Lanthanide-Containing Metallomesogens with Low Transition Temperatures

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Lanthanide-containing liquid crystals exhibiting a mesophase close to room temperature were obtained by adduct formation between a long-chain salicylaldimine Schiff base and tris(2-thenoyltrifluoroacetonato)-lanthanide(III) complexes or tris(benzoyltrifluoroacetonato)lanthanide(III) complexes. The mesophase was identified as a smectic A phase. The temperature range of the mesophase was found to decrease over the lanthanide series, and no mesophase was observed for the complexes of the smallest lanthanide ions. The photoluminescence of the europium(III), samarium(III), neodymium(III), and erbium(III) complexes was studied. It is shown that the clearing point can be detected by monitoring the luminescence decay time as a function of the temperature.

Introduction

Liquid-crystalline metal complexes (*metallomesogens*) combine the unique properties of both liquid crystals and d-block or f-block metal complexes.[1−8] However, the study of the physicochemical properties of metallomesogens is often hampered by their high transition temperatures and/or low thermal stability. Many researchers are therefore suspicious about the usefulness of these compounds for applications and metallomesogens still remain an academic curiosity. The availability of metallomesogens that are liquid-crystalline at room temperature, that have a high thermal stability, and that have useful properties (magnetism, luminescence, and redox behavior) could change this situation. There is presently a strong research interest in light-emitting liquid crystals (photoluminescent or electroluminescent liquid crystals).[9,10] These materials can be obtained either by incorporating a luminophore in a mesogenic unit or by doping luminescent compounds into a liquid-crystalline host matrix (*host−guest systems*).[11−14] Aligned luminescent liquid crystals can be used for the design of a polarized light source without the need

of relying on external polarizers. From this point of view, luminescent films prepared by cross-linking of liquid crystals with polymerizable groups are very interesting.[15−19] Although most studies on light-emitting liquid crystals have been focusing on fluorescent organic compounds,[20−33] research is now also more and more being directed to luminescent metallomesogens.[34−41] Many authors are exploring the typical

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line emission of trivalent lanthanide ions in the visible and near-infared spectral region for the design of luminescent materials,[42−46] so it is not surprising that lanthanide-containing liquid crystals are considered as a promising class of light-emitting liquid crystals.[7,47,48] Although several studies were performed on liquid-crystalline lanthanide complexes, only few of them are luminescent and most of these compounds have transition temperatures well above room temperature.[49−66] Some researchers approached this problem by doping luminescent lanthanide complexes into a nematic liquid-crystal host matrix.[67−72] Bünzli and co-workers de-
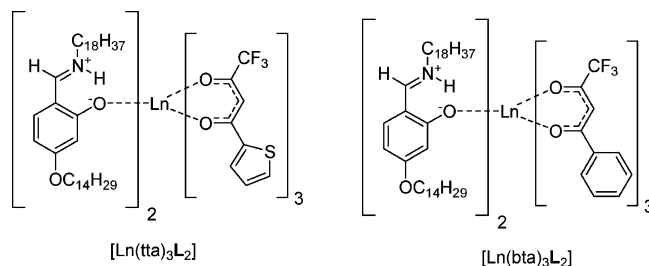
Figure 1. Structure of the lanthanide complexes [Ln(tta)$_3$**L**$_2$] and [Ln-(bta)$_3$**L**$_2$]. Here, Ln represent a trivalent lanthanide ion, tta is 2-thenoyltrifluoroacetonate, bta is benzoyltrifluoroacetonate, and **L** is the Schiff base.

tected luminescence of europium(III) and terbium(III) in the mesophase of a neat metallomesogen, albeit at elevated temperatures.[73,74] These authors also studied the luminescence properties of lanthanide(III) salts in room-temperature ionic liquid crystals.[75,76] Corkery and Martin studied the luminescence of glassy samples of mesomorphic europium-doped lanthanum(III) dodecanoate.[77] A related study focuses on the europium(III) alkanoates.[78]

Our research group synthesized a few years ago lanthanide-containing liquid crystals, based on salicylaldimine Schiff base ligands to tris(dibenzoylmethanato)lanthanide-(III) complexes.[79,80] The compounds showed a monotropic smectic A phase. To optimize the luminescence properties of these compounds, we replaced the dibenzoylmethanate ligand by 2-thenoyltrifluoroacetonate or benzoyltrifluoroacetonate (Figure 1). It is well-known that europium(III) complexes of this ligand exhibit a very intense red photoluminescence upon irradiation by UV light.[81−89] Surprisingly, we found that the complexes of the 2-thenoyltrifluoroacetonate and the benzoyltrifluoroacetonate ligand form more stable mesophases than the corresponding one of the dibenzoylmethanate ligand (the new complexes exhibit an enantiotropic mesophase) and have lower transition temperatures. The melting points of these mesogenic compounds are close to room temperature. This stimulated us to study the mesogenic, structural, and spectroscopic properties of these complexes in detail, and the present paper reports on this work. Throughout the paper, the Schiff base 2-[(E)-(octadecylimino)methyl]-5-(tetradecyloxy)-phenol (or *N*-octade-

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cyl-2-hydroxy-4-tetradecyloxybenzaldimine) is represented by **L** and the Schiff base 2-[(E)-(butylimino)methyl]-5-(methoxy)-phenol (or *N*-butyl-2-hydroxy-4-methoxybenzaldimine) by **L′**. 2-Thenoyltrifluoroacetonate is abbreviated by *tta* and benzoyltrifluoroacetonate by *bta*.

