

ARTICLES

Polarized Luminescence of Non-mesogenic Europium(III) Complexes Doped into a Nematic Liquid Crystal**Kris Driesen, Caroline Vaes, Thomas Cardinaels, Karel Goossens, Christiane Görller-Walrand, and Koen Binnemans****Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. Box 2404, B-3001 Leuven, Belgium**Received: February 7, 2009; Revised Manuscript Received: June 9, 2009*

The luminescence spectra of europium(III) complexes dissolved in the liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB) were investigated. Upon alignment of the europium(III)-doped nematic liquid-crystal host in a liquid-crystal cell with alignment layers, polarization effects were observed in the emission spectra. These polarization effects were visible as differences in the relative intensities of the crystal-field components of the transitions. Although the europium(III) complexes do not need to be liquid-crystalline themselves, some structural anisotropy is required for good alignment in the liquid crystal host and for the generation of linearly polarized light.

Introduction

Although linearly polarized absorption spectra of lanthanide ions in single-crystal host matrices have often been used for the assignment of symmetry labels to crystal-field transitions, only a relatively limited number of linearly polarized emission spectra for lanthanide ions in single-crystal host matrices have been reported.¹ The emitted light originating from transitions between crystal-field levels of trivalent lanthanide ions embedded in a noncubic single-crystal host matrix is linearly polarized, and the polarization directions of the emission lines depend on the selection rules for the symmetry point group of the lanthanide site.² The polarization characteristics of the emission lines are useful in lanthanide spectroscopy for the assignment of symmetry labels to the different crystal-field levels. Emission of linearly polarized light has also been observed for lanthanide complexes embedded in less ordered anisotropic media than single crystals.³ For instance, polarized emission was detected for europium(III) β -diketonate complexes embedded in stretched polyethylene films.^{3a,b} Whereas polarized lanthanide luminescence in single crystals is of academic interest only, it has been proposed that polarized emission from oriented molecular materials can find applications in new types of emissive displays.⁴ Very recently, polarized luminescence was observed for a vitrified mesophase of a liquid-crystalline europium(III) complex and for this europium(III) complex dissolved in a nematic liquid-crystal mixture.⁵ Because polarized emission from lanthanide-doped liquid-crystal mixtures was first observed for a mesogenic lanthanide complex dissolved in a liquid-crystal host matrix, the question arises whether the lanthanide complex needs to be a liquid crystal itself to enable the generation of polarized luminescence or whether the presence of an aligned anisotropic solvent is a sufficient condition. Earlier studies of luminescent lanthanide complexes

doped into liquid-crystal solvents⁶ and of luminescent lanthanidomesogens⁷ have not considered possible polarization effects for the emission lines. Moreover, no polarized emission is expected from the randomly oriented liquid-crystal domains in unaligned samples. In this paper, we discuss the possibility to observe polarized luminescence from europium(III) complexes doped into a nematic liquid-crystal host and aligned in a liquid-crystal cell (LC cell).

Experimental Section

CHN elemental microanalyses were performed on a CE Instruments EA-1110 elemental analyzer. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz). Photoluminescence spectra in the visible region have been recorded on an Edinburgh Instruments FS900 spectrofluorimeter. This instrument was equipped with a 450 W xenon arc lamp and a red-sensitive photomultiplier (300–820 nm). The photoluminescence spectra were corrected for the wavelength-dependent sensitivity of the detector. 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 luminescence could be measured in transmission mode. The home-built sample holder containing the LC cells was temperature-controlled. A polarizer was placed between the sample and the emission monochromator. The polarization direction was chosen to be parallel (para) or orthogonal (ortho) to the alignment layer in the homogeneous (HG, planar) LC cell. All spectra were normalized for the transition at 612 nm. LC cells with an alignment layer for planar alignment (HG cells) or for homeotropic alignment (HT cells) were purchased from AWAT PPW (ul. Kaliskiego 9, 01-476 Warsaw, Poland). LC cells with different cell gaps were used (1.5, 3, 5, 20, and 50 μ m), but most experiments were performed with the 5 μ m cells. The europium(III)-doped liquid-crystal mixtures were prepared by dissolving about 5 mg of the

* To whom correspondence should be addressed: E-mail: koen.binnemans@chem.kuleuven.be. Fax: +32 16 32 7992.

