ADVANCED MATERIALS

Polarized Luminescence from Aligned Samples of Nematogenic Lanthanide Complexes**

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Liquid-crystalline lanthanide complexes (lanthanidomesogens) are a class of molecular materials that have intensively been studied during the last decade.[1] Whereas the first examples of lanthanidomesogens were phthalocyanine[2] or Schiff base complexes,[3] progressively new types of lanthanide-containing liquid crystals have been discovered. These include alkanoates,[4] β-diketonates,[5] β-enaminoketones,[6] imidazo[4,5-f]-1,10-phenanthrolines,[7] 2,6-bis(benzimidazol-2-yl)pyridines,[8] crown ethers,[9] polyoxometalate surfactant complexes,[10] and complexes of lanthanide salts with non-ionic surfactants.[11] The rationale for incorporating lanthanide ions into liquid crystals is that this approach allows to add unique magnetic and spectroscopic properties to the anisotropy-related properties of liquid crystals.[1a] For example, it is possible to obtain liquid crystals that can be more easily aligned in an external magnetic field[3c,12] or luminescent liquid crystals.[13] The coordination geometries of the metal ion in f-block metallomesogens differ from those of the d-block metallomesogens, in the sense that the coordination number of the lanthanides is high (typically eight or nine). It is a challenge to obtain liquid-crystalline lanthanide complexes, because it is difficult to make the bulky coordination sphere of the lanthanide ion compatible with the structural requirements for the existence of liquid-crystal phases (rod-like or disk-like molecules).[1a] The most often used approach is to attach a large number of long alkyl chains to the core of the lanthanide complex. This usually leads to smectic or columnar mesophases. From a technological point of view, it is very interesting to have access to lanthanide complexes that exhibit a nematic phase.[14,15] Indeed, a nematic phase has the lowest viscosity of all types of mesophases, and hence it is easier to realign a nematic phase in external electric or magnetic fields, and it allows faster switching. There are some reports on nematic liquid-crystal hosts doped with lanthanide complexes,[16] but examples of nematogenic lanthanide complexes are very rare. Some of the earliest claims of such compounds[17] are difficult to reproduce.[18] Recently, Binnemans and coworkers reported on nematic phases observed for lanthanide complexes of imidazo[4,5-f]-1,10-phenanthroline ligands.[7] However, these compounds had a quite extended structure with cyanobiphenyl mesogenic groups attached via long alkyl spacers to the lanthanide core and the order of the molecules in these nematic phase is low. In this Communication, we describe the first examples of low-molecular-weight liquid-crystalline lanthanide complexes that exhibit a nematic phase over a rather broad temperature range, are thermally stable, and have interesting optical properties.

The novel nematogenic lanthanide complexes are ternary complexes consisting of three β-diketonate ligands and one substituted 2,2'-bipyridine ligand (Fig. 1). The β-diketonate ligand is rather unconventional in the sense that it incorporates the cyclohexyl moiety. The 2,2'-bipyridine ligand is 5,5'-bis(heptadecyl)-2,2'-bipyridine. By comparison with other lanthanide tris β-diketonates that contain a bidentate coligand, it can be assumed that the coordination number of the lanthanide ion in these complexes is eight.[19] Complexes of

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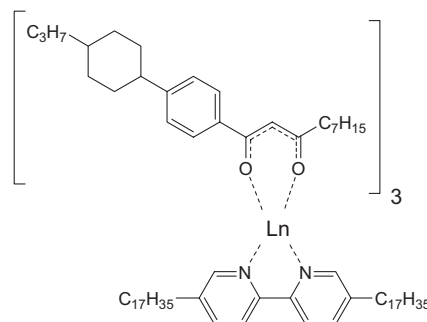E-mail: koen.binnemans@chem.kuleuven.be

