ISSN 1991–3966. Жидк. крист. и их практич. использ. / Liq. Cryst. and their Appl. 2016, 16 (4), 22–26

UDC 547.595+535.012

***A. A. Knyazev*[1], *A. S. Krupin*[1], *W. Haase*[2], *Yu. G. Galyametdinov*[1]**

POLARIZED LUMINESCENCE OF ALIGNED FILMS BASED ON NEMATIC BLENDS OF PFO AND LANTHANIDOMESOGEN

[1]Kazan National Research Technological University,
68 K. Marx St., Kazan, 420015, Russian Federation
[2]Institute of Physical Chemistry, Darmstadt University of Technology,
5 Karolinenplatz, Darmstadt, 64289, Germany
E-mail: yugal2002@mail.ru

This work reports on the first research of the aligned film based on nematic blend of LC polymer PFO (poly(9,9-di-n-octylfluorenyl-2,7-diyl)) and lanthanidomesogen. Alignment of a blend was carried out by its deposition on a quartz substrate modified with orientant (Nylon 6). The film has polarized luminescence properties with twofold change of intensity due to film alignment.

Key words: *nematic blend, polymer PFO (poly(9,9-di-n-octylfluorenyl-2,7-diyl)), lanthanidomesogen, aligned film, polarized luminescence.*

DOI: 10.18083/LCAppl.2016.4.22

***А. А. Князев*[1], *А. С. Крупин*[1], *В. Хаазе*[2], *Ю. Г. Галяметдинов*[1]**

ПОЛЯРИЗОВАННАЯ ЛЮМИНЕСЦЕНЦИЯ ОРИЕНТИРОВАННОЙ ПЛЕНКИ НЕМАТИЧЕСКОЙ СМЕСИ НА ОСНОВЕ ПОЛИ(9,9-ДИ-*н*-ОКТИЛФЛУОРЕНИЛ-2,7-ДИИЛА) И ЛАНТАНИДОМЕЗОГЕНА

[1]Казанский национальный исследовательский технологический университет,
ул. К. Маркса, д. 68, 420015 Казань, Россия
[2]Институт физической химии, Дармштадтский технологический университет,
пл. Кэролайн, д. 5, 64289 Дармштадт, Германия
E-mail: yugal2002@mail.ru

В данной работе сообщается о первом исследовании ориентированных пленок на основе нематической смеси ЖК-полимера ПФО (поли(9,9-ди-н-октилфлуоренил-2,7-диил)) и лантанидомезогена. Ориентацию смеси проводили путем ее нанесения на модифицированную ориентантом (нейлон 6) кварцевую подложку. Пленка обладает поляризованной люминесценцией, интенсивность которой изменяется в 2 раза за счет ориентации.

Ключевые слова: *нематические смеси, полимер ПФО (поли(9,9-ди-н-октилфлуоренил-2,7-диил)), лантанидомезоген, ориентированные пленки, поляризованная люминесценция.*

Introduction

Liquid crystal (LC) complexes of lanthanides or lanthanidomesogens are promising polyfunctional materials for optoelectronics [1, 2]. In such materials, liquid crystalline behavior provide anisotropy of physical properties. The presence of lanthanide ions in liquid crystal molecules allows creating new media with polarized monochromatic luminescence [3, 4]. Following a general trend of development of organized defectless structures for molecular electronics, publications in the scientific literature report about materials with polarized emission which are based on liquid crystalline conducting polymers [5–8] and their blends with lanthanide complexes [9, 10]. Ligand environment in lanthanide complexes is a kind of "antenna" which is able to absorb energy and transfer it to an ion. Organic "envelope" in lanthanide complexes also reduces nonradiative relaxation [11]. In lanthanide complexes for molecular electronics, β-diketones and various Lewis bases are quite efficient as such "antennas" [12, 13].