Results and Dissussion

The [Ln(tta)₃**L**₂] and [Ln(bta)₃**L**₂] complexes were prepared for all the trivalent rare-earth ions, except for scandium(III), cerium(III), and promethium(III). Scandium(III) has been omitted because this ion prefers six-coordination so that as a rule the tris *β*-diketonato scandium(III) complexes do not form adducts with Lewis bases.[89] Cerium(III) tends to be oxidized to cerium(IV), and promethium is a radioactive element without long-living isotopes. The synthetic method consisted of addition of a solution of 1 equiv of the [Ln-(tta)₃(H₂O)₂] or [Ln(bta)₃(H₂O)₂] complexes dissolved in dry toluene to a solution of 2 equiv of the Schiff base **L** in dry toluene, followed by stirring of the solution for 3 h at 50 °C. The complexes were obtained in pure form after removal of the solvent under reduced pressure, and the compounds were characterized by CHN analysis and by FTIR spectroscopy. For the diamagnetic lanthanum(III) complexes, a well-resolved ¹H NMR spectrum could be recorded. The stoichiometry of the complexes is similar to that observed for the dibenzoylmethanate complexes: two Schiff bases add to a tris(*β*-diketonate)lanthanide(III) complex.

The molecular structures of the analogous compounds [La-(tta)₃**L′**₂] and [Nd(bta)₃**L′**₂], where **L′** is the Schiff base *N*-butyl-2-hydroxy-4-methoxybenzaldimine, were determined by single-crystal X-ray diffraction. The structures show very clearly that three *β*-diketonate ligands and two Schiff base ligands are bonded to the lanthanide ions. The coordination number of the lanthanide ion is eight, for both structures. In the [La(tta)₃**L′**₂] structure, the lanthanum(III) ion is surrounded by three bidentate 2-thenoyltrifluoroacetonate ligands and two monodentate neutral Schiff base ligands (Figure 2). The oxygen atoms of the Schiff base's OH group are deprotonated and the hydrogen atoms are transferred to the nitrogen atoms. As a consequence, a zwitterionic structure (negative charge on the phenolic oxygen atom, positive charge on the imine nitrogen atom) is generated. The coordination polyhedron of lanthanum(III) can be described as a distorted square antiprism. Intramolecular N−H···O hydrogen bonds appear between the protonated nitrogen and
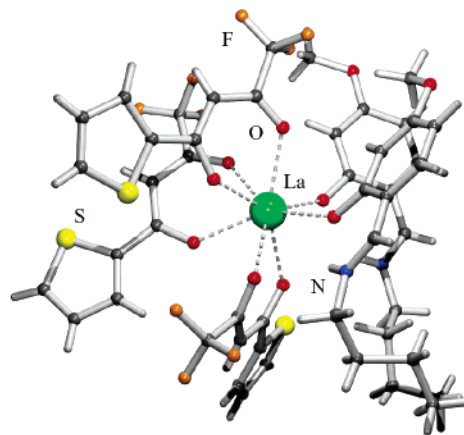
Figure 2. Molecular structure of [La(tta)₃**L′**₂], where **L′** is *N*-butyl-2-hydroxy-4-methoxybenzaldimine and tta is 2-thenoyltrifluoroacetonate.
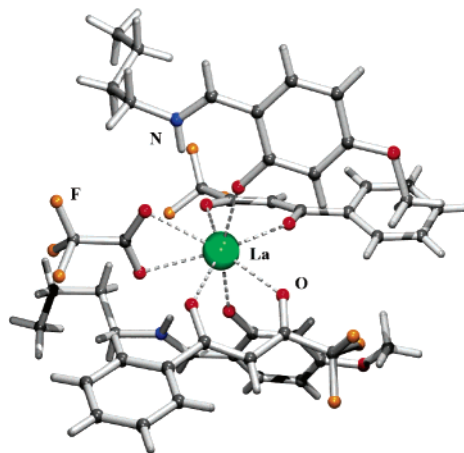
Figure 3. Molecular structure of [La(bta)₂**L′**₂(tfa)], where **L′** is *N*-butyl-2-hydroxy-4-methoxybenzaldimine, bta is benzoyltrifluoroacetonate, and tfa is trifluoroacetate.

