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# Liquid-Crystalline Ternary Rare-Earth Complexes

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The thermal behavior of the metallomesogens [Ln($C_{12}C_{16}$dbm)$_3$(phen)] (Ln = La, Nd, Eu, Gd, Tb, Dy, Er, Yb; $C_{12}C_{16}$dbm = 1-(4-dodecyloxyphenyl)-3-(4-hexadecyloxyphenyl)propane-1,3-dionate; phen = 1,10-phenanthroline) was investigated. The complexes of the light lanthanides (Ln = La, Nd) are not mesomorphic, whereas the complexes of the heavy lanthanides (Ln = Eu, Gd, Tb, Dy, Er, Yb) exhibit a monotropic smectic A phase (SmA). A model for the molecular organization of the molecules in the smectic A phase is proposed. The luminescence properties of the complexes [Eu($C_{12}C_{16}$dbm)$_3$(phen)], [Er($C_{12}C_{16}$dbm)$_3$(phen)], and [Yb($C_{12}C_{16}$dbm)$_3$(phen)] were investigated.

## Introduction

Most metal ions can form metal-containing liquid crystals (*metallomesogens*) after complex formation with suitable mesogenic ligands.[1–8] By incorporating a metal center into a liquid crystal, it is possible to obtain materials that combine the properties of liquid crystals with those of metal ions. It is very useful to choose d-block or f-block elements as the metallic centers in metallomesogens, because these metal ions often exhibit interesting properties like redox activity, paramagnetism, or photoluminescence. In the last decade, there has been considerable activity in the research field of lanthanide-containing liquid crystals (which are also called *lanthanidomesogens*).[2,9–11] Different types of ligands were used to design new classes of lanthanidomesogens: Schiff bases,[12–22] β-enamino ketones,[23] alkanoates,[24,25] 4-alkoxybenzoates,[26–28] phthalocyanines,[29,29–33] porphyrins,[34,35] imidazo[4,5-*f*][1,10]phenanthrolines,[36] β-diketonates,[37] crown ethers,[38–40] 2,6-bis(benzimidazol-2′-yl)pyridines,[11,41,42] and polyoxometalate-surfactant complexes.[43] Most examples of lanthanidomesogens are thermotropic liquid crystals, although some examples of lyotropic lanthanidomesogens have also been reported.[43–46] The rationale for the research interest in lanthanidomesogens is that, by incorporation of rare-earth ions in liquid crystals, it is possible to obtain magnetic[13,47,48] or luminescent liquid crystals.[49,50]

Although in some classes of lanthanidomesogens (like phthalocyanines[29] and imidazo[4,5-*f*][1,10]phenanthrolines[36]) the size of the lanthanide(III) ion has only limited or no effect on the transition temperatures, in many cases the lanthanide contraction has a very strong influence on the mesophase behavior. This was first illustrated by mesomorphic Schiff base complexes, where the temperature range over which the mesophase exists strongly decreases when going from lanthanum(III) to lutetium(III).[51] An even more dramatic temperature dependence is observed for the lanthanide(III) alkanoates, where a mesophase is often present for only the light lanthanides.[24] In all these examples, the lanthanide contraction results in a reduction of the mesophase stability over the lanthanide series. However, Piguet and co-workers have shown that the lanthanide contraction can also cause changes in the mesophase type.[41,42]

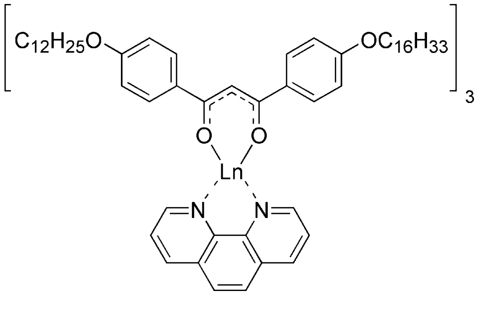

Figure 1. Structure of the lanthanide(III) β-diketonate complexes [Ln($C_{12}C_{16}$dbm)$_3$(phen)], where Ln = La, Nd, Eu, Gd, Tb, Dy, Er, Yb, and phen = 1,10-phenanthroline.

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In this paper, we present the mesophase behavior of new lanthanidomesogens of the type [Ln($C_{12}C_{16}$dbm)$_3$(phen)], where Ln = La, Nd, Eu, Gd, Tb, Dy, Er, Yb; $C_{12}C_{16}$dbm = 1-(4-dodecyloxyphenyl)-3-(4-hexadecyloxyphenyl)propane-1,3-dionate; phen = 1,10-phenanthroline (Figure 1).

