CONFINEMENT EFFECT IN A THICK LAYER OF NEMATIC LANTHANIDE COMPLEX

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Motivation

The recent years have witnessed considerable progress in the synthesis and studies of liquid-crystalline lanthanide complexes, owing to the progress in the physics of liquid crystals and in the coordination and organic chemistry. Systematic studies of metallomesogens revealed one more feature, which has not been deliberately investigated so far and is analyzed in this work. In particular, the first-order phase transition from the liquid-crystalline to isotropic phases can take place within a temperature range of one to several degrees. In the case of classical liquid crystals placed into a thin cell or porous matrix, this effect is manifested if the cell dimension is less than a micrometer.

Directions of studies

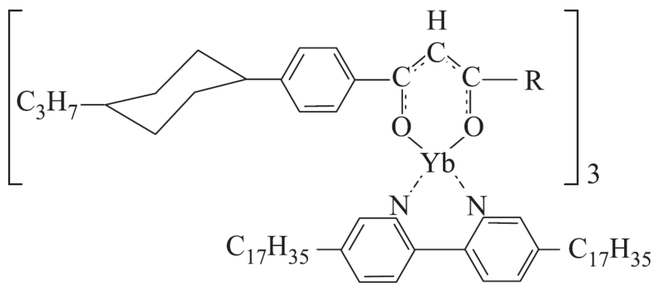
i. Electro-optical properties of the metallomesogen was investigated in **isotropic phase**;

ii. Electro-optical properties in isotropic phase was compared with the **optical** and **dielectric anisotropy** of **nematic phase**. Analysis of these data shows that the isotropic and anisotropic phases coexist on an interval of several degrees.

iii. The N–I **phase transition** was observed in the planar and wedge-like layers of various thickness by **polarization microscopy.**

Object of study

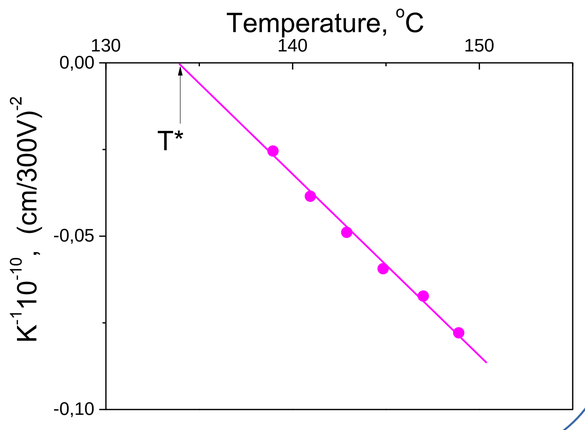
The liquid-crystalline complex studied in this work was tris[1-(4-(4-propylcyclohexyl)phenyl)octane1,3-diono]-[5,5′-di(heptadecyl)-2,2′-bipyridineytterbium, designated by $Yb(DDk_{3\text{-}5})_3Bpy_{17\text{-}17}$
The sample was synthesized at the Kazan National Research Technological University, Kazan, (Russia) [1].



Electro-optical properties

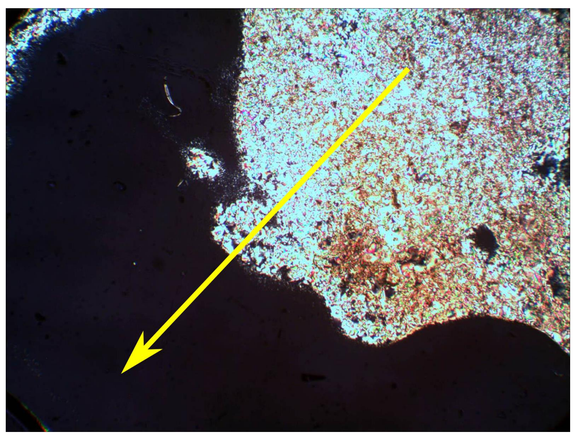
The electro-optical properties of an isotropic melt above the nematic–isotropic melt phase transition temperature were studied by considering the Kerr effect. The electric field-induced birefringence Δn_E is related to the Kerr constant K and the electric field strength E by the Kerr equation $\Delta n_E = KE^2$
.The electro-optical constant K(T– T*) was fined as $-2.0 \cdot 10^{-8}(\frac{cm}{300V})^{-2}K$

Temperature dependence of the reciprocal of the Kerr constant 1/K in an isotropic melt of the mesogenic complex. The limiting temperature of existence of the isotropic phase T* is designated.