the deprotonated oxygen atoms (average H···O distance: 1.99 Å). The asymmetric unit contains two crystallographically independent molecules with different conformations of the butyl chains of the Schiff bases. The Schiff bases of each complex are oriented in the same manner with respect to each other. This is in contrast to the structure of the corresponding complex with the dibenzoylmethanate ligands, in which the Schiff bases are directed oppositely to each other.[79] In the [Nd(bta)₃**L′**₂] structure, a similar distorted square antiprismatic coordination is observed for the neodymium(III) ion, surrounded by three bidentate benzoyltrifluoroacetonate ligands and two monodentate neutral Schiff base ligands (intramolecular average N−H···O distance: 2.02 Å). The asymmetric unit contains only one molecule.

During attempts to grow single crystals of lanthanide complexes of the benzoyltrifluoroacetonate ligands, the structure of a single crystal obtained from an ethanol solution turned out to have a quite unexpected structure: [La(bta)₂**L′**₂(tfa)] (Figure 3). Instead of three *β*-diketonate ligands, only two coordinate to the lanthanum(III) ion. Additionally, a trifluoroacetate anion (tfa) coordinates to the lanthanum(III) ion, as well as two Schiff base ligands. This is a rare example of a lanthanide bis *β*-diketonate complex.[89] The coordination polyhedron of the lanthanum(III) ion in [La(bta)₂**L′**₂(tfa)] can be described as a distorted bicapped trigonal prism, built up of eight oxygen atoms (four oxygens of the two benzoyltri-

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Table 1. Mesomorphic Behavior of the [Ln(tta)₃L₂] Complexes

compound	transition temperatures (°C)[a]	ΔH (kJ mol⁻¹)[b]
[Y(tta)₃**L₂**]	g 23 SmA 49 I	15.7
[La(tta)₃**L₂**]	g 23 SmA 68 I	15.2
[Pr(tta)₃**L₂**]	g 20 SmA 67 I	15.8
[Nd(tta)₃**L₂**]	g 22 SmA 65 I	15.4
[Sm(tta)₃**L₂**]	g 22 SmA 64 I	16.0
[Eu(tta)₃**L₂**]	g 22 SmA 62 I	15.3
[Gd(tta)₃**L₂**]	g 23 SmA 61 I	16.1
[Tb(tta)₃**L₂**]	g 23 SmA 57 I	15.4
[Dy(tta)₃**L₂**]	g 23 SmA 54 I	16.7
[Ho(tta)₃**L₂**]	g 22 SmA 52 I	16.1
[Er(tta)₃**L₂**]	g 24 SmA 48 I	16.4
[Tm(tta)₃**L₂**]	Cr 66 I	76.2
[Yb(tta)₃**L₂**]	Cr 64 I	80.3
[Lu(tta)₃**L₂**]	Cr 59 I	82.4

ᵃ g = glass transition; Cr = crystalline solid; SmA = smectic A phase; I = isotropic liquid. The error on the transition temperatures is estimated to be ±0.5 °C. *ᵇ* The enthalpy changes ΔH corresponds to the enthalpy change at the clearing point for the complexes Ln = La–Er, Y, while it corresponds to the melting enthalpy for the complexes Ln = Tm, Yb, Lu. The error on the ΔH values is estimated to be ±1 kJ mol⁻¹.

Table 2. Mesomorphic Behavior of the [Ln(bta)₃L₂] Complexes

compound	transition temperatures (°C)[a]	ΔH (kJ mol⁻¹)[b]
[Y(bta)₃**L₂**]	g 18 SmA 31 I	8.58
[La(bta)₃**L₂**]	g 19 SmA 50 I	8.70
[Pr(bta)₃**L₂**]	g 18 SmA 44 I	8.41
[Nd(bta)₃**L₂**]	g 19 SmA 43 I	8.62
[Sm(bta)₃**L₂**]	g 18 SmA 41 I	8.40
[Eu(bta)₃**L₂**]	g 18 SmA 40 I	8.75
[Gd(bta)₃**L₂**]	g 19 SmA 39 I	8.59
[Tb(bta)₃**L₂**]	g 18 SmA 37 I	8.54
[Dy(bta)₃**L₂**]	g 18 SmA 35 I	8.71
[Ho(bta)₃**L₂**]	g 18 SmA 33 I	8.72
[Er(bta)₃**L₂**]	g 18 SmA 29 I	8.53
[Tm(bta)₃**L₂**]	Cr 64 I	59.4
[Yb(bta)₃**L₂**]	Cr 60 I	59.1
[Lu(bta)₃**L₂**]	Cr 58 I	59.9

ᵃ g = glass transition; Cr = crystalline solid; SmA = smectic A phase; I = isotropic liquid. The error on the transition temperatures is estimated to be ±0.5 °C. *ᵇ* The enthalpy changes ΔH correspond to the enthalpy change at the clearing point for the complexes Ln = La–Er, Y, while it corresponds to the melting enthalpy for the complexes Ln = Tm, Yb, Lu. The error on the ΔH values is estimated to be ±1 kJ mol⁻¹.