## Results and Discussion

The β-diketone ligand 1-(4-dodecyloxyphenyl)-3-(4-hexadecyloxyphenyl)propane-1,3-dione is not liquid-crystalline and melts directly to give an isotropic liquid at 86 °C. The thermal behavior of the lanthanide(III) complexes is summarized in Table 1 and in the phase diagram shown in Figure 2. The melting point of the lanthanide(III) complexes does not depend much on the size of the lanthanide(III) ion, but a slight decrease of the melting point over the lanthanide series was observed. The lanthanum(III) and the neodymium(III) complexes are not liquid-crystalline. The europium(III), gadolinium(III), terbium(III), dysprosium(III), erbium(III), and ytterbium(III) complexes also melt directly to give isotropic liquids, but a monotropic mesophase can be observed upon cooling. On further cooling, the lanthanide(III) complexes do not crystallize but form a glass. The mesophase was identified as a smectic A phase by hot-stage polarizing optical microscopy. Upon cooling from the isotropic melt, typical bâtonnets are formed (Figure 3). These bâtonnets coalesce to give rise to a focal conic-like texture in which large pseudo-isotropic domains occur due to homeotropic alignment of the molecules in these domains (Figure 4). The clearing points of the lanthanide(III) complexes (Table 1, determined by reheating the monotropic smectic A phase) are virtually not dependent on the size of the lanthanide(III) ion. However, crystallization of the monotropic mesophase occurs much faster for the light lanthanides. Therefore, the mesophases of the europium(III) and gadolinium(III) complexes can only be observed by polarizing optical microscopy on fast cooling of the sample. For the same reason, it is impossible to determine accurately the clearing points of the europium(III) and gadolinium(III) complexes. The melting points and corresponding enthalpy and entropy changes for all the lanthanide(III) complexes could be determined by differential scanning calorimetry (DSC). Only for the erbium(III) and ytterbium(III) complexes also the clearing temperatures and corresponding enthalpy and entropy values could be obtained by DSC. The SmA phase of the lanthanide(III) complexes is metastable and can only be observed by supercooling the isotropic liquid to a temperature below the melting point of the crystal phase (i.e. the mesophase is monotropic).[52] The temperature difference between the melting point of the crystal phase and the clearing point of the monotropic mesophase decreases over the lanthanide series. Therefore, it is easier to obtain the mesophases of the heavy lanthanide(III) complexes and fast cooling rates are required to obtain the mesophases of the light lanthanide(III) complexes. The larger the temperature difference between the melting point of the crystal phase and the clearing point of the monotropic mesophase, the stronger is the crystallization tendency. This is also evident from the larger melting enthalpy values observed for the light lanthanide(III) complexes.

Table 1. Phase behavior, transition temperatures, transition enthalpies and melting entropies of the [Ln($C_{12}C_{16}$dbm)$_3$(phen)] complexes.

| Ln | Transition[a] | Temp. [°C] | $\Delta H$ [kJ mol$^{-1}$] | $\Delta S$ [J mol$^{-1}$ K$^{-1}$] |
|---|---|---|---|---|
| La | Cr → I | 145 | 28.7 | 67.9 |
| Nd | Cr → I | 146 | 37.8 | 90.3 |
| Eu | Cr → I[b] | 135 | 30.6 | 75.0 |
| Gd | Cr → I[b] | 136 | 26.0 | 63.5 |
| Tb | Cr → I | 129 | 16.4 | 40.1 |
| | I → SmA | 110 | –[c] | –[c] |
| Dy | Cr → I | 130 | 14.8 | 36.8 |
| | I → SmA | 114 | –[c] | –[c] |
| Er | Cr → I | 128 | 17.0 | 42.4 |
| | I → SmA | 114 | 1.1 | 2.9 |
| Yb | Cr → I | 121 | 14.9 | 37.8 |
| | I → SmA | 116 | 1.6 | 4.2 |

[a] Cr = crystalline phase; SmA = smectic A phase; I = isotropic liquid. [b] For the europium(III) and the gadolinium(III) complex, a metastable monotropic smectic A phase could be observed upon very fast cooling of the isotropic liquid. However, accurate transition temperatures could not be determined. [c] The $\Delta H$ and $\Delta S$ values of the I → SmA transition of the terbium(III) and dysprosium(III) complexes could not be detected by DSC.

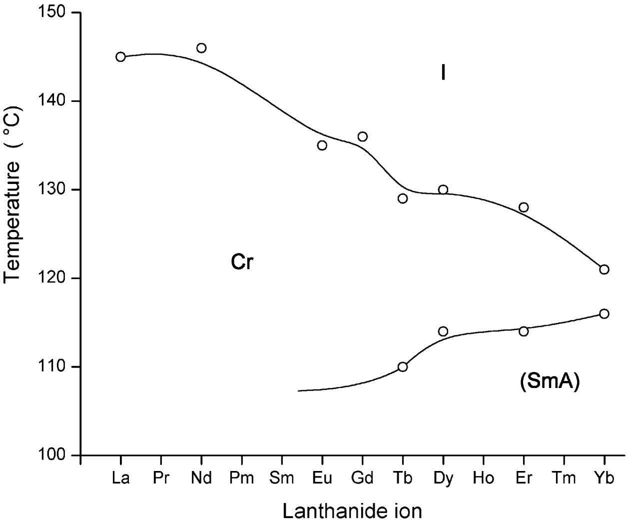

Figure 2. Phase diagram of the lanthanide(III) β-diketonate complexes [Ln($C_{12}C_{16}$dbm)$_3$(phen)], where Ln = La, Nd, Eu, Gd, Tb, Dy, Er, Yb, and phen = 1,10-phenanthroline. Abbreviations: Cr = crystalline phase; (SmA) = monotropic smectic A phase; I = isotropic liquid.