Until recently, the progress in creating lanthanide-containing luminescent liquid crystals with controlled alignment was restrained by the complexity of synthesis of calamite lanthanidomesogens with nematic mesophase. The number of scientific literature reports about nematic lanthanidomesogens with polarized luminescence is limited [14, 15]. The substances described in [14] decompose during transition to an isotropic state. Therefore, it is impossible to make these compounds aligned and develop respective anisotropic materials. A significant advantage of complexes described in [15, 16] is their ability to undergo glass transition without changing supramolecular packing obtained in mesophase. Due to this feature, application of these compounds is possible both in mesophase interval and at lower temperatures.

Due to their thermal and chemical stability, polymer directors (such as polyimide and nylon) offer the simplest solution for the synthesis of ordered layers of liquid crystals with uniaxial alignment of molecules. However, significant differences between the structure of lanthanidomesogens and the structure of the majority of organic liquid crystals make it difficult to select appropriate directing polymer.

This paper is focused on the original study of creation of substrate-oriented films from lanthanidomesogen – LC polymer nematic blends. The influence of alignment on luminescence is demonstrated.

Experimental section

Polymer PFO (*poly(9,9-di-n-octylfluorenyl-2,7-diyl)*); director *Nylon 6*; *Europium(III) chloride hexahydrate* ($EuCl_3 \cdot 6H_2O$) were purchased from Sigma Aldrich. Liquid crystal properties were studied by polarized optical microscopy (POM). Textures and phase transition temperatures were determined by "Olympus BX51" polarized microscope equipped with "Linkam" heating system. Luminescence spectra were taken by the original laboratory unit with the 90° geometry. This device is described in [17]. Nitrogen laser was used as an excitation source, the line λ_{ex}= 337 nm. The composition of the synthesized LC complex was determined by elemental analysis.

Tris[1-phenyl-3-(4-(4-propylcyclohexyl)phenyl) propane-1,3-dionato]-[5-heptadecyl-5'-methyl-2,2'-bipyridine]europium. The synthesis of a complex was carried out by the procedure described in literature [18–20]. An alcoholic solution of 0.01 mmol of $EuCl_3 \cdot 6H_2O$ was slowly dropped into a stirred hot alcoholic solution containing 0.03 mmol of β-diketone [21], 0.01 mmol of *5-heptadecyl-5'-methyl-2,2'-bipyridine* [22, 23] and 0.03 mmol of KOH. The suspension was stirred during 10 minutes. The light yellow precipitate that formed was isolated by hot filtration, washed with hot alcohol, and dried under vacuum over P_2O_5. Further, the product was dissolved in toluene, and the obtained solution was filtered off and evaporated under vacuum. The melting temperature: 180 °C. The yield: 0.166 г (62 %). Experimental values (%): C, 78.97; H, 7.09; N, 1.84. $C_{100}H_{107}N_2O_2Eu$. Calculated values (%): C, 78.49; H, 7.30; N, 1.77.

The surface and structure of films were studied by Solver P47 PRO NT-MDT atomic force microscope and EVO 50 XVP Carl Zeiss scanning electron microscope.

Results and Discussion

The following substances were used as blend components: a conjugated liquid crystalline polymer PFO (*poly(9,9-di-n-octylfluorenyl-2,7-diyl)*) (Fig. 1) and the LC adduct Eu(III) (Fig. 2); their ratio was 1:1. These substances demonstrate nematic mesomorphism in the 147–186 °C and 160–280 °C temperature ranges, respectively.