Figure 4. Schematic representation of the lanthanide complexes in the smectic A phase.
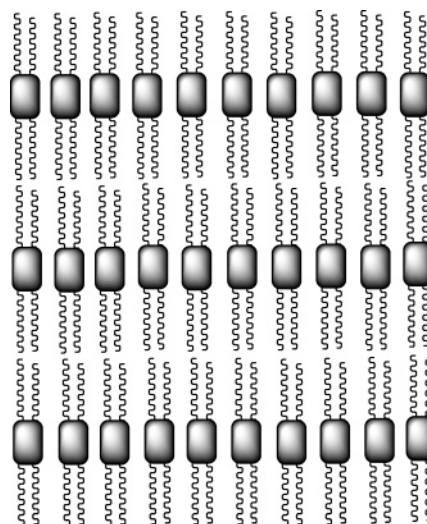
fluoroacetonate ligands, two oxygens of the two Schiff bases, and two oxygens of the trifluoroacetate group). The asymmetric unit contains two crystallographically independent molecules. For both molecules, the Schiff bases are coordinated approximately in a plane, opposite to each other. The β-diketonate ligands also coordinate oppositely, approximately in a plane perpendicular to the plane formed by the Schiff base coordination. The trifluoroacetate anion is very likely formed by decomposition of benzoyltrifluoroacetonate in ethanol by a reverse Claisen condensation reaction. By this reaction benzoyltrifluoracetonate ligands can decompose after protonation into acetophenone and ethyl trifluoroacetate. Ethyl trifluoroacetate can hydrolyze into trifluoroacetic acid and ethanol. Although there are reports in the older literature on the low stability of rare-earth β-diketonate complexes in alcoholic solvents,[90] the decomposition of lanthanide β-diketonates has not been studied in detail yet. Recently, we reported on the enhanced photostability of lanthanide β-diketonates in an ionic-liquid solvent.[91]

The thermal behavior of the lanthanide complexes is summarized in Tables 1 and 2. As mentioned in the Introduction, the complexes with dibenzoylmethanato ligands formed a monotropic mesophase. Unexpectedly, we observed for the [Ln(tta)₃**L₂**] and [Ln(bta)₃**L₂**] complexes not only a stabilization of the mesophase (formation of an enantiotropic mesophase) but also lower transition temperatures (liquid crystallinity at room temperature or at temperatures slightly above room temperature). For instance, compound [Eu-(tta)₃**L₂**] is obtained in the liquid-crystalline state after synthesis. Upon cooling the compound solidifies at 22 °C. No crystallization was observed. The clearing point of this compound is 62 °C. All the compounds exhibit a similar mesophase. The mesophase was identified as a smectic A phase on the basis of the very typical defect texture that could be observed by polarizing optical microscopy when the isotropic liquid was cooled into the mesophase. First bâtonnets were visible, and they coalesced to a fanlike texture. In

the smectic A phase, the molecules are situated in layers and the long molecular axis is on average perpendicular to the layer planes (Figure 4).

The transition temperatures of the benzoyltrifluoroacetonate complexes are lower than those of the 2-thenoyltrifluoroacetonate complexes. For the two series of compounds, the mesophase stability range decreases over the lanthanide series from the lanthanum(III) complex to the erbium(III) complex. The thulium(III), ytterbium(III), and lutetium(III) complexes are not mesomorphic and melt directly to the isotropic state. The transition temperatures of the yttrium-(III) are very comparable with those of the dysprosium(III) and holmium(III) complexes. This indicates that the size of the lanthanide ion has a strong influence on the transition temperatures of the mesogenic lanthanide complexes, a phenomenon that was also observed for other liquid-crystalline lanthanide complexes.[7,51] Although the thulium-(III), ytterbium(III), and lutetium(III) complexes have the same stoichiometry as the other lanthanide complexes, they are also different in the sense that they were obtained in crystalline form instead as a vitreous solid (glass).