The mesophase of [Yb($C_{12}C_{16}$dbm)$_3$(phen)] was further investigated by small-angle X-ray scattering (SAXS). The sample was first heated to the isotropic liquid (150 °C) for 5 min, after which it was cooled to 120 °C for the first measurement. Then, the sample was cooled further to the smectic A phase (100 °C) for the second measurement. The pattern at 120 °C exhibits a single broad peak with a maximum at $s = 0.033$ Å$^{-1}$ (Figure 5). There are no higher-order maxima, pointing at a highly disordered morphology, which

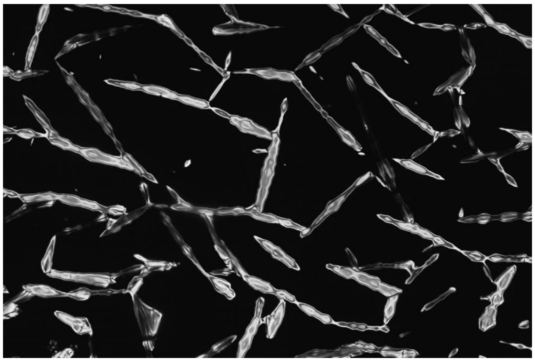

Figure 3. Formation of bâtonnets on cooling the isotropic melt of [Yb($C_{12}C_{16}$dbm)$_3$(phen)] at 113 °C (200 × magnification).

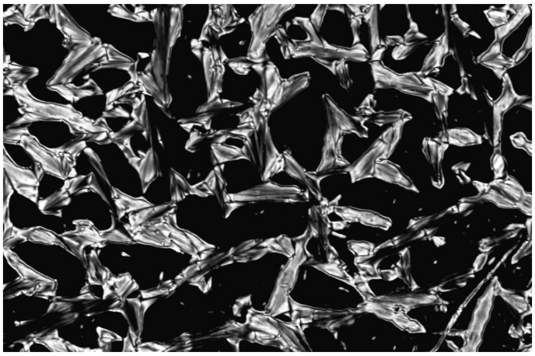

Figure 4. Focal conic-like texture of the monotropic smectic A phase of [Yb($C_{12}C_{16}$dbm)$_3$(phen)] at 108 °C, obtained upon cooling (500× magnification).

is typical for the isotropic liquid. On cooling from the isotropic liquid, the pattern at 100 °C displays a clear sharp maximum at $s$ = 0.03 Å$^{-1}$ and a weak corresponding second-order reflection at $s$ = 0.06 Å$^{-1}$ (Figure 5), characteristic of a layer-like (lamellar) structure with a periodicity of 33.3 Å (= $d_{001}$). The molecular organization within the smectic A layers can be described using the measured periodicities and the calculated molecular volume. The molecular volume can be estimated using the relation $V_M = (M/0.6022)f$ = 4028 Å$^3$, where $M$ is the molecular mass (2297.21 g mol$^{-1}$) and $f$ a temperature-correction factor ($f = 0.9813 + 7.474{\cdot}10^{-4}\,T = 1.056$ at 100 °C).[53] The density in the virtual mesophase is assumed to be close to 1 g cm$^{-3}$ at 25 °C. Using the molecular volume and the first-order reflection, the molecular area was calculated as $A_M = V_M/d_{001}$ = 121 Å$^2$. We propose a microsegregation of the compatible parts in such a way that two types of sublayers are formed: a sublayer of the molten aliphatic chains and a sublayer of the coordinated ytterbium(III) ions (Figure 6). If we assume that three of the six chains are pointing in one direction and the other three chains are pointing in the opposite direction (which is much more likely than six chains pointing in the same direction), a cross-sectional area per aliphatic chain $A_{ch} = A_M/3 \approx 40$ Å$^2$ is deduced. This value is much larger than the cross-sectional area of a stretched molten aliphatic chain ($A_{ch} \approx 22.5$ Å$^2$ at 100 °C)[54] and suggests that the molten aliphatic chains are interdigitating. In addition, the layer thickness $d_{001}$ (33.3 Å) is much smaller than the calculated length of the molecule ($L \approx 48$ Å) and is in good agreement with a lamellar structure with interdigitation of the molten aliphatic chains.

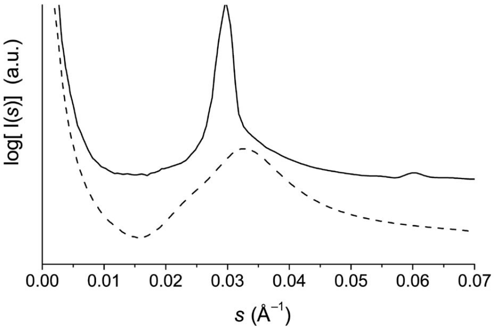

Figure 5. Desmeared SAXS intensities (on a logarithmic scale): sample at 120 °C (dashed line) and sample at 100 °C (full line). The pattern at 100 °C was shifted upwards for clarity.