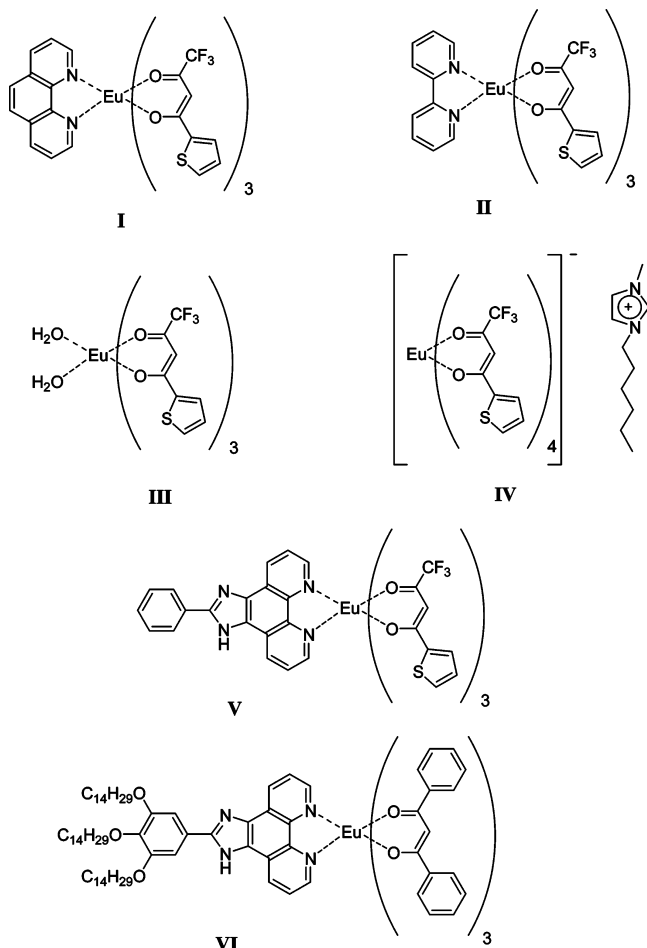


Figure 1. Structure of the europium(III) complexes. [Eu(tta)₃(phen)] (I), [Eu(tta)₃(bipy)] (II), [Eu(tta)₃(H₂O)₂] (III), [C₆mim][Eu(tta)₄] (IV), [Eu(tta)₃(imid)] (V), and [Eu(dbm)₃(imid3,4,5C₁₄)] (VI).

europium(III) complex in 1 mL of the liquid crystal 4'-pentyl-4-cyanobiphenyl (5CB). The LC cells were filled with the luminescent mixture by capillary forces after a drop of solution was placed at one side of the LC cell.

The liquid crystal 5CB was obtained from Merck AG. The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was prepared by a metathesis reaction between 1-butyl-3-methylimidazolium bromide and lithium bis(trifluoromethylsulfonyl)imide.¹² The europium(III) complexes were prepared according to procedures reported elsewhere: [Eu(tta)₃(phen)],¹³ [Eu(tta)₃(bipy)],¹³ [Eu(tta)₃(H₂O)₂],¹³ [Eu(acac)₃(H₂O)₂],¹³ [Eu(tta)₃(imid)],¹⁰ [Eu(dbm)₃(imid3,4,5C₁₄)],¹⁰ and [C₆mim][Eu(tta)₄].¹⁴

Results and Discussion

The choice of the europium(III) ion as the lanthanide ion for the polarized luminescence studies can be justified by the fact that none of the other trivalent lanthanide ions exhibits such a well-resolved crystal-field splitting pattern in the room-temperature spectra. Moreover, the spectra are simplified by the nondegenerate excited state ⁵D₀. For the europium(III) complexes, different types of β-diketonate complexes have been selected with varying degrees of shape anisotropy (Figure 1). These types of europium(III) complexes are well-known for their bright red photoluminescence.⁸ The liquid-crystal host was 5CB which forms a nematic phase at room temperature.⁹ The clearing point of this liquid crystal is 35 °C. The liquid crystal was used