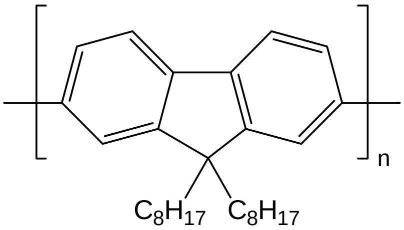

Fig. 1. The structure of PFO polymer

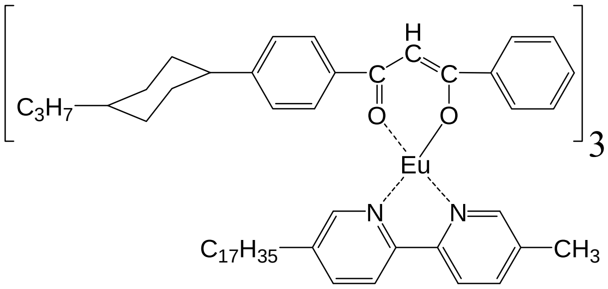

Fig. 2. The structure of Eu(CPDk$_{3\text{-Ph}}$)$_3$Bpy$_{17\text{-}1}$ complex

To obtain a homogeneous blend, the structure of the synthesized complex was selected in a way to provide coincidence temperature ranges of its and the polymer mesophases. The nematic mesomorphism temperature range of the prepared blend is within 170–270 °C. The type of mesophase was determined by polarized optical microscopy (Fig. 3).

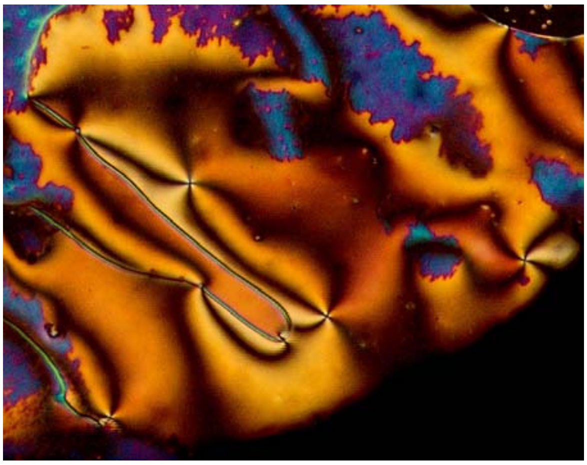

Fig. 3. The Schlieren texture of a blend in polarized microscope at 175 °C

Alignment of a blend was carried out by its deposition on a quartz substrate modified with director (Nylon 6). The director film was spin-coated from the 1 % blend solution in acetic acid and then modified by velvet fabric polishing. The atomic force microscopy photo of the modified support is shown in Fig. 4. The photo demonstrates regular texture of grooves formed by nylon on the entire polymer surface. The depth of these grooves is about 10–15 nm (Fig. 5).

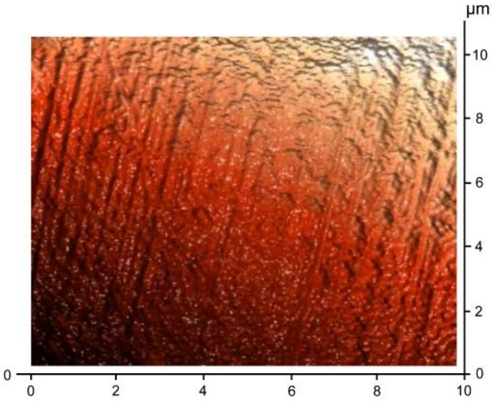

Fig. 4. The nylon surface polished by velvet fabric

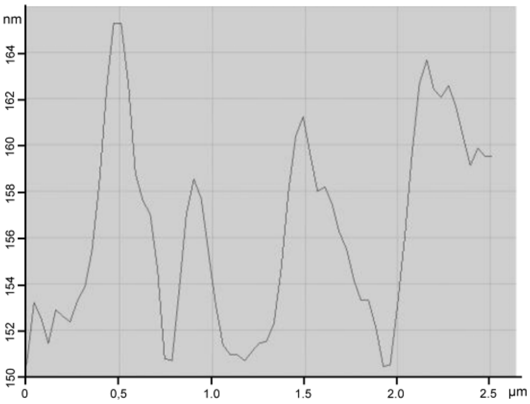

Fig. 5. Nylon surface profile after velvet fabric polishing

The next step was preparation of thin films (with ~100 nm thickness) in aligned and nonaligned states by spin-coating on quartz and modified quartz substrate with further heating up to 200 °C and cooling. The surface of films was studied by scanning electron microscopy (Fig. 6, 7).