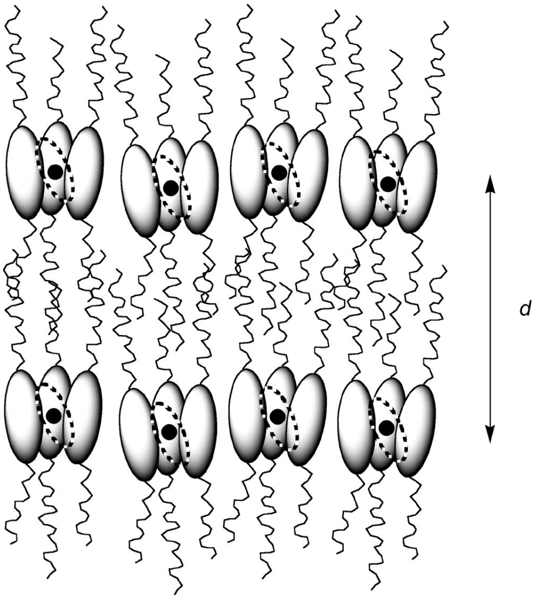

Figure 6. Model for the molecular organization of [Yb($C_{12}C_{16}$dbm)$_3$-(phen)] in the smectic A layers. The shaded ellipses represent the alkoxy-substituted β-diketonates, the dashed ellipses represent the 1,10-phenanthroline heterocycles and the spheres represent the ytterbium(III) ions.

The [Ln($C_{12}C_{16}$dbm)$_3$(phen)] complexes reported in this paper are among the rare examples of tris(β-diketonato) complexes that exhibit smectic mesomorphism. In 1982, Giroud-Godquin and Rassat investigated the tris[1,3-bis(4-dodecylphenyl)propane-1,3-dionato]iron(III) complex.[55,56] They observed a highly viscous mesophase, which was not further characterized. Swager and co-workers prepared related compounds,[57] including the dodecyloxy analog of the iron(III) complex reported by Giroud-Godquin and Rassat. X-ray diffraction showed that this compound with six alkoxy chains exhibited an unidentified smectic phase (SmX phase). An increase of the number of alkoxy chains on the β-diketonate ligands leads to columnar phases.[57,58] Also for tetrakis(β-diketonato) complexes, columnar mesophases were observed.[59] The thermal behavior of [$Eu(C_{12}C_{16}dbm)_3(phen)$] and [$Tb(C_{12}C_{16}dbm)_3(phen)$] is comparable with the thermal behavior of the previously reported complexes [$Eu(C_{14}C_{14}dbm)_3(phen)$] and [$Tb(C_{14}C_{14}dbm)_3(phen)$], which have symmetrically substituted dibenzoylmethanate ligands.[37] In both cases, the complexes show a monotropic smectic A phase. However, the transition temperatures of the unsymmetrically substituted complexes presented in this paper are lower.

The luminescence spectra of the europium(III), erbium(III), and ytterbium(III) complexes were recorded in the solid state. The europium(III) ion is known for its strong red photoluminescence, whereas erbium(III) and ytterbium(III) are good infrared emitters. The emission spectrum of [$Eu(C_{12}C_{16}dbm)_3(phen)$] is shown in Figure 7. The europium(III) compound showed a strong red photoluminescence upon irradiation with ultraviolet light. The luminescence spectra were measured upon excitation at 380 nm. 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 7). 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 lower). This is evident from the observation of three crystal-field components for the $^7F_1$ level at 588, 592, and 598 nm. The sharp $^5D_0 \rightarrow {}^7F_0$ line (579.5 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.[60–63] The most intense line is the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ around 611 nm. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is 12.2 (integration calculated in nm or in $cm^{-1}$ with $\lambda^2$ correction). Values larger than 10 are typical for europium(III) β-diketonate complexes.[64] The observed luminescence lifetime was determined from measurement of the luminescence decay curve and was found to be 0.53 ms at room temperature. This value is comparable with that of other europium(III) β-diketonate complexes.[64] For instance, a value of 0.46 ms was reported for [$Eu(dbm)_3(phen)$] by Bünzli and coworkers.[65] The decay curve was a single exponential curve. This supports the fact that only one type of europium(III) site is present. Only one line could be observed in the luminescence spectrum of the erbium(III) compound [$Er(C_{12}C_{16}dbm)_3(phen)$]: the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ line at 1530 nm in the near-infrared part of the spectrum (Figure 8). The emission spectrum of [$Yb(C_{12}C_{16}dbm)_3(phen)$] consists of several intense lines at 970 nm, corresponding to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition (Figure 9). The luminescence decay time of the $^2F_{5/2}$ level was found to be 10 μs.

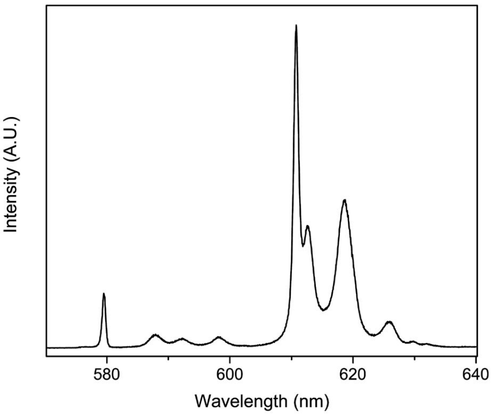

Figure 7. Room-temperature luminescence spectrum of [$Eu(C_{12}C_{16}dbm)_3(phen)$] in the solid state (the excitation wavelength was 380 nm). All transitions originate from the $^5D_0$ level.