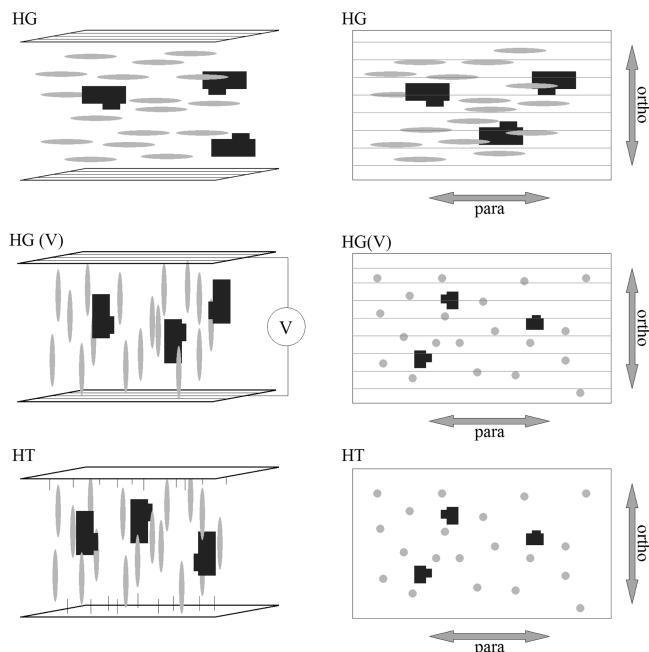


Figure 2. Schematic representation (side and top view) of the alignment of the 5CB molecules (gray) and a europium(III) complex (black) in an LC cell for planar or HG alignment, in the same cell with an applied potential difference (HG(V)) and in an LC cell for HT alignment. The emission polarizer can be either in a parallel (para) or orthogonal (ortho) position.

as an anisotropic solvent for the luminescent europium(III) complexes. 5CB is optically transparent for wavelengths longer than 330 nm. LC cells with a polyamide alignment layer for HG (planar) alignment were filled with the liquid-crystal mixtures by capillary forces. The alignment layers of the LC cell force the mesogenic molecules to line up with their long molecular axis parallel to the alignment layer and thus parallel to the glass plates of the LC cell. The filled LC cell was placed in the sample compartment of a spectrofluorimeter. The luminescence spectra were measured in transmission mode. A polarizer was placed between the luminescent sample and the emission monochromator. The luminescence intensity was evaluated in two polarization directions, with the polarizer either parallel to the alignment layer of the LC cell or perpendicular to it. The luminescence anisotropy has been determined as a function of the type of europium(III) complex, the temperature of the liquid-crystal mixture, and the cell thickness. In Figure 2, a schematic representation of the alignment of the molecules in the LC cells is shown.

Distinct polarization effects could be observed in the room-temperature photoluminescence spectra for most of the europium(III)-doped liquid crystal mixtures. The polarization effects were most easily observable by differences in the intensity of the crystal-field transitions within the ⁵D₀ → ⁷F₂ band around 612 nm. The luminescence spectra of europium(III) β-diketonate complexes are dominated by this intense transition. The polarized emission spectra of these europium(III) complexes dissolved in the liquid-crystal matrix show a degree of fine structure that is reminiscent to that of the polarized emission spectra of the europium(III) ion doped into single-crystal host matrices.¹ However, marked differences in the strengths of polarization effects were observed among the europium(III) complexes. The most pronounced polarization effects were observed for the more anisometric europium(III) complexes [Eu(tta)₃(imid)] and [Eu(dbm)₃(imid3,4,5C₁₄)]. It should be noticed that [Eu(dbm)₃(imid3,4,5C₁₄)] is not a liquid crystal.¹⁰

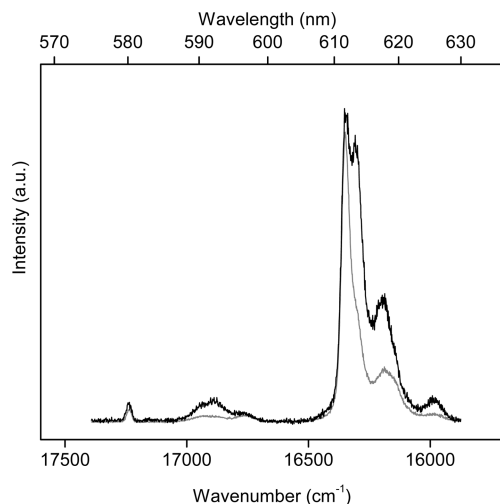


Figure 3. Normalized polarized luminescence spectra of $[\text{Eu}(\text{tta})_3(\text{imid})]$ dissolved in the liquid crystal 5CB. The two spectra are those obtained for the luminescent solution in an LC cell (cell gap: $5\ \mu\text{m}$) with an alignment layer for planar alignment. The polarizer was either parallel (gray line) or perpendicular (black line) to this alignment layer. The spectra were recorded at room temperature, and the excitation wavelength was 350 nm.

