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Tris(β-diketonates) lanthanum nematic adducts

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A series of new liquid-crystalline adducts of lanthanum tris(β-diketonates) displaying nematic and smectic mesomorphism was synthesised and investigated. The temperatures and thermodynamic parameters of the phase transitions were determined. Even–odd alternation of the nematic–isotropic transition was observed in the series of synthesised complexes. It was found that films of the obtained liquid-crystal complexes are vitrified when cooling, and packings of molecules, formed in the mesophase, are retained. Interlayer distances were determined and a model of packing of molecules in the mesophase was suggested based on data obtained by a small-angle X-ray scattering method.

Keywords: nematic lanthanidomesogens; vitrified mesophase; X-ray diffraction

1. Introduction

Liquid-crystalline complexes of lanthanides (lanthanidomesogens) are a class of molecular materials that have been intensively investigated in the past decade [1–3]. Multifunctional magnetocontrollable [4–6] and luminescent lanthanide-containing liquid crystals [7–8] can be obtained due to the high anisotropy of the magnetic susceptibility of Dy^{3+}, $Tb^{3+}$and Er^{3+} ions and the availability of luminescence with a narrow emission band in $Eu^{3+}$and Tb^{3+} ions. Difficulties in obtaining lanthanide mesogens occur because the lanthanide ion has a high coordination number and does not facilitate the formation of the anisometric (calamite) molecular geometry necessary for the development of liquid-crystal properties [10]. Therefore, the most applicable approach to lanthanide mesogens synthesis is the connection of long-chain alkyl-aryl substituents to the lanthanide ion, which facilitates the formation of smectic or columnar packing of molecules in the mesophase. However, for many reasons, lanthanide mesogens that have a nematic mesophase are more interesting [11, 12], especially because their viscosity is the lowest when compared to that of all other types of mesophase. This creates more manifold possibilities of liquid-crystal molecular orientation by means of orientations applied to the carrying base or weak electric or magnetic fields. There are two reports in the literature describing attempts to synthesise nematic lanthanide mesogens [13, 14]. However, the properties of the compounds described in the first article could not be reproduced, and an official contradiction of these results was published [15]. In adducts obtained in Professor Binnemans' group [14], liquid-crystal properties were given to complexes by connection of a ligand complicated nematogene molecule. The complexes had a very complex structure, narrow intervals of mesophase existence and a high clearing point (180°C), at which they broke down, which further complicated the investigation. In 2008 our group for the first time obtained complexes of lanthanides possessing a nematic mesophase based on non-mesogen ligands [16]. The most important advantage of this new class of compounds is their heat stability. They sustain a number of heating and cooling cycles and have a rather wide interval (up to 40°) of the nematic phase. They also show polymorphism; depending on the temperature, they develop smectic or nematic mesomorphism. Thus, it becomes possible to control material supramolecular organisation by means of temperature variation. Control of the physical and optical characteristics of an oriented lanthanide-containing nematic phase can be performed by the application of magnetic and electric fields. As the type of mesomorphism and temperature of the complexes' phase transitions are predetermined by the ligand composition and structure in many respects, the influence of the length of the alkyl substituent in the ligands (β-diketones) on the liquid-crystal properties of tris(β-diketonates) lanthanum adducts with 5,5'-diheptadecyl-2,2'-bipyridine was investigated.

2. Results and discussion

A series of β-diketones, $CPDK_{3\text{-}R}$, with different lengths of the alkyl terminal substituent $R{=}CH_3{-}C_8H_{17}$ (Figure 1) was synthesised according to the method of Adams and Hauser [17].

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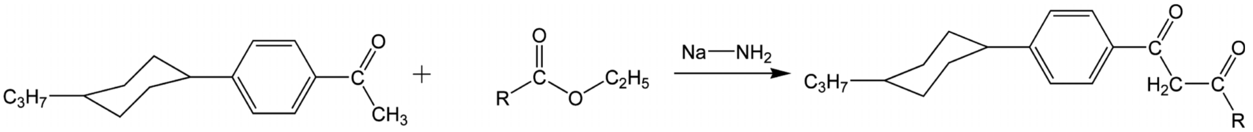

Figure 1. Synthesis of CPDK$_{3\text{-R}}$ β-diketones.