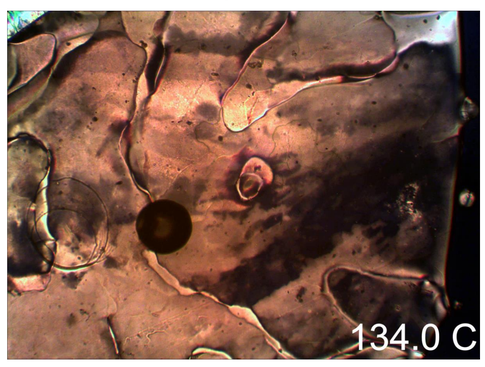


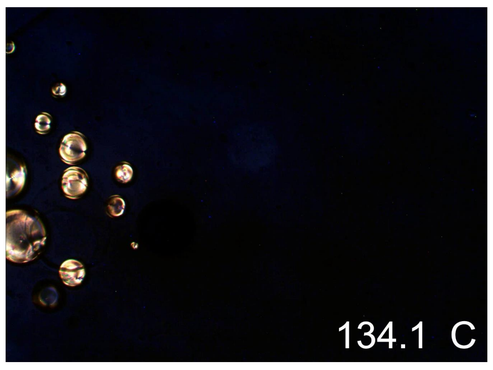
Polarization microscopy

Photomicrograph (80×) of a metallomesogen layer at 126.0°C. The polarizers are crossed. The arrow shows the direction in which the layer thickness linearly decreases from 200 μm to 5 μm. The nematic–isotropic phase interface moves along the same direction with temperature change in the interval of 118– 130°C.

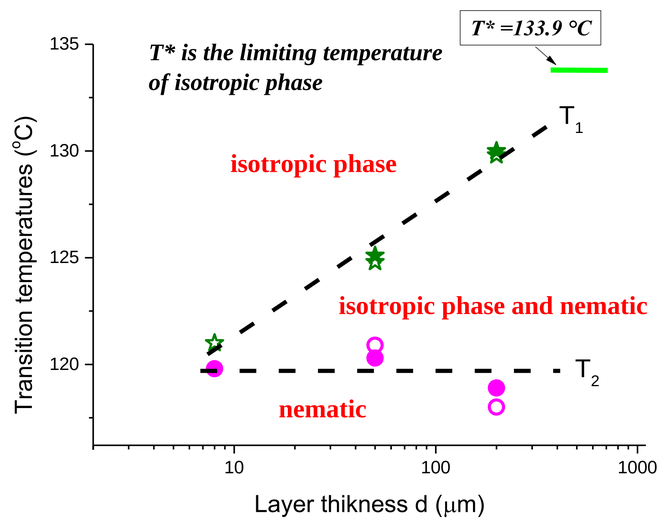


The phase transition in classical PAA (p, p'-di-n-methyloxyazoxybenzen) in the same cell occurs in the range of about 0.1 C or less.





Analysis of data



At a large thickness the phase transition occurs in approximately 10°C temperature interval between T_1 and T_2. Here T_1 is the higher temperature at which the mesophase is formed deep in the layer and T_2 is the minimal temperature at which the nematic phase is formed near the cell surface. In 8 and 50 μm thick planar layers, the temperature interval $T_1 - T_2$ narrows down to reach a minimal value of about 1°C in the thinnest layer

Analysis of optical, dielectric, and electro-optical data indicates that the isotropic and anisotropic phases coexist in the vicinity of phase transition in experimental optic and dielectric setups[2,3].
This is phase diagram, obtained using three samples with different layer thicknesses: 8, 50, and 200 μm. The nematic and isotropic phase regions and the coexistence region are designated. The temperature T* was determined by using the Kerr effect. During cooling (dark dots), the nematic–isotropic phase transition starts at the temperature $T_1$and ends at T_2. During heating (light dots), melting of the nematic starts at the temperature T_2 and ends at T_1.

The Landau–De Gennes theory makes it possible to express the dielectric $\Delta\varepsilon_c$ and optical Δn_c anisotropies of a liquid crystal at temperature Tc in terms of the electro-optical constant of the isotropic phase K(T – T*) in the following way:

$$\Delta n_c \Delta\varepsilon_c = 24\pi LK(T - T^*)/T_c$$

Using the measured electro-optical constant K(T– T*) and the heat of melting L= 8.0 × 10^6 erg/cm3 and **Tc= 127°C**, we calculated the anisotropy from relation (1) to be

$\Delta n_c \Delta\varepsilon_c$=−0,03

$\Delta n_c\Delta\varepsilon_c$ value		
1	2	3
Calculated from electro-optical data, equation (1)	Determined from experimental data n and ε (ref. 2 and 3)	Calculated from experimental data n and ε (ref. 2 and 3) far from Tc and corrected on order parameter S
−0,03	−0,00024	−0,05

Table indicates a coexistence near the transition of the nematic and isotropic phases.

Conclusions

It was found that the phase transition temperature drops in more than ten degrees when reducing of metallomesogenic layer thick form 200 to 5 microns. An anomalous confinement effect can be caused by a strong interaction of the complexes with each other.

Acknowledgements.
We thank Professor Y.G. Galyametdinov of Kazan National Research Technological University, Kazan, (Russia) for providing the LC material.

References.

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