Figure 1. Structure of the lanthanidomesogens (Ln = La, Nd, Eu, Yb)

lanthanum(III), neodymium(III), europium(III), and ytterbium(III) were prepared. This guaranteed that we had sufficient variation for the size of the lanthanide ion. Earlier studies have indicated that the nature of the lanthanide ion can have a large influence of the transition temperatures and even on the type of mesophase that can be observed.[1] The β-diketonate ligand (m.p. = 82 °C) and the 2,2'-bipyridine ligand (m.p. = 81.5 °C) are not mesomorphic, but the lanthanide complexes are liquid-crystalline. This shows that a mesophase is induced in the (mixture of) ligands by complex formation with the lanthanide ion. It is always an advantage that the ligands are not liquid-crystalline because it avoids the problem that in the case of unstable complexes the mesomorphism of the ligand is mistakenly considered as that of the corresponding metal complexes. The thermal behavior of the complexes was studied by polarizing optical microscopy (POM) and by differential scanning calorimetry (DSC). The results are summarized in Table 1. At room temperature, the complexes are glassy or amorphous solids. Upon heating, the compounds melt between 64 °C (lanthanum(III) complex) and 76 °C (ytterbium(III) complex) to a smectic A phase. Upon further heating, the smectic A phase transforms into a nematic phase (depending on the lanthanide ion between 98 °C and 108 °C). The nematic-to-isotropic transition occurs between 132 °C and 142 °C, with the lowest temperature for the lanthanum(III) complex and the highest temperature for the europium(III) complex. The same phase sequence was observed on cooling from the isotropic liquid. The mesophases were identified on the basis of their typical defect textures. The nematic phase formed as typical nematic droplets just below the clearing point, which coalesced to a threaded texture or a schlieren texture (with two-brushes and four-brushes schlieren point defects) (Fig. 2). A focal-conic texture was observed for the smectic A phase. No significant differences in the transition temperatures for the smectic A-to-nematic and for the nematic-to-isotropic transition were observed during
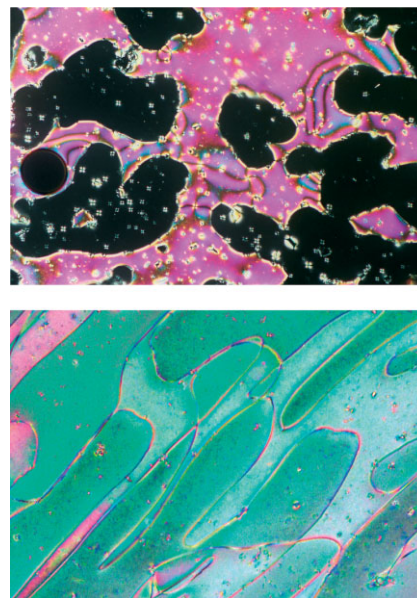
Figure 2. Top: Schlieren texture of the nematic phase [Eu(CPDK)$_3$(bpy17-17)] at 126 °C (magnification 200×). Bottom: Threaded texture of the nematic phase of [Nd(CPDK)$_3$(bpy17-17)] at 118 °C (magnification 200 ×).

subsequent heating-cooling cycles. The DSC trace of the europium(III) compound is shown in Figure 3. The values for the enthalpy and the corresponding entropy changes of the SmA-N and N-I transitions are very small (see Table 1), and these transitions are not easy to detect by differential scanning calorimetry. However, similar values have been observed for different classes of liquid crystals.[20] Several of these liquid crystals with small ΔH values for the SmA-N and N-I transitions have short terminal alkyl chains and/or a cyclohexyl group, i.e., structural features that are also present in the β-diketonate ligand of this study. Additionally, the very bulky metal fragment can prevent strong ordering of the molecules.

The small enthalpic changes indicate that the order of the molecules in the smectic A and in the nematic phase is low, resembling that in the isotropic liquid state. Our lanthanidomesogens are not only of interest because of the existence of a nematic phase, but also because these compounds are among the rare examples of liquid-crystalline lanthanide complexes that exhibit polymorphism of mesophases. Other examples of polymorphism were observed for the 2,6-bis(benzimidazol-2-yl)pyridines lanthanidomesogens described by Piguet and co-workers, which exhibit for one and the same compound a lamellar-columnar phase and a cubic phase.[8b] Ohta and co-workers described an ordered rectangular columnar phase and hexagonal columnar phase for bis(octaalkoxyphthalocyaninato)lutetium(III) complexes.[21]

The availability of samples of nematic phases of lanthanide complexes invites to perform studies on the re-alignment or switching in an external elec-

Table 1. Phase behavior, transition temperatures, melting enthalpies, and melting entropies of the [Ln(CPDK)$_3$(bpy17-17)] complexes.