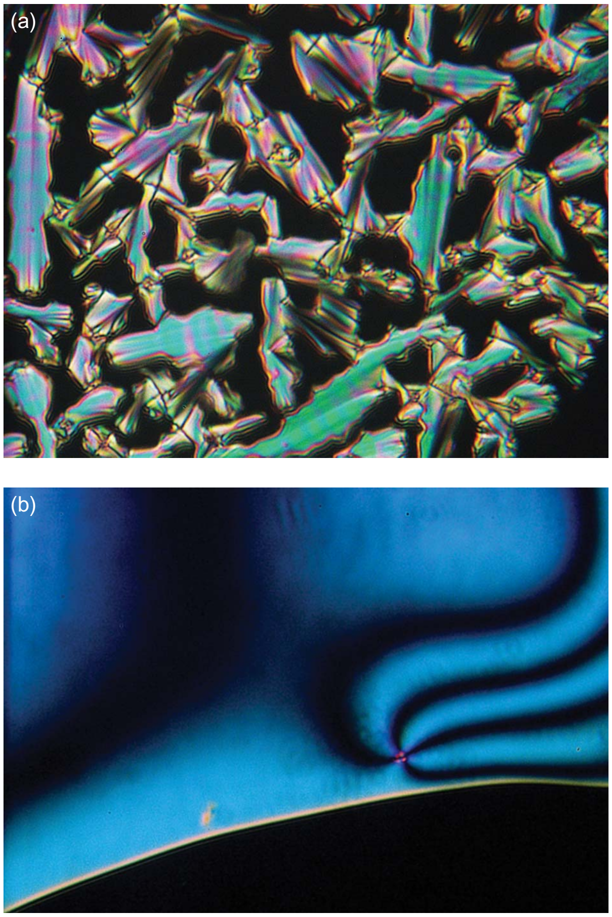

Figure 2. (a) Batonnets of the smectic A phase CPDK$_{3\text{–}2}$ at 76°C (magnification 96×). (b) Schlieren texture of the nematic phase CPDK$_{3\text{–}2}$ at 80°C (magnification 96×).

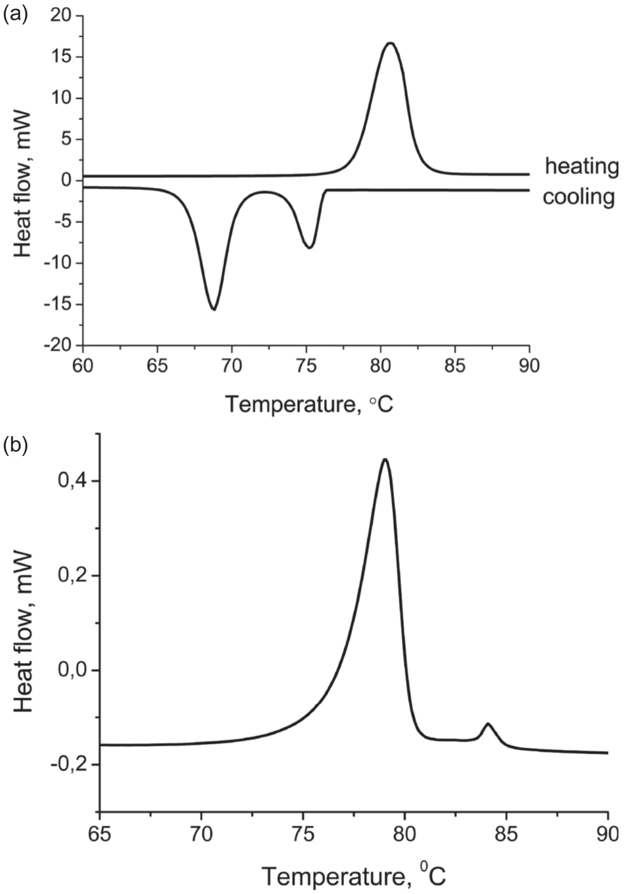

Figure 3. (a) Differential scanning calorimetry curve of CPDK$_{3\text{–}6}$. Endothermic peaks are upwards. The heating and cooling rates were 5°C min^{-1}. (b) Differential scanning calorimetry curve of CPDK$_{3\text{–}2}$. Endothermic peaks are upwards. The heating rate was 5°C min^{-1}.