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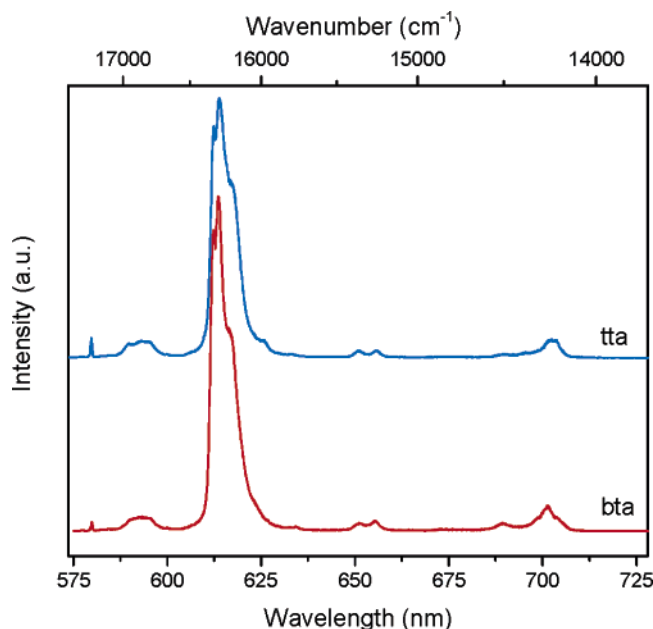
Figure 5. Luminescence spectra of [Eu(tta)$_3$L$_2$] (blue curve) and [Eu-(bta)$_3$L$_2$] (red curve) as a thin film in the mesophase at 25 °C. The excitation wavelength was 370 nm. All transitions start from the $^5D_0$ level and end at the different *J* levels of the ^7F term (*J* = 0−4 in this spectrum).
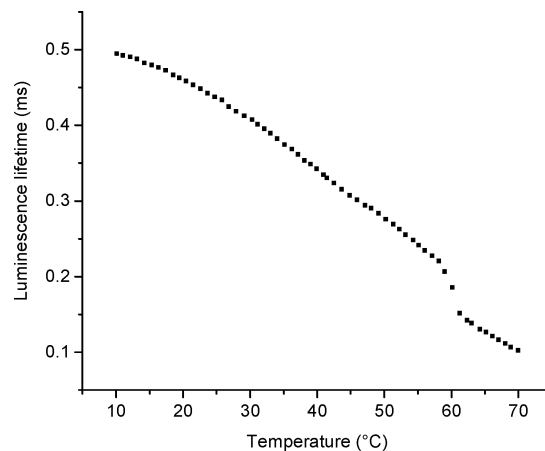

Figure 6. Luminescence decay time of the $^5D_0$ level of [Eu(tta)$_3$L$_2$] as a function of the temperature. The luminescence was monitored at 613 nm ($^5D_0 \rightarrow {}^7F_2$ line) and the excitation wavelength was 370 nm. The measurements were made during cooling of the sample.

The luminescence behavior of the europium(III) and samarium(III) complexes were studied in the vitrified mesophase at room temperature. The europium(III) compounds [Eu(tta)$_3$L$_2$] and [Eu(bta)$_3$L$_2$] show a strong red photoluminescence upon irradiation with ultraviolet light (Figure 5). The fine structure and intensity ratios for the two compounds are very similar. The luminescence spectra were measured with 370 nm as the excitation wavelength. The narrow peaks observed in the luminescence spectrum are transitions between the excited $^5D_0$ level and the different *J*-levels of the ground term ^7F (^7F_J, *J* = 0−4 in the spectrum shown in Figure 5). No transitions starting from the $^5D_1$ level could be seen. In the high-resolution luminescence spectra, crystal-field fine structure could be observed. The fine structure reveals that the site symmetry of the Eu^{3+} ion is low, C_{2v} or even lower. This is evident from the observation of three crystal-field components for the $^7F_1$ level at 595 nm. The $^5D_0 \rightarrow {}^7F_0$ line (580 nm) consists of one peak only, which gives a strong indication that all the Eu^{3+} ions occupy a site of the same symmetry and/or crystal-field strength.[92−95] The most intense line is the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ around 613 nm. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is 12.3 for [Eu(tta)$_3$L$_2$]. This is a typical value for europium(III) β-diketonate complexes.[89] The quantum yield of a solution of the europium complex for [Eu(tta)$_3$L$_2$] dissolved in dry dichloromethane was measured using an integrating sphere. A value of (29 ± 2)% was found for the

quantum yield. Because of the high viscosity of the mesophase, the europium(III) complex could not be aligned in the mesophase. Therefore, no polarized luminescence measurements were possible. The $^5D_0 \rightarrow {}^7F_1$ line is a magnetic dipole transition, whereas all the other transitions are induced electric dipole transitions. All the other induced electric dipole transitions are much weaker than the $^5D_0 \rightarrow {}^7F_2$ line.

The observed luminescence lifetime was determined from measurement of the luminescence decay curve. The decay curve is a single exponential. The luminescence lifetime of the $^5D_0$ level was measured as a function of the temperature upon cooling from 70 °C (isotropic) to 10 °C (vitrified mesophase). The luminescence lifetime increased from 103 μs at 70 °C to 495 μs at 10 °C (Figure 6). At the isotropic to smectic A transition (I $\rightarrow$ SmA transition) at 60 °C, a marked increase of the lifetime is observed. This increase can be attributed to a less efficient quenching of the excited states in the mesophase due to a reduction of the molecular mobility. It was shown earlier by Bünzli and co-workers that the melting point can be detected by luminescence lifetime measurements.[72,73] However, our work indicates that also the clearing temperature can be detected by this method. Notice that no change in the luminescence lifetime is observed upon vitrification of the mesophase. Monitoring of the luminescence lifetime is more accurate than monitoring of the luminescence intensity because the luminescence intensity can change upon flow or deformation of the liquid-crystalline sample.

