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LIQUID-CRYSTALLINE BEHAVIORS OF LANTHANIDE COMPLEXES CONTAINING HEMICYANINE

K. Z. Wang[a], C. H. Huang[a*], G. X. Xu[a] and Q. F. Zhou[b]

[a]State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing 100871, China
[b]College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

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The liquid crystalline behaviors of four lanthanide complexes, (*E*)-*N*-hexadecyl-4-(2-(4-(dimethylamino)phenyl)ethylene)pyridinium tetrakis(1-phenyl-3-methyl-4-benzoyl-5-pyrazolonato)lanthanide(La, Nd, Dy and Yb)(III) have been investigated by using differential scanning calorimetry (DSC), thermogravimetric and differential thermal analysis (TG-DTA) and polarized optical microscopy. Except for the lanthanum complex, the other three complexes display mesogenic behavior with typical smectic mosaic textures. This is the second report on lanthanide metallomesogens since a discotic mesophase of substituted bis(phthalocyanine)lutetium was found.

Keywords: A. liquid crystals, D. phase transitions.

1. INTRODUCTION

Much interest has recently been paid to metallomesogens,[1, 2] not only because these compounds have usual properties of liquid crystals, but also they can exhibit fascinating and unexpected properties due to the presence of ordered distribution of metals. Many of d- and f-block metal complexes have easily changeable geometry, variations in oxidation state which usually give colored liquid crystals, unpaired electrons exhibiting paramagnetism and polarizable electron density on metal atom which often profoundly affects on the physical characteristics of mesogens. As a result, new theoretical studies[3,4] and practical applications[5, 6] are increasingly emerging for these complexes.

To our knowledge, most of metallomesogens were limited to transitional metals, only one liquid crystal of lanthanide complex, substituted bis(phthalocyanine)lutetium,[7] has so far been reported. In addition, high peculiarity and regularity of the molecular packing of this new class of liquid crystals, also offer exploitable properties such as second-order nonlinearity[8]which is necessary for the reorientation of mesogen in electric or magnetic field. Here, we reported a kind of novel liquid crystals of hemicyanine containing lanthanide complex.

2. EXPERIMENTAL

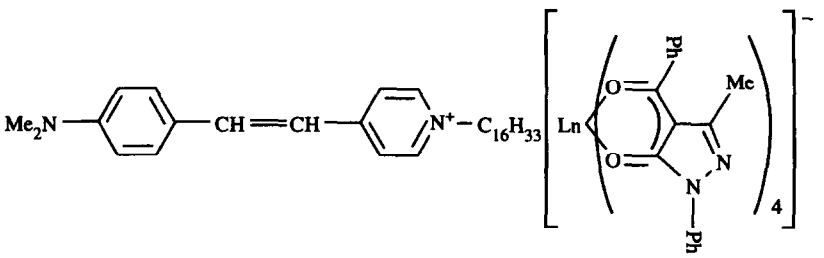
The four lanthanide complexes, (*E*)-*N*-hexadecyl-4-(2-(4-(dimethylamino)phenyl)ethylene)pyridinium tetrakis(1-phenyl-3-methyl-4-benzoyl-5-pyrazolonato)lanthanide(La, Nd, Dy and Yb)(III) (their molecular structures are shown in Fig. 1 and abbreviated to $A_{16}Ln(PMBP)_4$) were prepared as follows: to a mixture of 4 mmol 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone-one[9] in 20 ml of absolute ethanol, 4 mmol of aqueous NaOH solution (2 mol l^{-1}), 1 mmol (*E*)-*N*-hexadecyl-4-(2-(4-(dimethylamino)phenyl)-ethylene)pyridinium bromide ($A_{16}Br$)[10] were added 1 mmol of aqueous $Ln(NO_3)_3$ solution under vigorous stirring. The resulting solution was refluxed for 0.5 h. Isolated precipitate on cooling was filtered off and recrystalized from EtOH:H_2O, then extracted with dried benzene. The red substances, obtained after removing off the solvent under reduced pressure, were dried at 60 °C for 2 h. The details of characterization for the complexes by means of elemental analysis, UV-Vis, IR, ^1H NMR and X-ray photoelectron spectroscopy will be published elsewhere[10].

The differential scanning calorimetry (DSC) measurements were made on a du pont 1090 thermal analyser. Thermogravimetric and differential thermal analysis (TG-DTA) were carried out with a LCT-1 model thermal analyser. The polarizing microphotographs were taken on a Laborlux 12 optical polarized microscope.

3. RESULTS AND DISCUSSION

The results of TG-DTA show that the four lanthanide complexes are chemically stable from room temperature to 250 °C, over 253 °C, they undergo a series of decomposition and oxidation reactions and finally become Ln_2O_3 at about 560 °C,. The hemicyanine bromide $A_{16}Br$ is thermodynamically less unstable than corresponding lanthanide complexes and decomposes while heated to 253 °C. Prior to decomposition, both the hemicyanine bromide and the lanthanide complexes except for lanthanum complex appear two notable endothermic peaks, which are often known as birfraction phenomenon for liquid crystal compounds.

Fig. 2 shows DSC curves (curve a, b, c, d and e) for the hemicyanine bromide and the four complexes on a heating run and DSC curve (curve f) for the Yb complex on a cooling run. Interestingly, except for the lanthanum complex, each of other four compounds exhibits two visible endothermic peaks, the peak temperatures vary with



in which Ln = La, Nd, Dy and Yb

Fig. 1. Molecular structure of the four lanthanide complexes, in which Ln = La, Nd, Dy and Yb.

lanthanide central ions. The data of DSC are given in Table 1.