The obtained β-diketones are not liquid crystalline, except for CPDK$_{3\text{–}6}$ and CPDK$_{3\text{–}8}$, which show monotropic smectic A mesomorphism (Figure 2(a)), and β-diketone CPDK$_{3\text{–}2}$, which develops enantiotropic nematic mesomorphism within a temperature range of 76°C to 84°C (Figure 2(b)). Differential scanning calorimetry (DSC) data of CPDK$_{3\text{–}6}$ and CPDK$_{3\text{–}2}$ are shown in Figures 3(a) and (b) respectively.

Based on the synthesised ligands according to Knyazev *et al.* [18], a series of tris(β-diketonates) lanthanum adducts with 5,5'-diheptadecyl-2,2'-bipyridine La(CPDK$_{3\text{-R}}$)$_3$Bpy$_{17\text{–}17}$ (Figure 4) was obtained,

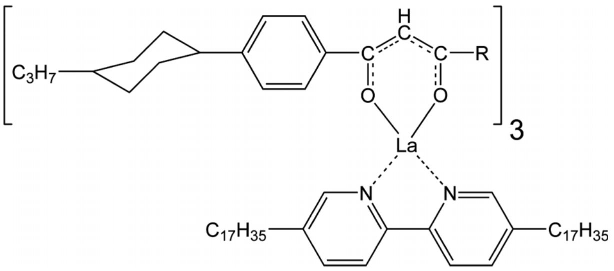

Figure 4. Synthesis of [La(CPDK$_{3\text{-R}}$)$_3$Bpy$_{17\text{–}17}$], where R=CH$_3$–C$_8$H$_{17}$.

Table 1. Temperatures, enthalpies and entropies of phase transitions in the complexes $La(CPDK_{3\text{-}R})_3Bpy_{17\text{–}17}$.

Number	Complex	Phase transition	Temperature (°C)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
1	$La(DDk_{3\text{–}1})_3Bpy_{17}$	Cr → I	252	–	–
2	$La(DDk_{3\text{–}2})_3Bpy_{17}$	Cr → SmA	133	9.73	23.97
		SmA → N	146	1.49	3.56
		N → I	160	3.79	8.75
3	$La(DDk_{3\text{–}3})_3Bpy_{17}$	Cr → N	106	37.58	99.16
		N → I	136	0.70	1.71
4	$La(DDk_{3\text{–}4})_3Bpy_{17}$	Cr → SmA	74	–	–
		SmA → N	102	–	–
		N → I	142	–	–
5	$La(DDk_{3\text{–}5})_3Bpy_{17}$	Cr → SmA	76	31.16	89.28
		SmA → N	94	0.11	0.30
		N → I	134	1.15	2.83
6	$La(DDk_{3\text{–}6})_3Bpy_{17}$	Cr → SmA	73	49.60	143.35
		SmA → N	89	–	–
		N → I	138	1.01	2.46
7	$La(DDk_{3\text{–}7})_3Bpy_{17}$	Cr → SmA	64	–	–
		SmA → N	98	0.11	0.30
		N → I	132	1.01	2.49
8	$La(DDk_{3\text{–}8})_3Bpy_{17}$	Cr → SmA	74	9.34	26.92
		SmA → N	93	–	–
		N → I	132	1.34	3.31

Note: Cr: crystal; N: nematic mesophase; I: isotropic liquid; SmA: smectic A mesophase.

where $CPDK_{3\text{-}R}$ are β-diketones ($R{=}CH_3$–C_8H_{17}), and $Bpy_{17\text{–}17}$ is 5,5'-diheptadecyl-2,2'-bipyridine. Synthesis was performed in an ethanol environment at 60°C. The complexes are light-yellow and white in colour, and they are highly soluble in chloroform and benzene. Liquid-crystal properties were examined by polarised optical microscopy (POM), DSC and small-angle X-ray scattering.