In Figure 7, the luminescence spectrum of the compound [Sm(bta)$_3$L$_2$] is shown. The narrow peaks observed in the emission spectra are transitions between the excited $^4G_{5/2}$ level and the different *J*-levels of the ^6H term.[96,97] The most intense transition is the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ line at 648 nm. Just as in the case of the europium(III), it was found that the monitoring of the luminescence lifetime can be used to detect the clearing point of a samarium(III)-containing liquid crystal.

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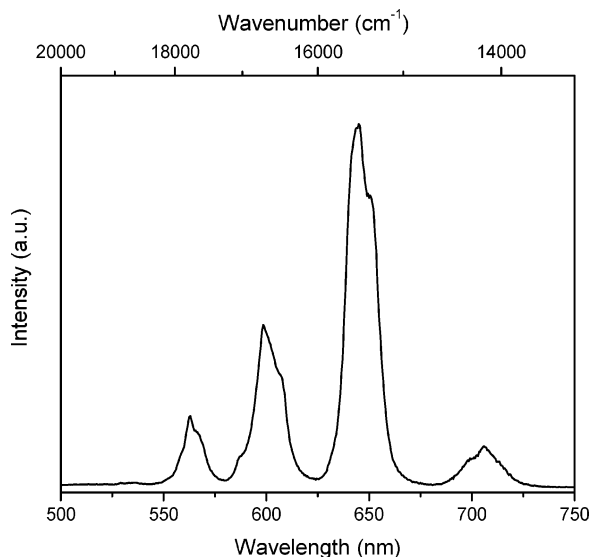
Figure 7. Emission spectrum of $[Sm(bta)_3L_2]$ in the mesophase at 25 °C. The excitation wavelength was 350 nm. All the transitions start from the $^4G_{5/2}$ level.
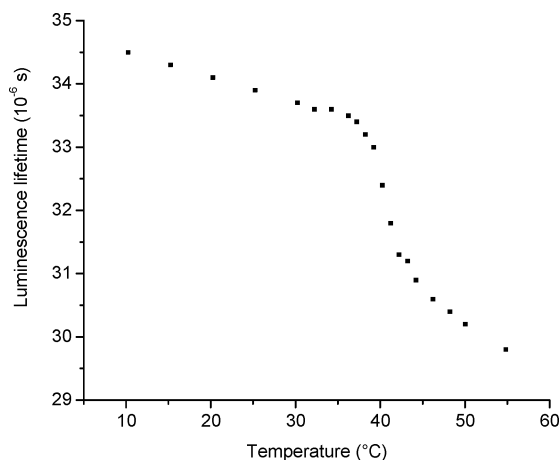
Figure 8. Luminescence decay time of the $^4G_{5/2}$ level of $[Sm(btta)_3L_2]$ as a function of the temperature. The luminescence was monitored at 648 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$ line) and the excitation wavelength was 350 nm. The measurements were made during cooling of the sample.

The luminescence lifetime increased from 30 μs at 54 °C to 34.5 μs at 10 °C (Figure 8). The luminescence lifetime increases sharply at 40 °C, and this temperature corresponds to the clearing temperature as determined by optical microscopy. Notice that the luminescence lifetime of samarium-(III) is much shorter than that of the corresponding europium-(III) compound.

