A red-emitting molecular europium(III) complex has been doped into liquid-crystalline (LC) physical gels consisting of 4-pentyl-4′-cyanobiphenyl (5CB) with amino acid-based gelators. Light scattering cells on the basis of these LC physical gels could be switched between a non-transparent off-state and a transparent on-state by on–off application of electric fields. The gels produced intense red light when they were irradiated with UV-light.

1. Introduction

Liquid-crystalline (LC) physical gels are a new class of soft functional materials, which are prepared by the simple mixing of liquid crystals and low-molecular-weight gelators. Liquid crystals show anisotropy and fluidity, which have been utilized in electrooptical shutters in informational displays. The physical gelation of liquid crystals leads to enhancement of electro-optical and electronic properties of liquid crystals through the formation of microphase-separated structures. For example, nematic LC physical gels show efficient electrooptical switching in light-scattering mode based on the LC polydomain structures induced by the introduction of fibrous aggregates of gelators. Incorporation of opto- and photo-active components is a promising approach to further functionalization of LC physical gels. The LC gels with photo-responsive fibers have been applied to rewritable optical memory. The introduction of fluorescent fibers and CdSe/ZnS quantum dots leads to light-scattering cells with tunable photoluminescence.

Narrow-band luminescence with a high color purity can be obtained by taking advantage of the line emission of the trivalent lanthanide ions. The color of the luminescence light depends on the nature of the lanthanide ion: red for Eu³⁺, green for Tb³⁺ and blue for Tm³⁺.

In this work, LC physical gels containing phosphorescent europium(III) complexes were developed. The effects of the introduction of a metal complex on the optical and photo-physical properties of the LC gels were studied. These LC gels were prepared by doping the luminescent europium(III) complex [Eu(tta)₃phen] (tta = 2-thienyltrifluoroacetanate, phen = 1,10-phenanthroline) into liquid crystal 4-pentyl-4′-cyanobiphenyl (5CB) followed by gelating of the LC matrix by the gelators 1 and 2 (Scheme 1). [Eu(tta)₃phen] is an efficient red-emitting molecular europium(III) complex, which was previously used as a dopant for obtaining luminescent liquid crystals.

2. Experimental

2.1 General

Optical textures of the LC gel phases were observed with Olympus BX51 equipped with a Mettler FP82HT hot stage. Photoluminescence spectra were recorded on a JASCO FP-6300 spectrofluorometer. 5CB (nematic–isotropic transition temperature: 35 °C, Δν = +17.9, Δn = +0.23) was purchased from Tokyo Kasei, and used without further purification.

2.2 Synthetic procedures

Synthesis and basic physical properties of 1 and 2 have been described elsewhere. The europium(III) complex [Eu(tta)₃phen] were prepared according to literature procedures.

2.3 Preparation of the LC gels

The gelator (1 or 2, 1 wt%), 5CB (98.99 wt%) and [Eu(tta)₃phen] (0.1 wt%) were added to a sample container and dissolved in chloroform. The mixture was heated at 65 °C until most of the chloroform was evaporated. Then the mixture was heated at 80 °C for three hours in order to remove the remaining chloroform. Finally, the mixture was heated to the isotropic form. The gelation of the LC gel was monitored by recording the experimentally observed optical textures with an optical microscope.
2.4 Measurements of electrooptical properties

The electrooptical effects of the LC gels on light-scattering mode were measured in ITO (indium tin oxide) glass sandwich cells (1 cm × 1 cm × 16 μm). The mixtures in the isotropic states were introduced into the cells, and then cooled to room temperature. A He–Ne laser (632.8 nm) was used as the incident light source. AC electric fields (300 Hz) were applied to the cells. The transmitted light intensity was measured with a photodiode. The light intensity for the empty ITO cell was assumed to be full-scale intensity. The rise was evaluated as the time periods required to reach 90% of maximum transmittance change upon application of electric fields.