Practically all the synthesised complexes are polymorphous and have two mesophases, smectic and nematic. The exception is the $La(CPDK_{3\text{–}1})_3Bpy_{17\text{–}17}$ complex, which is not a liquid crystal, and the $La(CPDK_{3\text{–}3})_3Bpy_{17\text{–}17}$ complex, which shows only nematic mesomorphism. According to the obtained data, the liquid-crystal properties of adducts are not predetermined by the liquid-crystal properties of the ligands. The temperatures and thermodynamic parameters of the phase transitions are shown in Table 1 and Figure 5.

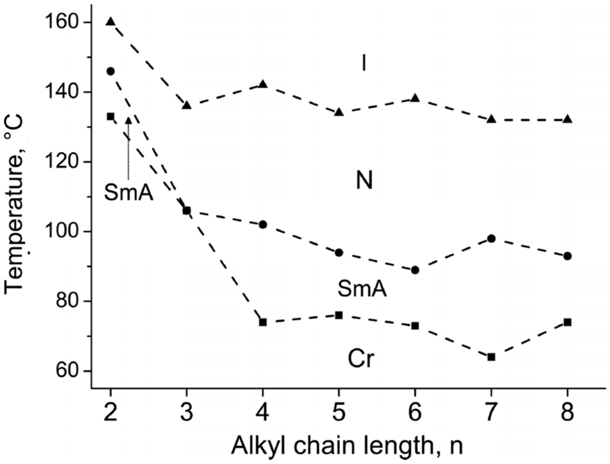

Figure 5. Dependence of phase transition temperatures on the length of alkyl substituent in complexes $[La(CPDK_{3\text{-}R})_3Bpy_{17\text{–}17}]$, where $R{=}CH_3$–C_8H_{17}.

Even–odd alternation of the nematic–isotropic transition temperatures, which is characteristic of a homologous series of liquid crystals and stipulated by alternation of even and odd substituent contributions to the general anisotropy of the molecular polarisability and geometrical anisometry [19], was observed in the synthesised complex series. On heating the polymorphous complexes, two types of textures were observed in POM. These were a fan-like texture (Figure 6) typical of the smectic A phase and a schlieren texture (Figure 7), which is typical of the nematic phase.

The DSC thermogram (Figure 8) characteristic of the series of synthesised complexes also confirms the existence of phase transitions: crystal–smectic A–nematic–isotropic liquid. There is no crystallisation peak in the thermograms on cooling (Figure 9), or it is only slightly shown (Figure 8), which gives evidence of sample vitrification. Small ΔH and ΔS values of the crystal–smectic A–nematic–isotropic liquid phase

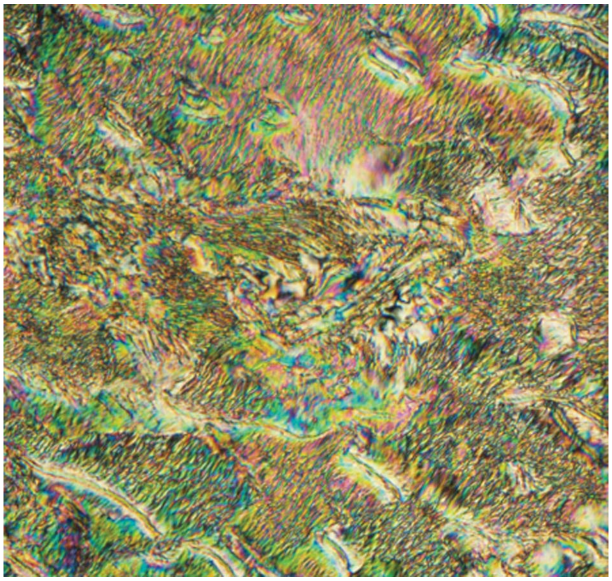

Figure 6. Fan-like texture of the smectic A phase of [La(CPDK$_{3-8}$)$_3$Bpy$_{17-17}$] at 90°C (magnification 96×).