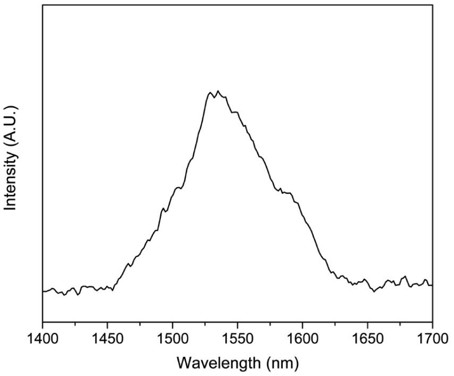

Figure 8. Room-temperature luminescence spectrum of [$Er(C_{12}C_{16}dbm)_3(phen)$] in the solid state (the excitation wavelength was 380 nm), showing the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ line.

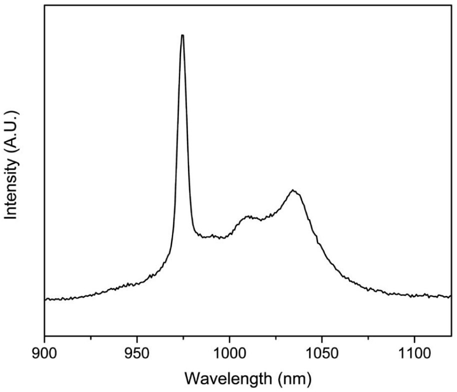

Figure 9. Room-temperature luminescence spectrum of [$Yb(C_{12}C_{16}dbm)_3(phen)$] in the solid state (the excitation wavelength was 380 nm), showing the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ line.

## Conclusions

In this paper, one of the few examples of liquid-crystalline lanthanide(III) β-diketonate complexes are presented.[37] In most of the earlier examples, the mesomorphism was not induced by the β-diketonate ligand, but rather by a mesogenic Schiff base ligand.[14,22,66] No liquid-crystal phases are observed for the complexes of the light lanthanides (Ln = La, Nd), whereas the complexes of the heavy lanthanides exhibit a monotropic smectic A phase. In the smectic A phase, the complexes are arranged in layers with interdigitation of the molten aliphatic chains. The modification of the dibenzoylmethanate ligand by addition of long alkyl chains to obtain liquid-crystal phases has no influence on the excellent luminescent properties of these materials. As luminescent materials, these lanthanide(III) β-diketonate complexes offer an alternative to the luminescent liquid crystals that are obtained by doping luminescent non-mesomorphic lanthanide(III) β-diketonate complexes in a liquid-crystalline host matrix.[67–70]

## Experimental Section

**General:** CHN elemental microanalyses were performed with a CE Instruments EA-1110 elemental analyzer. $^1$H NMR spectra were recorded with a Bruker Avance 300 spectrometer (operating at 300 MHz). Differential scanning calorimetry measurements were recorded with a Mettler-Toledo DSC 822e module. Optical textures of the mesophase were observed with an Olympus BX60 polarizing optical microscope equipped with a Linkam THMS 600 hot-stage and a Linkam TMS 93 programmable temperature controller. Photoluminescence spectra in the visible region were recorded with an Edinburgh Instruments FS900 spectrofluorimeter. This instrument was equipped with a 450 W xenon arc lamp, a microsecond flash lamp, and a red-sensitive photomultiplier (300–850 nm). The luminescence spectra in the infrared region were measured with an Edinburgh Instruments FS920P near-infrared spectrometer. The excitation source was a 450 W xenon lamp connected to a double-excitation monochromator. A liquid-nitrogen-cooled near-infrared photomultiplier tube was used for the detection. All photoluminescence spectra were recorded at room temperature and excited at 380 nm. A YAG:Nd laser operating at 355 nm was used to measure lifetimes. The photoluminescence spectra were corrected for the sensitivity of the detector at the different wavelengths. Small-angle X-ray scattering patterns were recorded with a Rigaku Kratky camera on a Rigaku Rotaflex RU-200B rotating Cu anode at a power of 4 kW. Cu-$K_\alpha$ radiation ($\lambda$ = 1.54 Å) was obtained by filtering with nickel foil and data were collected with a Braun linear position sensitive detector. The scattering angles, $2\theta$, are expressed as a function of $s$, the modulus of the scattering vector, which is defined as $s = 2\lambda^{-1}\sin\theta$ and scattered intensities were recorded over the $s$-range 0.002–0.07 Å$^{-1}$. The slit smeared scattering patterns were desmeared by the Guinier–Dumond procedure[71] as implemented in "TOPAS" software developed by Dr. N. Stribeck at the University of Hamburg (Germany). Desmeared intensities will be referred to as $I$ ($s$). Samples were measured in 1 mm glass capillaries for 1 h at respectively 120 °C and 100 °C, thereby allowing 5 min for temperature equilibration prior to each measurement. A home-made heating device controlled the temperature.

