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GIANT SHIFT OF THE NEMATIC–ISOTROPIC PHASE TRANSITION TEMPERATURE IN LAYER OF A METALLOMESOGENIC COMPLEX

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The successful synthesis of *nematic* metallomesogens [1] opened up the possibility to obtain and study macroscopically ordered liquid-crystalline phases in metallomesogen. 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 [2]. This should give rise to coexistence of the anisotropic and isotropic phases and to effective anisotropy of physical properties being lower in this range than the anisotropy of the proper liquid-crystalline phase.

The liquid-crystalline complex studied in this work was tris[1-(4-(4-propylcyclohexyl)phenyl)octane-1,3-diono]-[5,5′-di(heptadecyl)-2,2′-bipyridineytterbium. It has both smectic A and nematic phases [1]. We compared the electro-optical properties of the metallomesogen in isotropic (I) phase with the optical and dielectric anisotropy of the metallomesogen determined in the nematic (N) phase on the basis of the Landau–de Gennes theory. The anisotropy measured experimentally near the transition proved to be many times lower than the calculated value.

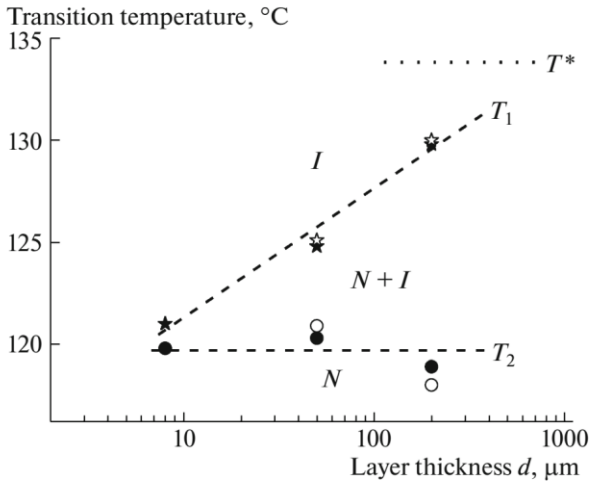

Figure 1. *Phase diagram of a metallomesogen obtained using three samples with different layer thicknesses: 8, 50, and 200 μm. The nematic and isotropic phase regions and the coexistence phase region are designated. The T*is the temperature of virtual second order phase transition. It was determined 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 cause for phase coexistence was determined by monitoring the phase transition by polarization microscopy. According to polarization microscopy data, the phase transition temperature decreases by more than 10°C as the metallomesogen layer thickness is reduced from 200 to 5 μm. This is the effect of boundaries of the cell containing the sample on the N–I phase transition temperature, i.e., the confinement effect. In the case of classical liquid crystals placed into a thin cell or porous matrix, this effect is manifested if the cell (pore) characteristic dimension is less than a micrometer. The confinement effect found in metallomesogens for order of magnitude greater layer thicknesses was a new and unexpected finding.

Thus, for the first time it was shown that very strong confinement effect exist in metallomesogen complexes. The reason seems to lie in the physical-chemical nature of the complexes, namely in the presence of coordination bonds.

[1] Dzhabarov, V.I.; Knyazev, A.A.; Strelkov, M.V.; Molostova, E.Yu.; Schustov, V.A.; Haase, W.; and Galyametdinov, Y.G. Liq. Cryst., 2010, 37, no. 3, 285–291.

[2] Polushin, S.G.; Rogozhin, V.B.; Polushina, G.E.; Lezova, I.E.; at al. Doklady Physical Chemistry, 2016, 471, Part 2, 197-200.