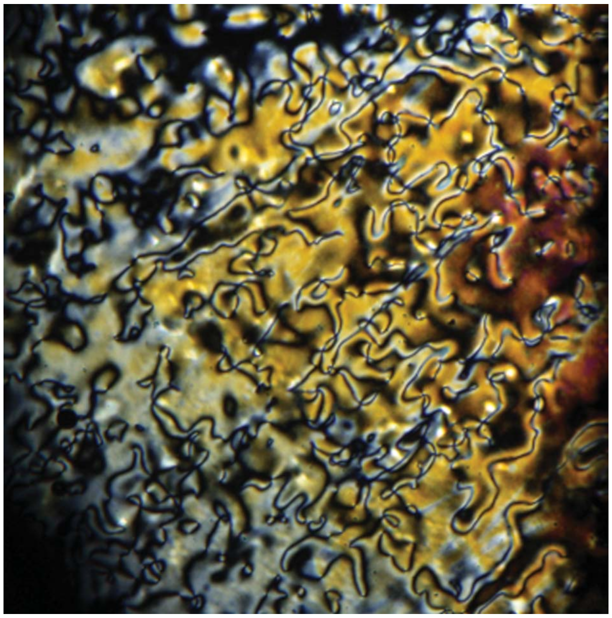

Figure 7. Schlieren texture of the nematic phase of [La(CPDK$_{3-8}$)$_3$Bpy$_{17-17}$] at 120°C (magnification 96×).

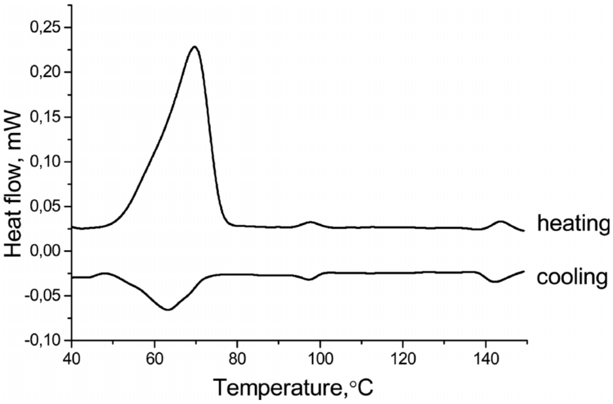

Figure 8. Differential scanning calorimetry curve of [La(CPDK$_{3-4}$)$_3$Bpy$_{17-17}$]. Endothermic peaks are upwards. The heating and cooling rates were 5°C min^{-1}.

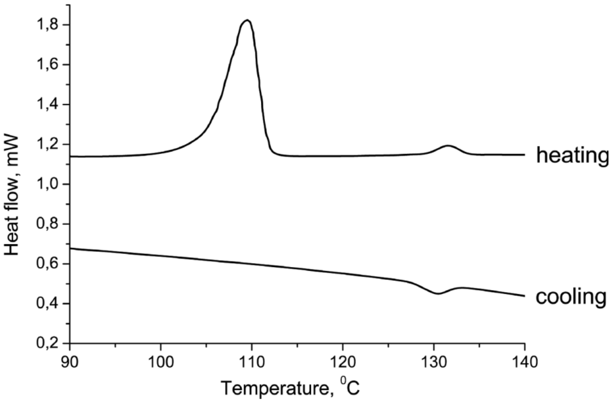

Figure 9. Differential scanning calorimetry curve of [La(CPDK$_{3-3}$)$_3$Bpy$_{17-17}$]. Endothermic peaks are upwards. The heating and cooling rates were 5°C min^{-1}.

transitions show that the packing of molecules in the mesophase has a low order and the phases have a low viscosity. Such ΔH and ΔS values are typical of liquid crystals [16, 20–25]. ΔH and ΔS of smectic A–nematic phase transitions could not be calculated from the DSC data for some adducts (because of weak signals in the DSC thermogram).

As seen from the DSC thermogram (Figure 9), the La(CPDK$_{3-3}$)$_3$Bpy$_{17-17}$ complex has only two transitions corresponding to the existence of only one mesophase, which was identified as the nematic phase by POM. The absence of a crystallisation peak during cooling also gives evidence of sample vitrification.