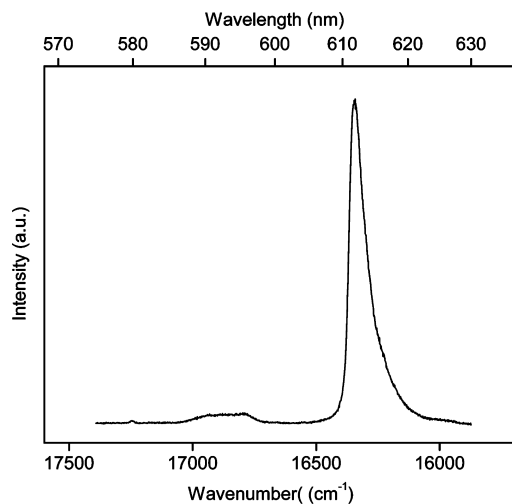


Figure 4. Luminescence spectrum of $[\text{C}_6\text{mim}][\text{Eu}(\text{tta})_4]$ dissolved in the liquid crystal 5CB in an LC cell (cell gap: $5\ \mu\text{m}$) designed for planar alignment. The spectrum was recorded at room temperature, and the excitation wavelength was 350 nm. The polarizer was parallel to the alignment layer of the LC cell. No differences were observable between this spectrum and the spectrum with the polarizer perpendicular to the alignment layer.

The (normalized) polarized luminescence spectra of $[\text{Eu}(\text{tta})_3(\text{imid})]$ are shown in Figure 3. To evaluate the degree of polarization of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ band, the quantity $[I(\text{ortho})/I(\text{para})]$, with $I(\text{ortho})$ being the integrated intensity of the spectrum with the polarizer in the orthogonal/perpendicular position and $I(\text{para})$ the integrated intensity for the spectrum with the parallel position, was calculated and found to be 1.74. Easily observable polarization effects were present in the luminescence spectra of the liquid-crystal mixtures doped with $[\text{Eu}(\text{tta})_3(\text{bipy})]$ or $[\text{Eu}(\text{tta})_3(\text{phen})]$. On the other hand, the polarization effects were much weaker in the $[\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2]$ -containing samples and were virtually absent in the luminescence spectra of the tetrakis β -diketonate complex $[\text{C}_6\text{mim}][\text{Eu}(\text{tta})_4]$ (Figure 4). It can be expected that $[\text{C}_6\text{mim}][\text{Eu}(\text{tta})_4]$ exists as an ion-pair in the liquid-crystal host because of the relatively low electric permittivity of the host matrix. These experiments

show that a rigid planar coligand like 1,10-phenanthroline or imidazo[5,6-*f*]-1,10-phenanthroline has a beneficial effect on the alignment of the europium(III) tris β -diketonate complexes in the nematic liquid-crystal host. The shape of the (hydrated) tris β -diketonate complexes and the tetrakis β -diketonate complexes is globular and thus too isometric to allow good alignment in the liquid-crystal host. However, the absence of polarization effects could also be intrinsic to the tetrakis first-coordination sphere and the resulting crystal field. In the case of the tetrakis β -diketonate complexes, the counter cations bearing a long alkyl chain are not aiding to a good alignment of the europium(III) complex.

The polarization effects were studied as a function of the temperature. For all of the europium(III)-doped liquid-crystal mixtures, the polarization effects decreased with increasing temperatures, and they totally disappeared above the clearing point at $35\ ^\circ\text{C}$. This can be related to a gradual decrease of the order parameter of the 5CB host matrix, which is reduced to zero above the clearing point. These experiments show that a liquid-crystal solvent is required to observe polarized luminescence. Simultaneously, the total luminescence intensity decreased with increasing temperature because of a more efficient nonradiative relaxation of the $^5\text{D}_0$ excited state. Although most of the experiments were performed with LC cells with a cell gap of $5\ \mu\text{m}$, LC cells with other gaps were tested as well: 1.5, 3, 5, 20, and $50\ \mu\text{m}$. These experiments show that an LC cell with a gap of $5\ \mu\text{m}$ is the best choice. It is very difficult to completely fill the narrow-gap cells with the liquid-crystal mixture by capillary forces. For the LC cells with larger gaps, the polarization effects were less pronounced. Probably, this can be explained by a worse alignment of the liquid-crystal molecules at larger distances from the alignment layers.