| Ln	Transition [a]	Temperature [b] [°C]	ΔH [c] [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]
La	g → SmA	64	–	–
	SmA → N	98	0.11	0.30
	N → I	132	1.02	2.51
Nd	g → SmA	74	–	–
	SmA → N	106	0.19	0.50
	N → I	140	1.26	3.05
Eu	g → SmA	72	–	–
	SmA → N	108	0.16	0.42
	N → I	142	0.95	2.29
Yb	g → SmA	76	–	–
	SmA → N	101	0.19	0.51
	N → I	134	0.98	2.41

[a] g = glass; SmA = smectic A phase; N = nematic phase; I = isotropic phase. [b] Transition temperatures were determined by polarizing optical microscopy. [c] The g → SmA transition could not be detected by differential scanning calorimetry.
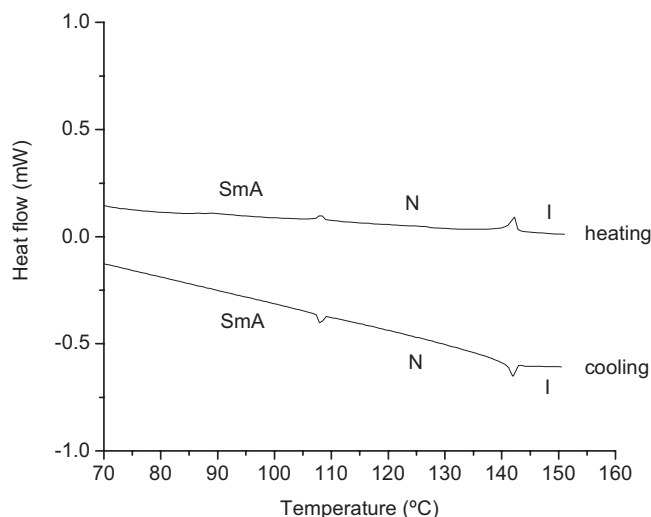
Figure 3. DSC curve of [Eu(CPDK)$_3$(bpy17-17)] (second heating). Endothermic peaks are upwards. The heating rate was 10 °C min^{-1}.

tric or magnetic field. Here, we investigated the polarized emission of the europium(III) complex [Eu(CPDK)$_3$(bpy17-17)] in two types of liquid-crystal cells (LC cells) with a thickness of 5 μm: a homogeneous cell with a parallel polyimide alignment layer for the two surfaces inducing a planar alignment (HG-cell) and a homeotropic cell inducing a 90° alignment perpendicular to the surface of the cell (HT-cell). The HG-cell is electrically switchable by use of a dc or ac power supply. At the temperatures at which the nematic phase is stable (108 to 142 °C for the europium complex), the radiationless deactivation is dominant so that only weak luminescence could be observed. Under these conditions, it was impossible to perform detailed measurements of the luminescence polarization in our current luminescence setup. Upon cooling of the sample in the LC cell, a vitrified aligned mesophase sample was obtained. The alignment of the vitrified smectic A mesophase was verified by polarizing optical microscopy before and after the luminescence measurements. For the HG-cell, no defects were observed and the sample showed a uniform color. For the HT-cell, the sample was entirely black with no appearances of any defects. The europium(III) complex [Eu(CPDK)$_3$(bpy17-17)] exhibits a strong red photoluminescence upon excitation with UV-irradiation at 350 nm. The polarization direction was chosen either parallel (para, π-spectrum) or orthogonal (ortho, σ-spectrum) to the alignment layer in the HG-cell. All spectra were normalized for the intensity of the transition at 611 nm. An unaligned thin film of the europium complex [Eu(CPDK)$_3$(bpy17-17)] showed no difference in luminescence polarization (Fig. 4A). The emission spectrum in an HT-cell,