It is important to note that films of the obtained liquid-crystal complexes are vitrified with the retention of the packing of molecules formed in the mesophase, when cooling below room temperature (according to the polythermal polarised microscopy data). This behaviour of the samples under investigation made it possible to examine the vitrified samples at room temperature by a small-angle X-ray scattering method. As polymorphous complexes are vitrified with the retention of the packing of the smectic A mesophase, the obtained diffractogram of the vitrified film (Figure 10) looked typical for the smectic mesophase [26]. Peaks in the diffractogram at $2\theta = 2.84°$ and 5.7° correspond to the first (001) and second (002) reflexes of the layer spacing $D_w = 31$ Å, which

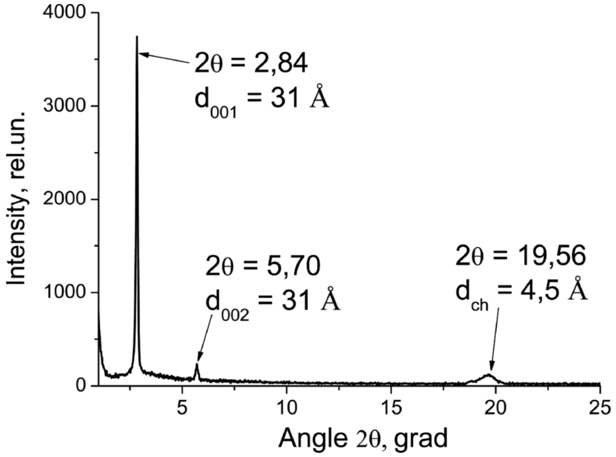

Figure 10. X-ray diffractogram of [La(CPDK$_{3-5}$)$_3$Bpy$_{17-17}$] vitrified in the smectic A mesophase.

confirms the existence of an ordered smectic mesophase. A wide peak at $2\theta = 19.56°$ corresponds to the intermolecular distance $D_w = 4.5$ Å.

A quantum chemical calculation of the molecular equilibrium structure was performed for all the synthesised complexes. As a result, the geometrical parameters of the molecules of the complexes were obtained. The calculation was performed using the Priroda 6 program [27] in the Multiple-access Supercomputing Centre of the Kazan Scientific Centre of the Russian Academy of Sciences. Optimisation of the geometrical structure using density functional theory (DFT) was carried out using the Stevens–Basch–Krauss–Jasien–Cundari (SBK) effective core potential [28–30] for the La atom and the 3z basis for other atoms [31]. The Perdew–Burke–Ernzerhof (PBE) functional was used in the DFT calculations [32]. As the calculated La(CPDk$_{3-5}$)$_3$Bpy$_{17}$ complex molecule length is 54 Å, a model of packing in beds was suggested (Figure 11), where alkyl fragment interfingering occurs.

Only one diffuse peak at $2\theta = 3.1°$ corresponding to the distance 29 Å is observed in the diffractogram for the La(CPDK$_{3-3}$)$_3$Bpy$_{17-17}$ complex having only a nematic phase (Figure 12). According to the data from the quantum chemical calculation of the complexes' structure, the width of the molecule of the La(CPDK$_{3-3}$)$_3$Bpy$_{17-17}$ nematic adduct is 29.1 Å and, therefore, the obtained value can be interpreted as the molecule width. Similar diffractograms for nematic liquid crystals are examined in Demus *et al.* [26].

3. Conclusion

New tris(β-diketonates) lanthanum liquid-crystalline adducts with 5,5'-diheptadecyl-2,2'-bipyridine were obtained. The temperatures and thermodynamic parameters of the phase transitions were determined. Practically all the synthesised complexes are polymorphous and have two mesophases, smectic and nematic. The exception is the La(CPDK$_{3-1}$)$_3$Bpy$_{17-17}$ complex, which is not liquid-crystalline and the La(CPDK$_{3-3}$)$_3$ Bpy$_{17-17}$ complex, which shows only nematic mesomorphism. The influence of the alkyl substituent length in the ligands (β-diketones) on the liquid-crystal properties of the adducts was determined. Even–odd alternation of the nematic–isotropic transition characteristic of a homologous series of liquid crystals, stipulated by inequality of the even and odd substituent contributions to the anisotropy of the molecular polarisability and geometrical anisometry, was observed in the synthesised complex series. Films of the obtained liquid-crystal complexes are vitrified with the retention of the packing of the molecules formed in the mesophase when cooling below room temperature. According to data obtained by small-angle X-ray scattering and quantum chemical calculations, interlayer distances were determined and a model of the packing of the molecules in the mesophase suggested.