In a series of control experiments, the influence of the alignment layer of the LC cells was investigated. It was not clear whether the role of the alignment layer is restricted to the alignment of the molecules of the liquid-crystal host matrix or whether there is also a direct interaction between the polyamide alignment layer and the europium(III) complexes. Crystallization or adsorption of the complexes on the polyamide layer can cause orientational effects and can thus induce the generation of polarized luminescence. For the experiments, the europium(III) complexes were dissolved in a nonmesogenic solvent: ethanol, toluene, benzonitrile, and the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Experiments with ethanol or toluene as solvent were unsuccessful, because the solvents so rapidly evaporated from the LC cell that the luminescence measurements could not be finished before all of the solvent had disappeared, leaving behind solid speckles of the luminescent product that showed no polarized emission. Therefore, the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ was chosen as a nonvolatile solvent with a moderate viscosity. Moreover, ionic liquids are known to be interesting solvents for spectroscopic studies of lanthanide complexes.¹¹ Benzonitrile (cyanobenzene) was selected as a solvent because it has some structural similarity with the aromatic core of the liquid crystal 5CB. In none of the experiments that were performed in $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ or in benzonitrile with $[\text{Eu}(\text{tta})_3(\text{phen})]$ and $[\text{Eu}(\text{tta})_3(\text{bipy})]$ as luminophor could any indication for polarized luminescence be detected. This indicates that the polarized emission we observe is a genuine effect due to the alignment of the europium(III) complexes in the liquid-crystal matrix and not

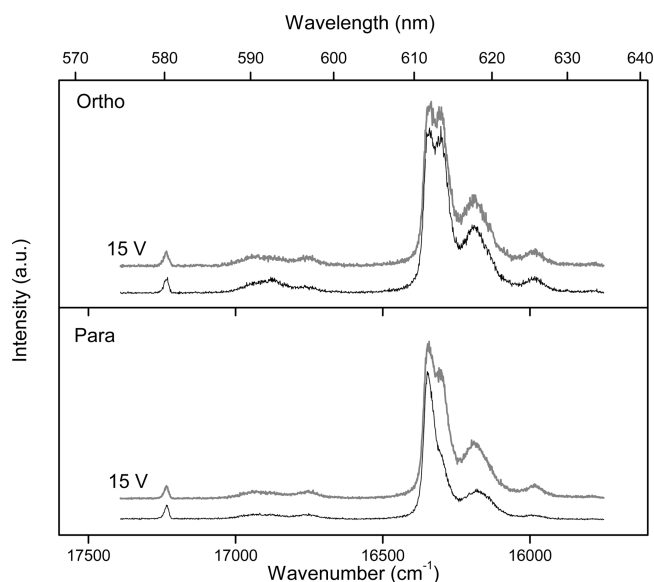


Figure 5. Luminescence spectra of $[\text{Eu}(\text{tta})_3(\text{phen})]$ dissolved in the liquid crystal 5CB in an LC cell (cell gap: $5\ \mu\text{m}$) designed for planar and electrical alignment. The spectra were recorded at room temperature, and the excitation wavelength was $350\ \text{nm}$. A difference in the spectrum was observed when an AC voltage difference of $15\ \text{V}$ was applied. The polarizer was parallel or orthogonal to the alignment layer of the LC cell.

to artifacts due to the alignment layer of the LC cell. An anisotropic solvent is required for polarized luminescence. This guest–host effect is attributed to the π – π interaction between the aromatic rings on the lanthanide ligands and the aromatic rings of 5CB. To test this hypothesis, we tried to record the luminescence spectra of the tris(acetylacetonato)-bis(aquo)europium(III) complex $[\text{Eu}(\text{acac})_3(\text{H}_2\text{O})_2]$, which contains no aromatic groups. However, these experiments were not conclusive, because the complex has a very low solubility in the 5CB host matrix and because direct excitation in the 4f levels (no sensitized luminescence is possible) gave a luminescence spectrum that was too weak and with a too low signal-to-noise ratio to study polarization effects.