To illustrate the possibility to observe near-infrared emission from trivalent lanthanide ions in the mesophase, we investigated the luminescence of the neodymium(III) and erbium(III) complexes. The ytterbium(III) complexes were not considered because they are not mesomorphic. The most intense near-infrared luminescence was found for the neodymium(III) complex (Figure 12). The observed transitions are the typical 4f−4f transitions of Nd^{3+}: $^4F_{3/2} \rightarrow {}^4I_J$ ($J = {}^9/_2$, $^{11}/_2$, $^{13}/_2$). The luminescence lifetime of the $^4F_{3/2}$ level at room temperature is 442 ns for $[Nd(tta)_3L_2]$ and 380 ns for $[Nd(bta)_3L_2]$. The luminescence of the erbium(III) compounds is much weaker than that of the corresponding neodymium-(III) compounds, due to stronger radiationless deactivation
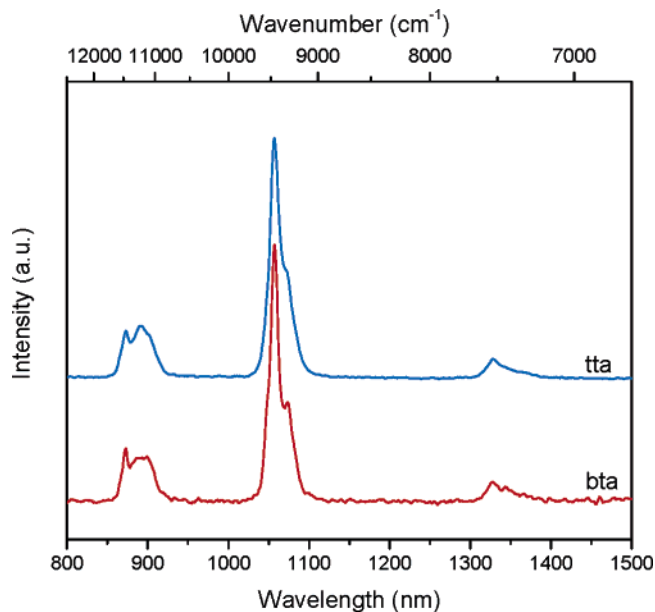
Figure 9. Luminescence spectra of $[Nd(tta)_3L_2]$ (blue curve) and $[Nd(bta)_3L_2]$ (red curve) as a thin film in the mesophase at 25 °C. The excitation wavelength was 317 nm. The observed lines belong to the $^4F_{3/2} \rightarrow {}^4I_J$ multiplet ($J = {}^9/_2$, $^{11}/_2$, $^{13}/_2$).

of the $^4I_{13/2}$ level of Er^{3+} than the $^4F_{3/2}$ level of Nd^{3+}. Only one line could be observed in the luminescence spectrum of the erbium(III) compounds in the mesophase: $^4I_{13/2} \rightarrow {}^4I_{15/2}$. The luminescence lifetime of the $^4I_{13/2}$ level at room temperature is 660 ns for $[Er(tta)_3L_2]$ and 560 ns for $[Er(bta)_3L_2]$.

Experimental Section

General. ^1H NMR spectra were recorded with a Bruker Avance 300 (300 MHz) using $CDCl_3$ as solvent. Elemental analyses (CHN) were obtained on a CE Instrument EA-1110 elemental analyzer. The optical textures of the mesophase were observed with an Olympus BX60 polarizing microscope equipped with a Linkam THMS-600 hot stage and a Linkam TMS-93 programmable temperature controller. DSC traces were recorded with a Mettler-Toledo DSC-821e module. The luminescence spectra of the europium(III) and samarium(III) complexes have been recorded on an Edinburgh Instruments FS-900 spectrofluorimeter. Luminescence lifetime measurements were made on the same instrument. This instrument is equipped with a xenon arc lamp, a microsecond flash lamp, and a red-sensitive photomultiplier (300−850 nm). The spectra were corrected for variations in the output of the excitation source and for variations in the detector response. The quantum yield of the europium(III) complex was determined using an integrating sphere (150 mm diameter, $BaSO_4$ coating) of Edinburgh Instruments, in combination with an Edinburgh Instruments FS920P spectrofluorimeter. The quantum yield can be defined as the following: the integrated intensity of luminescence signal divided by the integrated intensity of the absorption signal. Only the intense luminescence of the $^5D_0 \rightarrow {}^7F_2$ transition was measured by the integrating sphere, but this intensity value was corrected by taking into account the relative intensity of the other transitions (as determined from the steady-state luminescence spectrum). In this way, an intensity value that corresponds to the total luminescence output was obtained. The absorption intensity was calculated by subtracting the integrated intensity of the light source (with the sample in the integrating sphere) from the integrated intensity of the light source (with a blank sample in the integrating sphere).

The blank sample was a quartz measuring cell, filled with the solvent (dichloromethane).

Crystallography. Yellow single crystals of [La(tta)$_3$**L**′$_2$] and [Nd-(bta)$_3$**L**′$_2$] were obtained by slow evaporation of a solution of the compounds in chloroform at 4 °C in a refrigerator. Yellow crystals of [La(tta)$_2$**L**′$_2$(tfa)] were obtained by slow evaporation of a solution of the compound in ethanol at 4 °C in a refrigerator. X-ray intensity data were collected on a SMART 6000 diffractometer equipped with CCD detector using Cu Kα radiation (λ = 1.54178 Å). The images were interpreted and integrated with the program SAINT from Bruker.[98]

[La(tta)$_3$**L**′$_2$]: C$_{97}$H$_{93}$Cl$_3$F$_{18}$La$_2$N$_4$O$_{20}$S$_6$, M = 2553.35, triclinic, $P\bar{1}$ (No. 2), a = 12.7129(12) Å, b = 19.784(3) Å, c = 22.611(2) Å, α = 103.268(6)°, β = 97.491(4)°, γ = 102.145(10)°, V = 5315.0(11) Å^3, T = 100(2) K, Z = 2, ρ_{calc} = 1.595 g cm^{-3}, μ(Cu Kα) = 8.792 mm^{-1}, $F(000)$ = 2572, crystal size 0.3 × 0.15 × 0.1 mm, 19426 independent reflections (R_{int} = 0.1302). Final R = 0.0752 for 12702 reflections with $I > 2\sigma(I)$ and ωR2 = 0.1900 for all data.

