Cr 175 I	I 161 Cr
2c	Cr 170 I	I 150 Cr
2d	Cr 151.7 (12.1) Col 156 (0.43) Col 165.8 (6.3) I	I 164 (3) Col 155 (0.3) Col 148 (12) Cr
2e	Cr 71.9 (42) Col 121 (1.5) Col 146.2 (4.7) I	I 144.2 Col 118.0 Col 67.1 Cr

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