Additionally, it was experimentally found that LC cells for HG (planar) alignment have to be used to observe polarized luminescence. No polarization differences between orthogonal and parallel polarizer positions were observed for europium(III)-doped 5CB filled in an LC cell constructed for HT alignment, but the spectra clearly differed from the spectra in a bulk liquid crystal and from those observed in the LC cell for planar alignment.

The LC cells with a polyamide alignment layer for HG (planar) alignment have an indium tin oxide (ITO) layer, and a liquid crystal in these cells can be switched by an external electric field. The 5CB molecules are oriented homeotropically (perpendicular to the ITO surface) after applying a $15\ \text{V}$ alternating current (AC) potential difference over the two electrodes of the LC cell (Figure 5). This also caused a reorientation of the europium(III) complex molecules. The luminescence spectrum changed distinctly and resembled the spectrum for the cells with a HT alignment, but the polarization effects were weak. These experiments demonstrate that at specific spectral regions (e.g., $612\ \text{nm}$ for $[\text{Eu}(\text{tta})_3(\text{phen})]$) the polarization can be electrically switched. It would be interesting to find an europium(III) complex with a even more pronounced change in polarized emission upon switching.

The polarization effects observed in the luminescence spectra of europium(III) complexes in a liquid–crystal host are comparable to those seen by Srdanov et al. for the tris(dinaphthoylemethanato)(1,10-phenanthroline)europium(I–II) complex in a stretched polyethylene film, for which the authors also reported differences in the relative intensities of the crystal-field transitions.^{3a} In both cases (liquid crystal or stretched polymer film) a preferential orientation of the europium(III) complex is induced. However, the effects observed for the europium(III) complexes in the liquid–crystal matrix are different from the polarized luminescence described by Wu et al. for $[\text{Eu}(\text{tta})_3(\text{phen})]$ in photoaligned azopolymer films.^{3c} In that case, the polarized emission was caused by the “polarizer effect” of the aligned azobenzene groups. The oriented polymer matrix acted as a polarizer towards the emission light that travels through it. Therefore, the intensity of the emission light was stronger when the direction of the electric-field vector was parallel to the alignment layer and lower when the direction of the electric field was perpendicular to it. As a consequence, the luminescence spectra showed differences in the relative intensities of the crystal-field components rather than differences in the absolute intensities in the two polarization directions. It should be realized that neither for europium(III) complexes in a liquid–crystal matrix nor for europium(III) complexes in a stretched polymer film the polarization effects are as pronounced as in a single-crystal host matrix, but these systems are easier to prepare than large single crystals.

Conclusions

Polarized luminescence spectra can be observed for small molecular europium(III) complexes in solution, provided that an anisotropic solvent like a liquid crystal is selected to dissolve the europium(III) complexes. The europium(III) complexes do not need to exhibit liquid–crystalline behavior themselves, although a structural anisotropy of the complex seems to be necessary to obtain a good alignment in the liquid–crystal host matrix. No polarization effects were observed for unaligned bulk samples of the europium(III)-doped liquid crystals. However, because the polarization effects are restricted to differences in the relative intensities of the crystal-field components within a $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transition rather than being a total on–off switch of the luminescence upon a change in the polarization direction of the polarizer, it might be difficult to make use of these polarization effects in emissive displays.

Acknowledgment. K.D. and T.C. are postdoctoral fellows of the FWO-Flanders (Belgium). K.G. is a research fellow of the FWO-Flanders (Belgium). Financial support by the K.U. Leuven (project GOA 03/03) and by the FWO-Flanders (project G.0508.07) is gratefully acknowledged.

References and Notes

- (1) (a) Lagerwey, A. A. F.; Blasse, G. *Chem. Phys. Lett.* **1975**, *31*, 27. (b) Peacock, R. D. *Chem. Phys. Lett.* **1975**, *35*, 420. (c) Moret, E.; Nicolo, F.; Bünzli, J.-C. G.; Chapuis, G. *J. Less-Common Met.* **1991**, *171*, 273. (d) Blanc, J.; Ross, D. L. *J. Chem. Phys.* **1965**, *43*, 1286.
- (2) Bünzli, J.-C. G. In *Lanthanide Probes in Life, Chemical and Earth Sciences*; Bünzli, J.-C. G., Choppin, G. R., Eds.; Elsevier: Amsterdam, 1989; Chapter 7, p 219.
- (3) (a) Srdanov, V. I.; Robinson, M. R.; Bartl, M. H.; Bu, X.; Bazan, G. C. *Appl. Phys. Lett.* **2002**, *80*, 3042. (b) Yang, C. Y.; Srdanov, V.; Robinson, M. R.; Bazan, C. G.; Heeger, A. J. *Adv. Mater.* **2002**, *14*, 980. (c) Wu, S.; Yu, X. W.; Huang, J. T.; Shen, J.; Yan, Q.; Wang, X.; Wu, W. X.; Luo, Y. H.; Wang, K. Y.; Zhang, Q. *J. Mater. Chem.* **2008**, *18*,