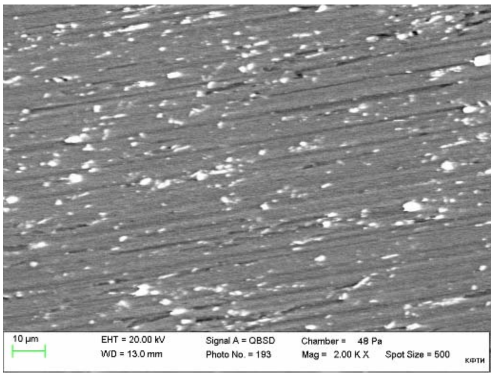

Fig. 6. Scanning electron microscopy image of an aligned film surface

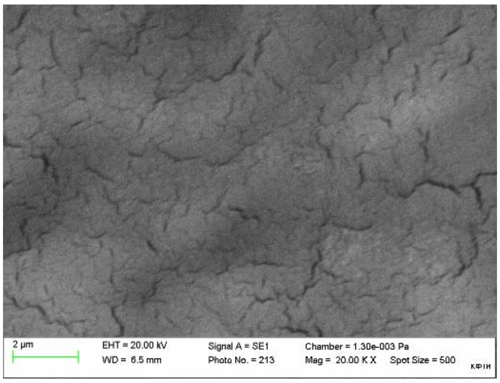

Fig. 7. Scanning electron microscopy image of a nonaligned film surface

As we can see from Fig. 6, the aligned film surface is more homogeneous and its alignment is predominantly directed according to microscopic grooves formed on nylon surface. Figure 7 represents the surface made from the same blend by its deposition on a quartz support without a director. According to Fig. 7, the film is non-uniform, contains microfractures, and no predominant alignment of its layers can be observed.

To determine the influence of alignment on luminescent properties, the aligned film was studied by polarized luminescence (Fig. 8). Irradiation by a laser with 337 nm wavelength results in intensive red luminescence of a film with the maximum at 612 nm wavelength. Figure 8 represents luminescence spectra of samples with parallel (---) and perpendicular (—) alignment relative to the polarization plane of an excitation source. We can see from the spectrum that the film has polarized luminescence properties with twofold change of luminescence due to film alignment.

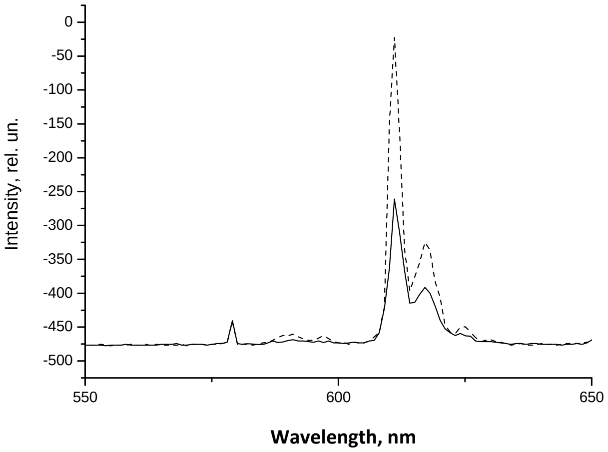

Fig. 8. The spectrum of polarized luminescence of a blend's film with parallel (---) and perpendicular (—) alignment relative to the polarization plane of an excitation source

Conclusion

The aligned films based on nematic LC polymer – lanthanidomesogen blends have been produced for the first time. A twofold increase of the film's luminescence intensity is observed when this aligned film undergoes transition from a perpendicular to a parallel position relative to the excitation source.

Acknowledgment

The work was supported by the Ministry of Education and Science of the Russian Federation (project № 4.323.2014/K)

A.A. Knyazev thanks the grant of the President of the Russian Federation № MD-6102.2016.3 for supporting synthesis of the individual complexes.

