

Narrow band photoluminescence of europium-doped liquid crystals

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Luminescent materials with liquid-crystalline properties at room temperature were obtained by doping the nematic liquid-crystal host matrices MBBA and 5CB with the europium(III) β -diketonate complex [Eu(TTA)₃(phen)]; very well resolved crystal-field fine structure is observed in the europium(III) emission spectra.

The main disadvantages of liquid-crystal displays (LCDs) are their low brightness and energy efficiency. These limitations are due to the use of dichroic sheet polarisers and absorbing colour filters in the LC cell which result in absorption losses. Major improvements in colour LCD performance can be expected when an LC cell without polarisers and colour filters could be designed. A very promising concept is the *luminescent LCD* (or *fluorescent LCD*), which is an emissive type of display. Different approaches to luminescent LCDs are possible, e.g. the use of photoluminescent sheets acting as active colour filters,¹ or the use of luminescent liquid crystals.² Many organic liquid crystals fluoresce on their own, albeit mostly in the blue spectral region (e.g. 5CB).^{2b} Several research groups are trying to create liquid crystals that emit at longer wavelengths.³ The broad band emission by organic molecules (typically several tens of nanometers) could be a disadvantage for the development of full-colour emissive LCDs. For such a device blue, green and red emitting liquid-crystalline matrices are necessary, but overlap of the emission bands should be avoided. Lanthanide-containing liquid crystals can offer a solution to this problem. The narrow band photoluminescence of lanthanide complexes and their high luminescence quantum yield is currently being explored to improve the performance of organic light emitting diodes (OLEDs).⁴ Although several types of lanthanide-containing liquid crystals have been described in the literature, none of them are liquid crystalline at room temperature and their photoluminescence efficiency is often low.⁵ Other mesogenic systems with interesting photo-physical behaviours failed to form a liquid-crystalline phase.⁶ An alternative approach is that of Yu and Labes who doped the nematic liquid crystal 4-*n*-pentyl-4'-cyanobiphenyl (5CB) with europium(III) thenoyltrifluoroacetate trihydrate [Eu(TTA)₃·3H₂O].^{2b} Hapiot and coworkers have investigated the luminescence of a comparable complex in a cholesteric liquid-crystal mixture.^{2f,g}

In this communication we show that it is possible to obtain liquid-crystalline materials with narrow band red photoluminescence by doping a nematic host matrix with highly luminescent europium(III) complexes. By taking advantage of the guest–host effect it is possible to optimise the luminescent and liquid-crystalline properties of the system independently. Liquid crystals are shown to be an excellent solvent for high resolution spectroscopic studies of lanthanide complexes.

Lanthanide complexes are the obvious choice for designing luminescent materials with narrow emission bands. Depending on the lanthanide(III) ion, different emission colours can be

achieved, for instance, red photoluminescence by Eu^{III} and green emission by Tb^{III}. Blue photoluminescence by a lanthanide(III) ion is more difficult to achieve in an organic matrix, but some studies mention blue emission by Tm^{III} complexes. We restricted ourselves in this study to Eu^{III} complexes. β -Diketonates (1,3-diketonates) are very good ligands with which to obtain highly luminescent europium(III) complexes. The β -diketonates form three types of complexes with the trivalent lanthanide ions, depending on the ligand-to-metal ratio: (1) tris-complexes; (2) Lewis base adducts of tris complexes, and (3) tetrakis complexes. The tetrakis complexes exhibit a very strong photoluminescence, but have the disadvantage that they are negatively charged, so that a positive counter ion is necessary to achieve electric neutrality. Such ionic compounds can cause problems when they are used in LC cells switched by an external electric field. Because in the tris complexes the coordination sphere of the lanthanide ion is close to an octahedron (which contains an inversion centre), the intensity of the emission peaks will be weak. Moreover, the coordination sphere of the lanthanide ion is not saturated in the tris complexes, so that tris complexes easily form adducts with Lewis bases to achieve a higher coordination number (typically eight or nine). When no precautions are taken, water will add to the tris complexes to form di- or trihydrates. Water in the first coordination sphere of a lanthanide ion has to be avoided when one wants to obtain highly luminescent complexes, because water molecules can efficiently deactivate excited states by radiationless deactivation. Earlier workers, who doped liquid-crystalline matrices with lanthanide complexes, used hydrated lanthanide complexes, so that their systems had no optimal performance. A much better choice for a dopant in the liquid crystalline matrix are adducts of polydentate N-donor ligands such as 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy) to the tris complexes. The luminescence efficiency of the β -diketonate complexes can be increased by an appropriate choice of substituents on the β -diketone ligand, because in this way the position of the triplet level of the organic ligand can be tuned and good energy transfer between the β -diketone ligand and the lanthanide ion can be achieved. For this work, we prepared the europium(III) complex [Eu(TTA)₃(phen)], where TTA is thenoyltrifluoroacetate and phen is 1,10-phenanthroline. The complex was synthesised according to a literature method,⁷ and its purity has been checked by CHN microanalysis.