3223. (d) Hasegawa, M.; Ishii, A.; Furukawa, K.; Ohtsu, H. *J. Photopolym. Sci. Technol.* **2008**, *21*, 333.

(4) Grell, M.; Bradley, D. D. C. *Adv. Mater.* **1999**, *11*, 895.

(5) Galyametdinov, Y. G.; Knyazev, A. A.; Dzhabarov, V. I.; Cardinaels, T.; Driesen, K.; Görrler-Walrand, C.; Binnemans, K. *Adv. Mater.* **2008**, *20*, 252.

(6) (a) Binnemans, K.; Moors, D. *J. Mater. Chem.* **2002**, *12*, 3374. (b) Van Deun, R.; Moors, D.; De Fré, B.; Binnemans, K. *J. Mater. Chem.* **2003**, *13*, 1520. (c) Palewska, K.; Miniewicz, A.; Bartkiewicz, S.; Legendziewicz, J.; Strek, W. *J. Lumin.* **2007**, *124*, 265. (d) Boyaval, J.; Hapiot, F.; Li, C.; Isaert, N.; Warenghem, M.; Carette, P. *Mol. Cryst. Liq. Cryst.* **1999**, *330*, 1387. (e) Puntus, L. N.; Schenk, K. J.; Bünzli, J.-C. G. *Eur. J. Inorg. Chem.* **2005**, 4739. (f) Guillet, E.; Imbert, D.; Scopelliti, R.; Bünzli, J.-C. G. *Chem. Mater.* **2004**, *16*, 4063. (g) Yu, L. J.; Labes, M. M. *Appl. Phys. Lett.* **1977**, *31*, 719. (h) Binnemans, K. *J. Mater. Chem.* **2009**, *19*, 448.

(7) (a) Yang, Y. T.; Driesen, K.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Binnemans, K. *Chem. Mater.* **2006**, *18*, 3698. (b) Suarez, S.; Mamula, O.; Imbert, D.; Piguet, C.; Bünzli, J.-C. G. *Chem. Commun.* **2003**, 1226. (c) Suarez, S.; Imbert, D.; Gumy, F.; Piguet, C.; Bünzli, J.-C. G. *Chem. Mater.* **2004**, *16*, 3257.

(8) Binnemans, K. Rare-earth Beta-diketonates. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Bünzli, J.-C. G., Pecharsky, V. K., Eds.; Elsevier: Amsterdam, 2005; Vol. 35, Chapter 225, p 107.

(9) Gray, G. W.; Harrison, K. J.; Nash, J. A. *Electron. Lett.* **1973**, *9*, 130.

(10) Cardinaels, T.; Ramaekers, J.; Nockemann, P.; Driesen, K.; Van Hecke, K.; Van Meervelt, L.; Lei, S. B.; De Feyter, S.; Guillon, D.; Donnio, B.; Binnemans, K. *Chem. Mater.* **2008**, *20*, 1278.

(11) Arenz, S.; Babai, A.; Binnemans, K.; Driesen, K.; Giernoth, R.; Mudring, A. V.; Nockemann, P. *Chem. Phys. Lett.* **2005**, *402*, 75.

(12) Nockemann, P.; Binnemans, K.; Driesen, K. *Chem. Phys. Lett.* **2005**, *415*, 131.

(13) Melby, L. R.; Rose, N. J.; Abramson, E.; Caris, J. C. *J. Am. Chem. Soc.* **1964**, *86*, 5117.

(14) Lunstroo, K.; Driesen, K.; Nockemann, P.; Görrler-Walrand, C.; Binnemans, K.; Bellayer, S.; Le Bideau, J.; Vioux, A. *Chem. Mater.* **2006**, *18*, 5711.

JP901145Z