References:

1. Binnemans K. Lanthanidomesogens. *Handbook on the Physics and Chemistry of Rare Earths* / Ed. by J.-C. G. Bünzli, V. K. Pecharsky. Amsterdam: Elsevier Science, 2013, **43**, Ch. 254, 1–158. **DOI:** 10.1016/B978-0-444-59536-2.00001-5.
2. Donnio B., Guillon D., Deschenaux R., Bruce D.W. Metallomesogens. *Comprehensive coordination chemistry II* / Ed. by J. A. McCleverty T. J. Meyer. Oxford, UK: Elsevier, 2003, **7**, Ch. 7.9, 357-627. **DOI:** 10.1016/B0-08-043748-6/06150-8.
3. Driesen K., Moors D., Beeckman J., Neyts K., Görller-Walrand C., Binnemans K. Near-infrared luminescence emitted by an electrically switched liquid crystal cell. *Journal of Luminescence*, 2007, **127** (2), 611-615. **DOI:** 10.1016/j.jlumin.2007.03.022.

4. Knyazev A.A., Molostova E.Y., Krupin A.S., Heinrich B., Donnio B., Haase W., Galyametdinov Y.G. Mesomorphic behaviour and luminescent properties of mesogenic-diketonate lanthanide adducts with 5, 5′-di (heptadecyl)-2, 2′-bipyridine. *Liquid Crystals*, 2013, **40** (7), 857-863. **DOI**: 10.1080/02678292.2013.795626.
5. Schmidt-Mende L., Fechtenkötter A., Müllen K., Moons E., Friend R.H., MacKenzie J.D. Self-organized discotic liquid crystals for high-efficiency organic photovoltaics. *Science*, 2001, **293** (5532), 1119–1122. **DOI:** 10.1126/science.293.5532.1119.
6. Hulvat J.F., Sofo, M., Tajima K., Stupp S.I. Self-Assembly and Luminescence of Oligo (p-phenylene vinylene) Amphiphiles. *Journal of the American Chemical Society*, 2005, **127** (1), 366–372. **DOI:** 10.1021/ja047210m.
7. Amrutha S.R., Jayakannan M. Structure control of π-conjugated polymers for enhanced solid-state luminescence: synthesis and liquid crystalline and photophysical properties of new bulky poly (p-phenylenevinylene) s and oligo (phenylenevinylene)s bearing tricyclodecane pendants. *Macromolecules*, 2007, **40** (7), 2380–2391. **DOI:** 10.1021/ma062764q.
8. Yang Q., Xu Y., Jin H., Shen Z., Chen X., Zou D., Fan X., Zhou Q. A novel mesogen-jacketed liquid crystalline electroluminescent polymer with both thiophene and oxadiazole in conjugated side chain. *Journal of Polymer Science. Part A,* 2010, **48** (7), 1502–1515. **DOI:** 10.1002/pola.23908.
9. Wu S., Yu X., Huang J., Shen J., Yan Q., Wang X., Wu W., Luo Y., Wang K., Zhang Q. Optically controllable polarized luminescence from azopolymer films doped with a lanthanide complex. *Journal of Materials Chemistry*, 2008, **18** (27), 3223-3229. **DOI:** 10.1039/B802198H.
10. Yan Q., Wu Y., Wang X., Luo Y., Zou G., Zhang Q. Effects of absorption overlap on the modulation of the polarized fluorescence of Eu $(DBM)_3$Phen-doped azobenzene polymer films. *Journal of Polymer Research*, 2010, **17** (5), 707-712. **DOI:** 10.1007/s10965-009-9359-7.
11. Binnemans K. Luminescence of metallomesogens in the liquid crystal state. *Journal of Materials Chemistry*, 2009, **19** (4), 448-453. **DOI:** 10.1039/B811373D.
12. de Bettencourt-Dias A. Lanthanide-based emitting materials in light-emitting diodes. *Dalton Transactions*, 2007, (22), 2229–2241. **DOI:** 10.1039/B702341C.