For these preliminary investigations, we have chosen two nematic liquid crystals as the host matrix: *N*-(4-methoxybenzylidene)-4-butylaniline (MBBA) and 4-*n*-pentyl-4'-cyanobiphenyl (5CB). However, the choice of LC solvent is a less critical factor than the choice of the lanthanide complex in determining the luminescence properties. Therefore, a liquid-crystal host with desirable mesophase properties (typically this will be a LC mixture) can be selected. The europium complex can be dissolved directly in the liquid crystal host by heating

the liquid crystal first to the isotropic liquid state. Alternatively both the liquid crystal and the europium complex can be dissolved in an inert, non-coordinating organic solvent (e.g. chloroform or dichloromethane) and after mixing of the two solutions the solvent can be evaporated under reduced pressure. This method ensures that no particles of undissolved europium complex remain dispersed in the liquid crystal host and that solvation at the molecular level can be achieved. Clustering of the europium complex has to be avoided because this is detrimental for luminescence efficiency. The solubility of the lanthanide complexes in the liquid crystal solvents we tested is only a few wt%, but only low doping concentrations are necessary for luminescence applications.

Photoluminescence spectra have been recorded on an Edinburgh Instruments FS900 steady-state spectrofluorimeter. The samples have been excited at 396 nm. The liquid-crystalline mixtures were either added to a quartz cuvette (2 mm thickness) or squeezed between two quartz plates. Luminescence was measured at an angle of 90° with respect to the excitation light beam. For comparison, the luminescence spectra of the europium(III) in KBr pellets have been measured too. In Fig. 1 the luminescence spectrum of [Eu(TTA)₃(phen)] in a KBr pellet is shown and in Fig. 2 the luminescence spectrum of the same complex in the liquid crystal MBBA. The two spectra are very comparable. The differences in intensities are mainly due to the differences in sample preparation and in sample geometry. We were surprised to observe that the linewidth of the crystal-field transitions of [Eu(TTA)₃(phen)] dissolved in MBBA at room temperature were even smaller than those of [Eu(TTA)₃(phen)] in KBr at 77 K. The spectra in 5CB are similar with those in MBBA.

The transitions observed in the 575–725 nm region are

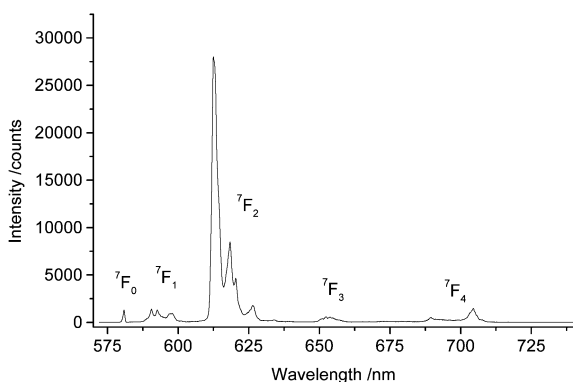


Fig. 1 Luminescence spectrum at 77 K of [Eu(TTA)₃(phen)] in a KBr pellet. The excitation wavelength is 396 nm. All the transitions start from the ⁵D₀ excited state.

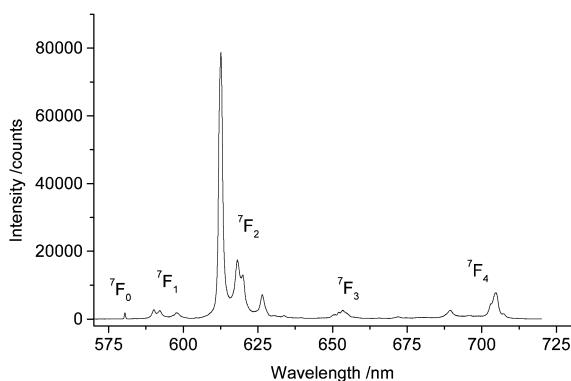


Fig. 2 Room temperature luminescence spectrum of [Eu(TTA)₃(phen)] in the nematic liquid crystal MBBA. The doping concentration was 4 wt%. The excitation wavelength is 396 nm. All the transitions start from the ⁵D₀ excited state.

emission transitions from the ⁵D₀ excited state to the ⁷F_J (J = 0–4) levels. The most intense transition in the luminescence spectrum is the ⁵D₀→⁷F₂ transition at around 612 nm. This transition is a so-called *hypersensitive transition* and is responsible for the bright red emission colour of the complex.⁸ The fact that only one peak is observed for the ⁵D₀→⁷F₀ transition and not more than three peaks for the ⁵D₀→⁷F₁ transition, provides evidence for one complex species in both the KBr and MBBA matrix. The presence of three peaks for the ⁵D₀→⁷F₁ transition shows that the site symmetry of the europium(III) is low, C_{2v} at a maximum.⁹ All the transitions in the luminescence spectrum are induced electric dipole transitions, except for the ⁵D₀→⁷F₁ transition which is allowed by the magnetic dipole mechanism. The intensity ratio I(⁵D₀→⁷F₂)/I(⁵D₀→⁷F₁) is 13.9 for [Eu(TTA)₃(phen)] in MBBA. High ratios are desirable for high color purity.

In conclusion, we can make the following statements. (1) Narrow band photoluminescence can be obtained by lanthanide-containing liquid crystals. (2) From a technical (and practical) point of view, a good approach by which to obtain luminescent liquid crystals is to dope a liquid-crystalline host matrix with highly luminescent lanthanide complexes rather than trying to obtain lanthanide complexes which exhibit a mesophase at room temperature. This guest–host effect allows the luminescence and mesomorphic properties of the liquid-crystal mixture to be optimised independently. (3) Liquid crystals can be used as solvents for high-resolution spectroscopy of lanthanide complexes. Further work is in progress to measure polarised luminescence of lanthanide-doped liquid crystals in LC cells.

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