with the molecules aligned perpendicular to the cell surfaces, is different from the spectrum of the unaligned thin film but also independent of the position of the polarizer. A most interesting effect is the observation of polarized luminescence by the europium(III)-containing vitrified mesophase in the HG-cell. Distinct polarization effects could be observed, depending on the position of a polarizer placed in the light beam of the emitted light, with respect to the alignment direction of the rod-like molecules in the HG-cell (Fig. 4B). These polarization effects are visible as differences in the relative intensities of the crystal-field transitions within a spectroscopic line. The most pronounced effects were observed for the $^5D_0 \to {}^7F_2$ transition (indicated 1-5 in the Figures 4 and 5), which is the most intense emission line in the luminescence spectrum of the nematogenic europium(III) complex. The intensity differences within the $^5D_0 \to {}^7F_1$ transition (indicated 1', 2', 3' in the Figures 4 and 5) are also easy to recognize. The $^5D_0 \to {}^7F_0$ line (indicated 0 in the Figures 4 and 5) remained unchanged when the polarizer was turned. In principle, it should be possible to determine the site symmetry of the europium(III) ion on the basis the number of crystal-field components and the polarization information. Because three components can be observed for the $^5D_0 \to {}^7F_1$ transition and five components for the $^5D_0 \to {}^7F_2$ transition, the actual site symmetry is low (C$_1$, C$_2$, or C$_s$ symmetry).[22] However, a discrimination
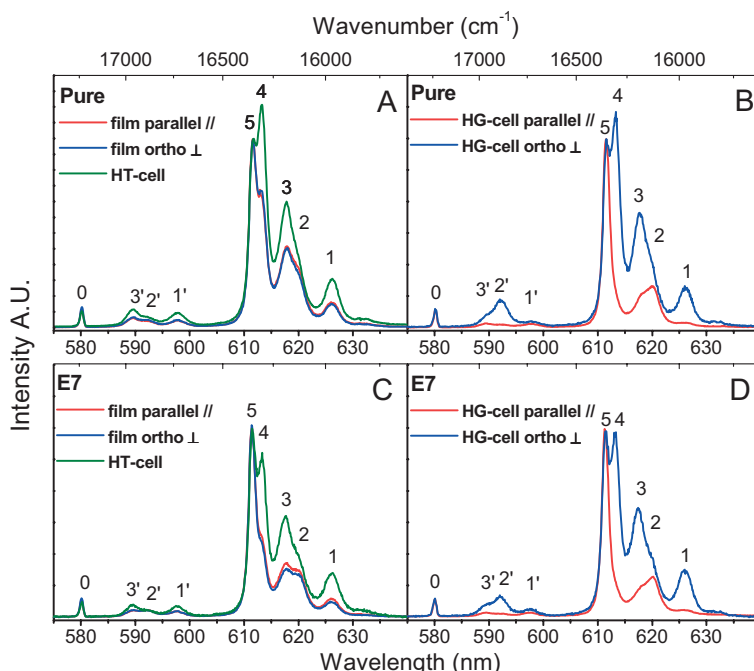
Figure 4. Polarized luminescence spectra of (A) pure [Eu(CPDK)$_3$(bpy17-17)] as a supercooled thin film and in a HT-cell (homeotropic alignment); (B) pure [Eu(CPDK)$_3$(bpy17-17)] as an aligned supercooled phase in a HG-cell (homogeneous or planar alignment; (C) [Eu(CPDK)$_3$(bpy17-17)] dissolved in the nematic liquid-crystal mixture E7 as a thin film and in a HT-cell (D) [Eu(CPDK)$_3$(bpy17-17)] dissolved in the nematic liquid-crystal mixture E7 aligned in a HG-cell. All spectra were measured at room temperature and the excitation wavelength was 350 nm. The intensity was normalized for the transition at 611 nm. The transitions shown in the spectra are the $^5D_0 \to {}^7F_J$ (J = 0, 1, 2) lines.
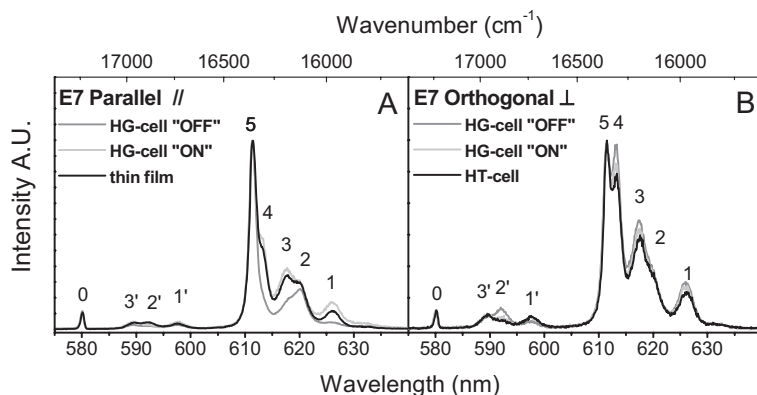
Figure 5. Influence on the application of a voltage difference (30V DC-current) on the polarized luminescence spectra of [Eu(CPDK)$_3$(bpy17-17)] dissolved in the nematic liquid-crystal mixture E7 for the (A) parallel and (B) orthogonal polarization. For comparison the spectrum of an unaligned thin film and a HT-cell are presented in (A) and (B) respectively. All spectra were measured at room temperature and the excitation wavelength was 350 nm. The intensity was normalized for the transition at 611 nm. The transitions shown in the spectra are the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2) lines.