4. Experimental

4.1 General

CHN elemental microanalyses were performed on a CE Instruments EA-1110 elemental analyser. Infrared spectra were recorded on a Bruker-IFS66V/S in Nujol between KBr pellets and were distributed on the surface of a thin polyethylene film. ^{1}H nuclear magnetic

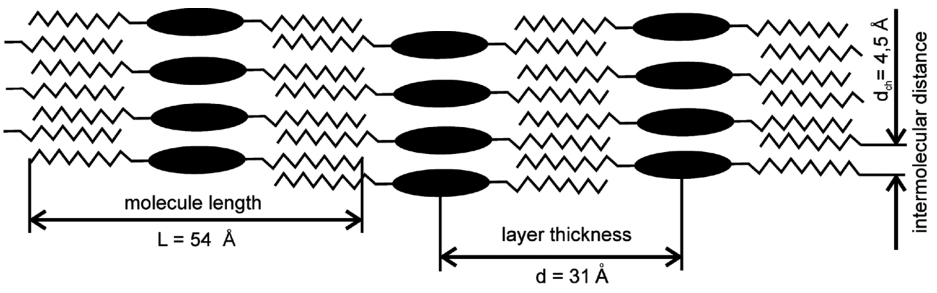

Figure 11. Scheme of molecular organisation in the vitrified smectic mesophase of [La(CPDK$_{3-5}$)$_3$Bpy$_{17-17}$].

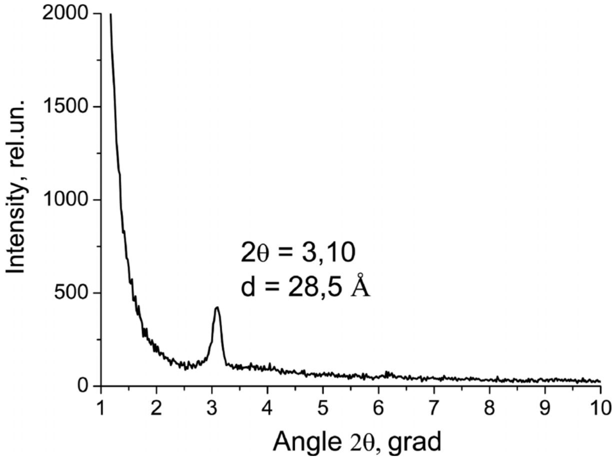

Figure 12. X-ray diffractogram of [La($CPDK_{3-3}$)$_3$$Bpy_{17-17}$] vitrified in the nematic mesophase.

resonance (NMR) spectra were recorded on a Bruker ARX-300 spectrometer. DSC measurements were made on a Mettler-Toledo DSC 1 Star module. Optical textures of the mesophase were observed with an Nagema K8 POM equipped with a Boëtius hot-stage. X-ray scattering patterns were recorded on a DRON-7 X-ray diffractometer with a copper anode.

4.2 Chemicals

The source ketone [1-(4-(4-propylcyclohexyl)phenyl)-ethanone] was obtained from Professor R. Eidenschink (Nematel, Mainz-Hechtsheim, Germany). 5,5'-dimethyl-2,2'-bipyridine was purchased from Aldrich. Esters for β-diketones synthesis and a suspension of sodium amide were purchased from Acros (Geel, Belgium).

4.3 Synthetic procedures

The β-diketone ligands (abbreviated to $CPDK_{3\text{-}R}$) with different lengths of the alkyl terminal substituent R=CH_3–C_8H_{17} (Figure 1) were synthesised according to the method of Adams and Hauser [17]. To the stirred solution of the ketone (0.05 mol) in 100 ml of absolute ether, cooled to 10°C, the suspension of sodium amide in toluene (0.1 mol) was added. After 5 min the calculated amount of ester (0.1 mol) in 100 ml of absolute ether was added over 20 min, and the stirring continued for 6 h. After 20 ml of water was added, the mixture was neutralised with dilute hydrochloric acid and extracted with ether. The solvent was evaporated from the ether solution and the residue dissolved in the minimum volume of ethanol. The β-diketone was recrystallised twice from this ethanol solution. Yields, elemental analysis and melting points are described below.