13. Katkova M.A., Vitukhnovskii A.G., Bochkarev M.N. Coordination compounds of rare-earth metals with organic ligands for electroluminescent diodes. *Russian Chemical Reviews*, 2005, **74** (12), 1089–1109. **DOI:** 10.1070/RC2005v074n12ABEH002481.
14. Cardinaels T., Driesen K., Parac-Vogt T.N., Heinrich B., Bourgogne C., Guillon D., Donnio B., Binnemans K. Design of high coordination number metallomesogens by decoupling of the complex-forming and mesogenic groups: Nematic and lamello-columnar mesophases. *Chemistry of materials*, 2005, **17** (26), 6589-6598. **DOI:** 10.1021/cm0513177.
15. Galyametdinov Yu.G., Knyazev A.A., Dzhabarov V.I., Cardinaels T., Driesen K., Görller-Walrand C., Binnemans K. Polarized luminescence from aligned samples of nematogenic lanthanide complexe. *Advanced materials*, 2008, **20** (2), 252–257. **DOI:** 10.1002/adma.200701714.
16. Dzhabarov V.I., Knyazev A.A., Strelkov M.V., Molostova E.Y., Schustov V.A., Haase W., Galyametdinov Y.G. Tris (β-diketonates) lanthanum nematic adducts. *Liquid Crystals*, 2010, **37** (3), 285–291. **DOI:** 10.1080/02678290903506040.
17. Lapaev D.V., Nikiforov V.G., Knyazev A.A., Dzhabarov V.I., Lobkov V.S., Salikhov K.M., Galyametdinov Y.G. Intramolecular energy transfer in mesogenic europium (III) adduct. *Optics and Spectroscopy*, 2008, **104** (6), 851-857. **DOI:** 10.1134/S0030400X08060088.
18. Dzhabarov V.I., Knyazev A.A., Nikolaev V.F., Galyametdinov Y.G. Anisotropy of the magnetic susceptibility of mesogeneous lanthanide complexes. *Russian Journal of Physical Chemistry A*, 2011, **85** (8), 1450–1453. **DOI:** 10.1134/S0036024411080085.
19. Knyazev A.A., Dzhabarov V.I., Molostova E.Y., Lapaev D.V., Lobkov V.S., Galyametdinov Y.G. Luminescence of nematic lanthanide-containing mixtures. *Russian Journal of Physical Chemistry A*, 2011, **85** (7), 1270–1273. **DOI:** 10.1134/S0036024411070132.
20. Knyazev A.A., Krupin A.S., Molostova E.Y., Romanova K.A., Galyametdinov Y.G. Influence of Structural Anisotropy on Mesogenity of Eu (III) Adducts and Optical Properties of Vitrified Films Formed on their Base. *Inorganic Chemistry*, 2015, **54** (18), 8987-8993. **DOI:** 10.1021/acs.inorgchem.5b01617.
21. Knyazev A.A., Dzhabarov V.I., Lapaev D.V., Lobkov V.S., Haase W., Galyametdinov Y.G. New nematogenic β-diketones for synthesis of lanthanidomesogens. *Russian Journal of General Chemistry*, 2010, **80** (4), 756–760. **DOI:** 10.1134/S1070363210040122.
22. Knyazev A.A., Karyakin M.E., Krupin A.S., Galyametdinov Y.G. Synthesis and luminescence properties of hybrid systems based on liquid crystal terbium (III) and europium (III) complexes. *Russian Journal of General Chemistry*, 2015, **85** (12), 2806–2812. **DOI:** 10.1134/S1070363215120245.
23. Knyazev A.A., Lobkov V.S., Galyametdinov Y.G. Liquid-crystalline complex of Eu^{III} β-diketonate with 5,5"-di(heptadecyl)-2,2"-bipyridine. *Russian Chemical Bulletin*, 2004, **53** (4), 942–943. **DOI:** 10.1023/B:RUCB.0000037869.44796.4c.

Поступила в редакцию 7.11.2016 г
Received 7 November 2016.