between C_1, C_2, or C_s symmetry is not possible with the available data.

In order to have an electrically switchable nematic phase at room temperature, the europium(III) complex [Eu-(CPDK)$_3$(bpy17-17)] was dissolved in the commercially available room-temperature nematic liquid-crystal mixture E7 (Merck), which consists of an eutectic mixture of 4-cyanobiphenyls and 4-cyanoterphenyls.[23] It was found that the solubility of the complex in E7 was quite good. The polarized luminescence spectra are comparable with those observed for the aligned sample of the vitrified mesophase (Figure 4C and D). Switching of the pure compound was not possible, but switching could be easily induced by application of an electric potential (10–30 V ac or dc) over a HG-cell filled with a liquid crystalline solution of the lanthanide complexes in E7. The reversible change in the luminescence spectrum by turning the cell "on" and "off" is shown in Figure 5. Upon switching the cell, the re-alignment of the molecules from the planar to the homeotropic alignment is not perfect because still some polarization effects were noticed. This can be caused by the fact that the molecules in the neighborhood of the alignment layer retain their planar alignment. When the polarization is parallel to the alignment, the spectrum in the "on" state is similar to spectrum in an unaligned thin film. When the polarization is orthogonal to the alignment, the spectrum of the HG-cell in the "on" state similar to the spectrum of the HT-cell.

The alignment of the nematic doped E7 mixture was confirmed by polarizing optical microscopy in the same way as for the vitrified pure sample (see above). It should be noted that the polarization effects are in the first place caused by the site symmetry of the europium(III) ion.[24] By redesigning the first coordination of the europium(III) ion, it is possible to change the polarization effects observed in the photoluminescence spectra. On the basis of theoretical considerations, it is

possible to predict what should be the structure of the europium(III) coordination polyhedron to have very pronounced polarization effects. In the most extreme case, it should be possible to have a very high contrast ratio for the luminescence visible for the two polarization states. First of all the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ should be very intense in comparison to the other transitions, so that most of the emission intensity is emitted via this line. To have an intense $^5D_0 \rightarrow {}^7F_2$ transition, the europium(III) ion should be surrounded by polarizable ligands. Ideally, the coordination sphere should have D_{3h} symmetry. According to the selection rules for D_{3h} symmetry, only one crystal-field transition is allowed for $^5D_0 \rightarrow {}^7F_2$ when the polarizer is orthogonal to the alignment direction (σ spectrum), whereas no transition is allowed for $^5D_0 \rightarrow {}^7F_2$ when the polarizer is parallel to the alignment direction (π spectrum).

Although the phenomenon of polarized emission is well known for lanthanide(III) ions doped into non-cubic host crystals,[25,26,27] only few examples of polarization effects in the luminescence spectra of oriented molecular lanthanide-containing materials have been reported in the literature. Bazan and coworkers described polarized emission by stretched polyethylene films doped with a europium(III) β-diketonate complex.[28,29] It has been recognized that polarized luminescence from oriented molecular materials is an important topic in materials sciences.[30] Most studies on linearly polarized photoluminescence make use of oriented polymer films,[31] whereas some workers have investigated polarized luminescence by aligned liquid crystal samples.[32]

To conclude, we presented here the first examples of lanthanidomesogens that exhibit a low viscous nematic phase. The compounds are one of the rare examples of liquid-crystalline lanthanide complexes that show polymorphism in the mesophase region (smectic A and nematic phases). The temperatures at which the nematic phase occurs are low and the nematic temperature range is broad, which makes these materials interesting for further physical studies. Moreover, the compounds are thermally stable. We illustrated for the first time that aligned samples of lanthanidomesogens can emit linearly polarized light. Further work will be directed to modification of the complex in order to lower the transition temperatures. The ultimate goal is to obtain for a lanthanide complex a nematic phase that is stable at room temperature.