Typical ^{1}H-NMR spectra for 1-(4-(4-propylcyclohexyl)phenyl)undecane-1,3-dione: δH (300 MHz, CDCl3): 0.88–0.94 m (6H, CH_3); 1.29–1.69 m (21H, CH_2, C_6H_{10}); 1.89–1.92 m (4H, C_6H_{10}); 2.42 t (2H, CH_2-CO, $J = 6.8$ Hz); 2.51–2.59 m (1H, C_6H_{10}); 4.06 s (0.2 H, CH_2 keto); 6.15 s (1 H, CH enol); 7.28–7.31 m (2H, C_6H_4); 7.83 d (2H, C_6H_4, $J = 8.1$ Hz); 16.26 s (0.8 H, CH enol).

4.3.1 Synthesis of 5,5'-di(heptadecyl)-2,2'-bipyridine

The ligand 5,5'-diheptadecyl-2,2'-bipyridine (abbreviated to bpy_{17-17}) was synthesised according to a method of alkylation of 5,5'-dimethyl-2,2'-bipyridine with 1-bromohexadecane and lithium diisopropylamide in tetrahydrofuran at –40°C [33]. Melting point (m.p.): 81.5°C. MS (ESI) m/z: 634 (M+). Anal. calcd for $C_{44}H_{76}N_2$ (M_w=633.09 g mol^{-1}): C, 83.48; H, 12.10; N, 4.42%; found: C, 83.15; H, 12.12; N, 4.42%. δH (300 MHz, CDCl3) 0.84–0.91 (m, 6H, CH3), 1.15–1.36 (m, 56H, CH2), 1.60–1.70 (m, 4H, CH2CH2-Pyr), 2.66 (t, 4H, CH2-Pyr $J = 7.3$ Hz), 7.61 (dd, 2H, H4 $J_1 = 2.0$ Hz, $J_2 = 1.9$ Hz) 8.26 (d, 2H, H3 $J = 8.2$ Hz), 8.47–8.52 (m, 2H, H6).

4.3.2 Synthesis of lanthanum complexes

The [La($CPDK_{3\text{-}R}$)$_3$(bpy_{17-17})] complexes were synthesised following a modified procedure of Knyazev *et al.* [18] The complexes were prepared by mixing the β-diketone ligand (3 eq.), sodium hydroxide (3 eq.) and the bipyridine ligand (1 eq.) in absolute ethanol at 66–68°C, followed by dropwise addition of an ethanolic solution of the lanthanide chloride salt (1 eq.). The reaction time was 30 min.

Yields and elemental analysis: $C_{122}H_{193}LaN_2O_6$: yield 71%; anal. calcd: C, 76.21; H, 10.12; N, 1.46; found: C, 76.20; H, 10.05; N, 1.50 %. $C_{119}H_{187}$ LaN_2O_6: yield 64%; anal. calcd: C, 76.00; H, 10.02; N, 1.49%; found: C, 76.20; H, 10.00; N, 1.54%. $C_{116}H_{181}LaN_2O_6$: yield 63%; anal. calcd: C, 75.78; H, 9.92; N, 1.52 %; found: C, 76.20, H, 10.00; N, 1.51%. $C_{113}H_{175}LaN_2O_6$: yield 61%; anal. calcd: C, 75.55; H, 9.82; N, 1.56%; found: C, 75.70; H, 9.90; N, 1.59%. $C_{110}H_{169}LaN_2O_6$: yield 68%; anal. calcd: C, 75.31; H, 9.71; N, 1.60%; found: C, 75.00; H, 9.80; N, 1.59%. $C_{107}H_{163}LaN_2O_6$: yield 57%; anal. calcd: C, 75.05; H, 9.59; N, 1.64%; found: C, 74.70; H, 9.60; N, 1.66%. $C_{104}H_{157}LaN_2O_6$: yield 66%; anal. calcd C, 74.78; H, 9.47; N, 1.68%; found: C, 74.22; H, 9.39; N, 1.72%. $C_{101}H_{151}LaN_2O_6$: yield 53%; anal. calcd: C, 74.50; H, 9.35; N, 1.72%; found: C, 74.32; H, 9.40; N, 1.79%.

Complex formations were identified by the appearance of signals on infrared spectra at 412–403 cm^{-1} (La-O) and 208 cm^{-1} (La-N).

Acknowledgements

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