[Nd(bta)$_3$**L**′$_2$]: C$_{54}$H$_{52}$F$_9$N$_2$NdO$_{10}$, M = 1323.59, triclinic, $P\bar{1}$ (No. 2), a = 12.354(3) Å, b = 12.972(4) Å, c = 19.357(4) Å, α = 101.524(16)°, β = 93.225(15)°, γ = 108.121(16)°, V = 2865.3(13) Å^3, T = 100(2) K, Z = 2, ρ_{calc} = 1.534 g cm^{-3}, μ(Cu Kα) = 8.960 mm^{-1}, $F(000)$ = 1338, crystal size 0.3 × 0.25 × 0.15 mm, 7663 independent reflections (R_{int} = 0.1061). Final R = 0.0673 for 5460 reflections with $I > 2\sigma(I)$ and ωR2 = 0.1747 for all data.

[La(tta)$_2$**L**′$_2$(tfa)]: C$_{46}$H$_{46}$F$_9$LaN$_2$O$_{10}$, M = 1096.76, triclinic, $P\bar{1}$ (No. 2), a = 15.1196(11) Å, b = 18.5236(10) Å, c = 20.6386(12) Å, α = 70.890(3)°, β = 80.255(4)°, γ = 66.575(4)°, V = 5006.5(6) Å^3, T = 100(2) K, Z = 4, ρ_{calc} = 1.455 g cm^{-3}, μ(Cu Kα) = 7.377 mm^{-1}, $F(000)$ = 2216, crystal size 0.4 × 0.25 × 0.1 mm, 14108 independent reflections (R_{int} = 0.1000). Final R = 0.0627 for 9376 reflections with $I > 2\sigma(I)$ and ωR2 = 0.1684 for all data. Disordered solvent in voids of 109, 79, and 79 Å^3 at positions ($^1/_2$, 0, $^1/_2$), (0.061, 0.327, 0.711), and (−0.061, 0.673, 0.289), respectively, were modeled with SQUEEZE[99] (total contribution of 37 e$^-$).

All three structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.[100] Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). CCDC-273180 ([La(tta)$_3$**L**′$_2$]), CCDC-601963 ([La-(tta)$_2$**L**′$_2$(tfa)]), and CCDC-601964 ([Nd(bta)$_3$**L**′$_2$]) contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving-.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

Synthesis. The Schiff base ligand **L** and the [Ln(tta)$_3$(H$_2$O)$_2$] and [Ln(bta)$_3$(H$_2$O)$_2$] complexes were synthesized by following a literature procedure.[79] The synthesis of the europium(III) complex [Eu(tta)$_3$**L**$_2$] is described below, and all the other complexes were prepared by the same method. See Supporting Information for the analysis results.

Synthesis of [Eu(tta)$_3$L$_2$]. A solution of [Eu(tta)$_3$(H$_2$O)$_2$] (0.1 mmol, 0.085 g) in dry toluene was added dropwise to a solution of 2-hydroxy-*N*-octadecyl-4-tetradecyloxybenzaldimine (**L**) (0.2 mmol, 0.117 g) in dry toluene. The reaction mixture was stirred at 50 °C for 3 h. After the solution was allowed to cool to room temperature, the solvent was removed under reduced pressure and the product was dried in vacuo. The compound is obtained as a light yellow sticky solid with a red hue (due to photoluminescence) at room temperature. Yield: 0.198 g (99%). Elemental analysis: calcd (%) for C$_{102}$H$_{154}$EuN$_2$O$_{10}$F$_9$S$_3$ (1987.5): C, 61.64; H, 7.81; N, 1.41. Found: C, 61.60; H, 7.87; N, 1.29.

Conclusions

We optimized the design of liquid-crystalline Schiff base adducts lanthanide β-diketonate complexes. By a proper choice of the β-diketonate ligand (2-thenoyltrifluoroacetonate or benzoyltrifluoroacetonate instead of dibenzoylmethanate) the transition temperatures could be reduced and the mesophases could be stabilized. The materials exhibit a smectic A phase at temperatures close to room temperature. A major advantage of this type of lanthanide-containing metallomesogens is their intense luminescence output, both in the mesophase and in the vitrified mesophase.

Supporting Information Available: CHN analysis results for the lanthanide complexes; IR data of the tta complexes; NMR spectrum of [La(bta)$_3$**L**$_2$]; CIF files of the crystal structures; molecular structure of [Nd(bta)$_3$**L**′$_2$]; texture of [Eu(tta)$_3$**L**$_2$] in the smectic A phase. This material is available free of charge via the Internet at http://pubs.acs.org.

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