It was confirmed by polarizing microscopic observations that the first small endothermic peaks of each compounds in the heating run belong to melting points, and latter ones are the transitions from liquid crystalline states to isotropic liquids. Under 90° polarizing microscope, the hemicyanine bromide A16 melts at 96°, followed by the change of view from dark background to brightened one, that means going into the liquid crystalline state and appearing birfraction. Fig.3 (a) indicates that A16 is typical focal conical texture. But the lanthanum complex did not show typical liquid crystalline texture after melting. While other three complexes show similar behavior to A16 under polarizing microscope. Prior to melting, they are in dark background, and then exhibiting birfraction while heated over their melting points of 85, 68, and 72 °C , respectively, typical mosaic textures as shown in Fig.3 (b, c and d) remained until they are at a temperature of 135, 164 and 152 °C, respectively, then changed into isotropic liquid being characteristics of the disappearance of the birfraction. All of these agree well with the DSC results

It should be pointed out that birfraction near melting point is very weak and gradually enhances. This is due to the facts that at first stage of melting, the samples were very poor fluid and were strong optical absorption. As the temperature was elevated, the samples become more fluid. As a result, strong birfraction was observed.

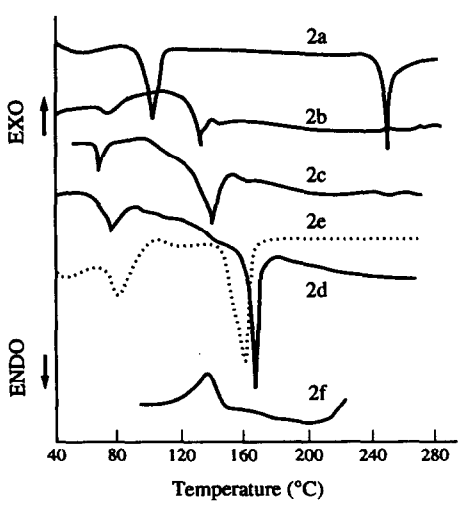


Fig. 2. DSC curves for the hemicyanine bromide (a)–(e) and the DSC curve (f).

Table 1. Phase transition temperatures of the liquid crystalline compounds

compound	m.p.(°C)	c. p. (°C)	$\Delta T=T_{cl}-T_m$
A16Br	96.3	246.3	150
A16Nd(PMBP)4	66.7	132.9	66.2
A16Dy(PMBP)4	65.4	163.7	98
A16Yb(PMBP)4	67.0	149.8	82.8

It is noteworthy that the phase transitions of both hemicyanine bromide and three complexes are reversible. In other words, they are enantiotropic liquid crystals. This can be seen by the cooling DSC curve (curve f in Fig.2) for ytterbium complex. However, the peak in the cooling curve moved to lower temperature side compared with that in the heating curve, this is so-called supercooled phenomenon. Polarized microscope revealed that this kind of irreversible process occurred for all the liquid crystalline compounds in this study.

It should also be pointed out that the incorporation of lanthanide complexes into hemicyanine made melting points T_m, clear point T_{cl} and temperature range $\Delta T(\Delta T=T_{cl}-T_m)$ of liquid crystal decrease. This phenomenon is similar to most reported liquid crystals of transitional metal complexes. However, in this case, the combination of hemicyanine chromophore having large second-order molecular hyperpolarizability with functional lanthanide complexes made this kind of liquid crystalline compounds attractive.

4. SUMMARY

In conclusion, the hemicyanine bromide was characterized to be a smectic liquid crystal with focal conical texture. The replacement of bromide ion in the hemicyanine by the lanthanide complexes results in a new mosaic texture, the decrease of the melting points, clear points and temperature ranges of the liquid crysatls. This study may provide a simple approach to obtain multifunctional liquid crystals of metal complexes.

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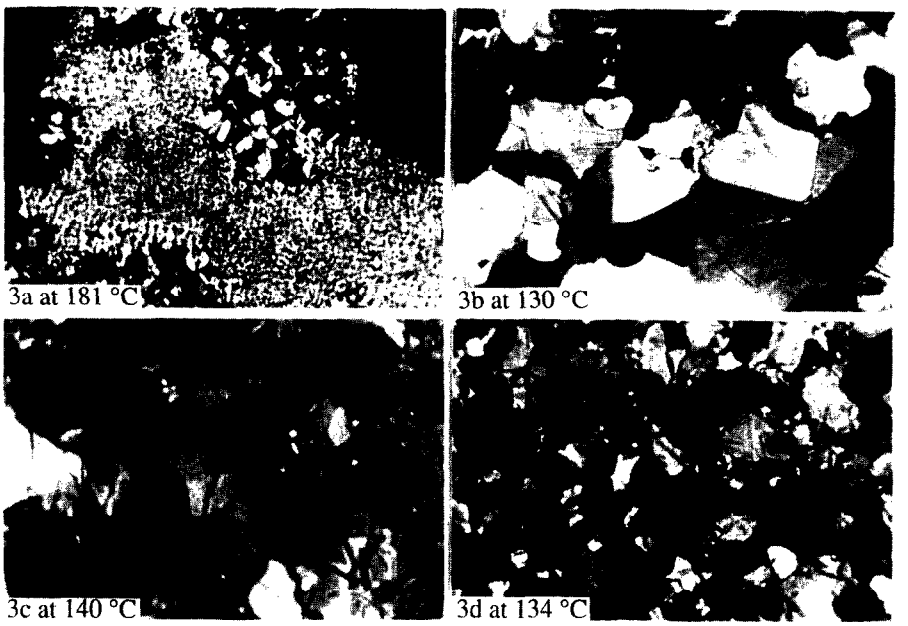

Fig. 3. Polarizing microscopic observations of A_{16}.

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