**Synthetic Procedures:** The β-diketone ligand 1-(4-dodecyloxyphenyl)-3-(4-hexadecyloxyphenyl)propane-1,3-dione (abbreviated to HC$_{12}$C$_{16}$dbm) was synthesized according to a modified literature method by a Claisen condensation reaction between the ethyl ester of 4-hexadecyloxybenzoic acid and 4-dodecyloxyacetophenone, with sodium hydride as the base.[72] M.p. 86 °C. MS: $m/z$ = 649 [M$^+$]. $C_{43}H_{68}O_4$ (649.00): calcd. C 79.58, H 10.56; found C 79.39, H 10.69. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.84–0.94 (m, 6 H, CH$_3$), 1.17–1.39 (m, 44 H, CH$_2$), 1.74–1.87 (m, 4 H, $\mathrm{C}H_2\mathrm{CH_2O}$), 4.03 (t, 4 H, CH$_2$O), 4.52 (s, 0.4 H, keto =CH$_2$), 6.73 (s, 0.8 H, enol =CH), 6.95 (d, 4 H, $J_o$ = 8.3 Hz), 7.95 (d, 4 H, $J_o$ = 8.3 Hz), 17.00 (s, 0.8 H, enol OH; keto:enol = 1:4) ppm. The [Ln(C$_{12}$C$_{16}$dbm)(phen)] complexes (Ln = La, Nd, Eu, Gd, Tb, Dy, Er, Yb) were synthesized according to a modified literature method.[73] All metal complexes were prepared by mixing the β-diketone HC$_{12}$C$_{16}$dbm (3 equiv.), sodium hydroxide (3 equiv.), and 1,10-phenanthroline (1 equiv.) in absolute ethanol at 70–75 °C, followed by a dropwise addition of an ethanolic solution of the lanthanide(III) chloride salt. The precipitate was filtered off, washed with hot absolute ethanol, and dried in vacuo. The yields varied between 70 and 80%. The purity of the compounds was verified by CHN elemental analysis (see electronic supporting information). All compounds are colored in different shades of yellow, except for the neodymium(III) complex, which has a green color.

**Supporting Information** (see also the footnote on the first page of this article): Yields and CHN analysis data of the lanthanide(III) complexes.

## Acknowledgments

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[1] J. L. Serrano (Ed.), *Metallomesogens, Synthesis Properties and Applications*, VCH, Weinheim, Germany, **1996**.

[2] K. Binnemans, C. Görller-Walrand, *Chem. Rev.* **2002**, *102*, 2303–2345.

[3] D. W. Bruce in *Inorganic Materials* (Eds.: D. W. Bruce, D. O'Hare), Wiley, Chichester, United Kingdom, **1996**, pp. 429–522.

[4] B. Donnio, D. Guillon, R. Deschenaux, D. W. Bruce in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Oxford, United Kingdom, **2003**, pp. 357–627.

[5] B. Donnio, D. W. Bruce, *Struct. Bonding (Berlin)* **1999**, *95*, 193–247.

[6] P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano, E. Sola, *Coord. Chem. Rev.* **1992**, *117*, 215–274.

[7] A. M. Giroud-Godquin, P. M. Maitlis, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 375–402.

[8] S. A. Hudson, P. M. Maitlis, *Chem. Rev.* **1993**, *93*, 861–885.

[9] K. Binnemans, D. W. Bruce, S. R. Collinson, R. Van Deun, Y. G. Galyametdinov, F. Martin, *Philos. Trans. R. Soc. London, Ser. A* **1999**, *357*, 3063–3077.

[10] C. Piguet, J. C. G. Bünzli, B. Donnio, D. Guillon, *Chem. Commun.* **2006**, 3755–3768.

[11] E. Terazzi, S. Suarez, S. Torelli, H. Nozary, D. Imbert, O. Mamula, J. P. Rivera, E. Guillet, J. M. Benech, G. Bernardinelli, R. Scopelliti, B. Donnio, D. Guillon, J. C. G. Bünzli, C. Piguet, *Adv. Funct. Mater.* **2006**, *16*, 157–168.

[12] K. Binnemans, Y. G. Galyametdinov, S. R. Collinson, D. W. Bruce, *J. Mater. Chem.* **1998**, *8*, 1551–1553.

[13] K. Binnemans, Y. G. Galyametdinov, R. Van Deun, D. W. Bruce, S. R. Collinson, A. P. Polishchuk, I. Bikchantaev, W. Haase, A. V. Prosvirin, L. Tinchurina, I. Litvinov, A. Gubajdullin, A. Rakhmatullin, K. Uytterhoeven, L. Van Meervelt, *J. Am. Chem. Soc.* **2000**, *122*, 4335–4344.

[14] K. Binnemans, K. Lodewyckx, *Angew. Chem. Int. Ed.* **2001**, *40*, 242–244.