Experimental

General: CHN elemental microanalyses were performed on a CE Instruments EA-1110 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz). Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC 822e module. Optical textures of the mesophase were observed with an Olympus BX60 polarized optical microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS

93 programmable temperature controller. Photoluminescence spectra in the visible region have been recorded on an Edinburgh Instruments FS900 spectrofluorimeter. This instrument is equipped with a 450 W xenon arc lamp, and a red-sensitive photomultiplier (300–850 nm). The photoluminescence spectra were corrected for the sensitivity of the detector at the different wavelengths. The excitation light beam with a wavelength of 350 nm was unpolarized. All samples were placed in the sample compartment of a spectrofluorimeter in such a position that the luminescence could be measured in transmission mode. A polarizer can be placed at the exit monochromator. The polarization direction is parallel (para) or orthogonal (ortho) to the alignment layer in the HG-cell. The arbitrary para(0°)- and ortho(+90°)-indication is maintained for the polarization direction in the thin film and HT-cell. To eliminate any influence of polarization by the instrument (e.g. gratings), different sample orientations (+45°, +90°) were used and compared. All spectra were normalized for the transition at 611 nm.

Liquid-Crystal Cells: Two types of liquid-crystal cells were purchased from AWAT (Warszawa, Poland). The cell thickness was 5 μm.The HG-cell was electrically switched by use of a home-made dc or ac power supply. The cells were filled at 150 °C for the pure compound and 40 °C for the E7 mixture. As a reference sample, a supercooled thin film and a nematic E7 mixture were prepared between two glass plates without alignment layer. The mechanism of polymer alignment of liquid crystals has been described by Geary et al.[53]

Synthetic Procedures: The β-diketone ligand 1-(4-*trans*-(4-propyl-cyclohexyl) phenyl)-1,3-decanedione (abbreviated to HCPDK3-7) was obtained from R. Eidenschink (Nematel, Mainz-Hechtsheim, Germany), m.p.: 82 °C. The ligand 5,5'-diheptadecyl-2,2'-bipyridine (abbreviated to bpy17-17) was synthesized according to a literature method by alkylation of 5,5'-dimethyl-2,2'-bipyridine with 1-bromo-hexadecane and lithium diisopropylamide in THF at –40 °C.[34] 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%. d_H (300 MHz, CDCl$_3$) 0.84–0.91 (m, 6H, CH$_3$), 1.15–1.36 (m, 56H, CH$_2$), 1.60–1.70 (m, 4H, CH$_2$CH$_2$-Pyr), 2.66 (t, 4H, CH$_2$-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$_o$ = 8.2 Hz), 8.47–8.52 (m, 2H, H6).

The [Ln(CPDK3-7)$_3$(bpy17-17)] complexes (Ln = La, Nd, Eu, Yb) were synthesized following a modified literature procedure.[35] 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 minutes. The yields were 67% (La), 68% (Nd), 72% (Eu), and 67% (Yb). The purity of the compounds was verified by CHN elemental analysis: Anal calcd. for $C_{119}H_{187}LaN_2O_6$ (M_w = 1880.67 g mol^{-1}): C, 76.00; H, 10.02; N, 1.49 %;. Found: C, 75.72; H, 10.25; N, 1.47 %. Anal calcd. for $C_{119}H_{187}N_2NdO_6$ (M_w = 1886.01 g mol^{-1}): C, 75.78; H, 9.99; N, 1.49 %;. Found: C, 75.66; H, 10.39; N, 1.48 %. Anal calcd. for $C_{119}H_{187}EuN_2O_6$ (M_w = 1893.73 g mol^{-1}): C, 75.47; H, 9.95; N, 1.48 %;. Found: C, 75.25; H, 10.18; N, 1.48 %. Anal calcd. for $C_{119}H_{187}N_2O_6Yb$ (M_w = 1914.81 g mol^{-1}): C, 74.64; H, 9.84; N, 1.46 %;. Found: C, 74.26; H, 10.20; N, 1.45 %.

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