[15] K. Binnemans, K. Lodewyckx, B. Donnio, D. Guillon, *Chem. Eur. J.* **2002**, *8*, 1101–1105.
[16] K. Binnemans, K. Lodewyckx, T. Cardinaels, T. N. Parac-Vogt, C. Bourgogne, D. Guillon, B. Donnio, *Eur. J. Inorg. Chem.* **2006**, 150–157.
[17] Y. G. Galyametdinov, M. A. Athanassopoulou, K. Griesar, O. Kharitonova, E. A. S. Bustamante, L. Tinchurina, I. V. Ovchinnikov, W. Haase, *Chem. Mater.* **1996**, *8*, 922–926.
[18] Y. G. Galyametdinov, G. I. Ivanova, I. V. Ovchinnikov, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1991**, *40*, 1109.
[19] Y. G. Galyametdinov, G. I. Ivanova, I. V. Ovchinnikov, K. Binnemans, D. W. Bruce, *Russ. Chem. Bull.* **1999**, *48*, 385–387.
[20] M. Marcos, A. Omenat, J. Barbera, F. Duran, J. L. Serrano, *J. Mater. Chem.* **2004**, *14*, 3321–3327.
[21] R. Van Deun, K. Binnemans, *Liq. Cryst.* **2001**, *28*, 621–627.
[22] Y. T. Yang, K. Driesen, P. Nockemann, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Chem. Mater.* **2006**, *18*, 3698–3704.
[23] I. Bikchantaev, Y. G. Galyametdinov, O. Kharitonova, I. V. Ovchinnikov, D. W. Bruce, D. A. Dunmur, D. Guillon, B. Heinrich, *Liq. Cryst.* **1996**, *20*, 489–492.
[24] K. Binnemans, L. Jongen, C. Görller-Walrand, W. D'Olieslager, D. Hinz, G. Meyer, *Eur. J. Inorg. Chem.* **2000**, 1429–1436.
[25] L. Jongen, D. Hinz, G. Meyer, K. Binnemans, *Chem. Mater.* **2001**, *13*, 2243–2246.
[26] L. Jongen, B. Goderis, I. Dolbnya, K. Binnemans, *Chem. Mater.* **2003**, *15*, 212–217.
[27] L. Jongen, B. Goderis, I. P. Dolbnya, K. Binnemans, *J. Rare Earths* **2004**, *22*, 193–196.
[28] M. K. Singh, B. Singh, R. Dhar, V. K. Agrawal, *Phase Transitions* **2005**, *78*, 495–506.
[29] K. Binnemans, J. Sleven, S. De Feyter, F. C. De Schryver, B. Donnio, D. Guillon, *Chem. Mater.* **2003**, *15*, 3930–3938.
[30] A. G. Gurek, T. Basova, D. Luneau, C. Lebrun, E. Kol'tsov, A. K. Hassan, V. Ahsen, *Inorg. Chem.* **2006**, *45*, 1667–1676.
[31] F. Maeda, K. Hatsusaka, K. Ohta, M. Kimura, *J. Mater. Chem.* **2003**, *13*, 243–251.
[32] C. Piechocki, J. Simon, J. J. Andre, D. Guillon, P. Petit, A. Skoulios, P. Weber, *Chem. Phys. Lett.* **1985**, *122*, 124–128.
[33] J. Sleven, C. Görller-Walrand, K. Binnemans, *Mater. Sci. Eng., C* **2001**, *18*, 229–238.
[34] J. Z. Li, H. Xin, M. Li, *Liq. Cryst.* **2006**, *33*, 913–919.
[35] H. Miwa, N. Kobayashi, K. Z. Ban, K. Ohta, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2719–2728.
[36] T. Cardinaels, K. Driesen, T. N. Parac-Vogt, B. Heinrich, C. Bourgogne, D. Guillon, B. Donnio, K. Binnemans, *Chem. Mater.* **2005**, *17*, 6589–6598.
[37] Y. G. Galyametdinov, L. V. Malykhina, W. Haase, K. Driesen, K. Binnemans, *Liq. Cryst.* **2002**, *29*, 1581–1584.
[38] K. Binnemans, B. Gundogan, *J. Rare Earths* **2002**, *20*, 249–255.
[39] S. Suarez, O. Mamula, D. Imbert, C. Piguet, J. C. G. Bünzli, *Chem. Commun.* **2003**, 1226–1227.
[40] S. Suarez, O. Mamula, R. Scopelliti, B. Donnio, D. Guillon, E. Terazzi, C. Piguet, J. C. G. Bünzli, *New J. Chem.* **2005**, *29*, 1323–1334.
[41] E. Terazzi, J. M. Benech, J. P. Rivera, G. Bernardinelli, B. Donnio, D. Guillon, C. Piguet, *Dalton Trans.* **2003**, 769–772.
[42] E. Terazzi, S. Torelli, G. Bernardinelli, J. P. Rivera, J. M. Benech, C. Bourgogne, B. Donnio, D. Guillon, D. Imbert, J. C. G. Bünzli, A. Pinto, D. Jeannerat, C. Piguet, *J. Am. Chem. Soc.* **2005**, *127*, 888–903.
[43] T. R. Zhang, C. Spitz, M. Antonietti, C. F. J. Faul, *Chem. Eur. J.* **2005**, *11*, 1001–1009.
[44] Y. G. Galyametdinov, H. B. Jervis, D. W. Bruce, K. Binnemans, *Liq. Cryst.* **2001**, *28*, 1877–1879.
[45] L. Jongen, K. Binnemans, *J. Rare Earths* **2003**, *21*, 101–104.
[46] N. M. Selivanova, V. S. Lobkov, V. P. Barabanov, K. M. Salikhov, W. Haase, Y. G. Galyametdinov, *Dokl. Chem.* **2005**, *401*, 51–54.
[47] K. Binnemans, R. Van Deun, C. Görller-Walrand, W. Haase, D. W. Bruce, L. V. Malykhina, Y. G. Galyametdinov, *Mater. Sci. Eng., C* **2001**, *18*, 247–254.
[48] V. S. Mironov, Y. G. Galyametdinov, A. Ceulemans, K. Binnemans, *J. Chem. Phys.* **2000**, *113*, 10293–10303.
[49] J. C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048–1077.
[50] S. Suarez, D. Imbert, F. Gumy, C. Piguet, J. C. G. Bünzli, *Chem. Mater.* **2004**, *16*, 3257–3266.
[51] K. Binnemans, R. Van Deun, D. W. Bruce, Y. G. Galyametdinov, *Chem. Phys. Lett.* **1999**, *300*, 509–514.
[52] D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill (Eds.), *Handbook of Liquid Crystals*, Wiley-VCH, Weinheim, **1998**.
[53] D. Felder-Flesch, L. Rupnicki, C. Bourgogne, B. Donnio, D. Guillon, *J. Mater. Chem.* **2006**, *16*, 304–309.
[54] M. Marcos, R. Gimenez, J. L. Serrano, B. Donnio, B. Heinrich, D. Guillon, *Chem. Eur. J.* **2001**, *7*, 1006–1013.
[55] A. M. Giroud-Godquin, *Coord. Chem. Rev.* **1998**, *180*, 1485–1499.
[56] A. M. Giroud-Godquin, A. Rassat, *C. R. Acad. Sci. Paris Ser. II* **1982**, *294*, 241–243.
[57] H. X. Zheng, T. M. Swager, *J. Am. Chem. Soc.* **1994**, *116*, 761–762.
[58] T. M. Swager, H. X. Zheng, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1995**, *260*, 301–306.
[59] S. T. Trzaska, H. X. Zheng, T. M. Swager, *Chem. Mater.* **1999**, *11*, 130–134.
[60] K. Binnemans, *Bull. Soc. Chim. Belg.* **1996**, *105*, 793–798.
[61] K. Binnemans, C. Görller-Walrand, *J. Rare Earths* **1996**, *14*, 173–180.
[62] J. C. G. Bünzli in *Lanthanide Probes in Life, Chemical and Earth Sciences: Theory and Practice* (Eds.: J. C. G. Bünzli, G. R. Choppin), Elsevier, Amsterdam, **1989**, pp. 219–293.
[63] C. Görller-Walrand, K. Binnemans in *Handbook on the Physics and Chemistry of Rare Earths* (Eds.: K. A. Gschneidner, L. Eyring), Elsevier, Amsterdam, **1996**, pp. 121–283.
[64] K. Binnemans in *Handbook on the Physics and Chemistry of Rare Earths* (Eds.: K. A. Gschneidner, J. C. G. Bünzli, V. K. Pecharsky), Elsevier, Amsterdam, The Netherlands, **2005**, pp. 107–272.
[65] J. C. G. Bünzli, E. Moret, V. Foiret, K. J. Schenk, M. Z. Wang, L. P. Jin, *J. Alloys Compd.* **1994**, *207*, 107–111.
[66] K. Binnemans, K. Lodewyckx, T. N. Parac-Vogt, R. Van Deun, B. Goderis, B. Tinant, K. Van Hecke, L. Van Meervelt, *Eur. J. Inorg. Chem.* **2003**, 3028–3033.
[67] K. Binnemans, D. Moors, *J. Mater. Chem.* **2002**, *12*, 3374–3376.
[68] J. Boyaval, F. Hapiot, C. Li, N. Isaert, M. Warenghem, P. Carette, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1999**, *330*, 1387–1394.
[69] L. N. Puntus, K. J. Schenk, J. C. G. Bünzli, *Eur. J. Inorg. Chem.* **2005**, 4739–4744.
[70] R. Van Deun, D. Moors, B. De Fré, K. Binnemans, *J. Mater. Chem.* **2003**, *13*, 1520–1522.
[71] J. W. M. DuMond, *Phys. Rev.* **1947**, *72*, 276–283.
[72] K. Ohta, H. Muroki, K. I. Hatada, I. Yamamoto, K. Matsuzaki, *Mol. Cryst. Liq. Cryst.* **1985**, *130*, 249–263.
[73] A. A. Knyazev, V. S. Lobkov, Y. G. Galyametdinov, *Russ. Chem. Bull.* **2004**, *53*, 942–943.

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