3. Results and discussion

The concentration of [Eu(tta)₃phen] was kept low (<0.1 wt%) in order to obtain stable LC gels. At higher [Eu(tta)₃phen] concentrations, the gel formation was disturbed and the gel was only partially formed. Two types of europium(III)-doped LC gels were prepared, namely 5CB/1/[Eu(tta)₃phen] (98.9/1/0.1 wt%) and 5CB/2/[Eu(tta)₃phen] (98.9/1/0.1 wt%). The LC physical gels were studied by polarizing optical microscopy (POM) to determine their phase behavior and to observe their morphology. Both mixtures show nematic gel (N gel) phases at room temperature. Thin and dispersed fibers combined with small domains of a europium(III)-doped nematic liquid crystal with the size of ca. 1 μm were observed.

The transition temperatures (in °C) for the phase transitions from a N gel to an isotropic gel (I gel) and to the isotropic liquid (I) is given in Table 1. The sol–gel transition temperatures of 5CB/1/[Eu(tta)₃phen] and 5CB/2/[Eu(tta)₃phen] were found to be comparable to those of the LC gels without metal complexes at similar gelator concentrations, indicating that the introduction of small amount (ca. 0.1 wt%) of [Eu(tta)₃phen] does not disturb the fibrous aggregation of gelators, and has only a small influence on the thermal behavior of the LC gels. At higher concentration of [Eu(tta)₃phen], fibrous aggregation of the gelators was inhibited and the gel was only partially formed.

The morphology of the [Eu(tta)₃phen]-doped LC physical gels seems to be suitable for the preparation of light-scattering cells because the size of LC domains is comparable to the wavelength of visible light. LC gels composed of thin, dispersed fibers combined with small domains of liquid crystal produce a higher contrast ratio and a lower threshold voltage compared to LC gels composed of thick fibers combined with large liquid-crystal domains. The mixtures of 5CB/1/[Eu(tta)₃phen] and 5CB/2/[Eu(tta)₃phen] were introduced into 16 μm thick indium tin oxide (ITO) sandwich cells in the isotropic state (65 °C) to examine the electrooptical properties of the LC physical gels in the light-scattering mode. The cells could be switched using an AC current of 70 V (300 Hz). In the off-state (0 V), the cell shows a light-scattering state, while in the on-state (70 V), the cell was light-transmitting (Fig. 1). The rise times (the time periods required to reach 90% transmittance change upon application of electric fields) were about 1 ms. In the off-state, the LC molecules have a random orientation and strongly scatter the incident light. In the on-state, the LC molecules reoriented themselves in the direction of the electric field (thus perpendicular to the glass plates—homeotropic alignment), and transmit the incident light. When the scattering cells were irradiated with UV-light of wavelength 365 nm, they produced intense, bright-red light and switching between a transparent on-state and non-transparent

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase transition temperature/°C</th>
<th>N gel</th>
<th>I gel</th>
<th>I</th>
</tr>
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<tr>
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<td>♦ 36°♦</td>
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<tr>
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<td>♦ 37°♦</td>
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<td>♦ 51°♦</td>
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<tr>
<td>5CB/2</td>
<td>♦ 33°♦</td>
<td>♦ 54°♦</td>
<td>♦</td>
<td>♦</td>
</tr>
</tbody>
</table>

*a* Phase transition temperatures from a nematic gel to the isotropic gel.

*b* Phase transition temperatures from an isotropic gel to the isotropic liquid.

Fig. 1 Scattering cell of 5CB/2/[Eu(tta)₃phen]. The scattering cells were placed above a black piece of paper with white text “LC GEL” (black paper was used because white paper shows blue luminescence when exposed to UV-light of 365 nm). UV-light with a wavelength of 365 nm was used. Top left: off-state; top right: on-state; bottom left: off-state, + UV-light; bottom right: on-state, + UV-light.

Fig. 2 Relationship between transmittance and applied voltage for 5CB/2, 5CB/2/[Eu(tta)₃phen], 5CB/1, and 5CB/1/[Eu(tta)₃phen].

8572 | J. Mater. Chem., 2010, 20, 8571–8574

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The introduction of the europium(III) complex \[\text{Eu(tta)}_3\text{phen}\] results in a more efficient absorption of the excitation light by the cell in the off-state. This observation can be rationalized by the threshold voltage was higher in the case of \[\text{Eu(tta)}_3\text{phen}\] (69.6) than for \[5\text{CB}/[\text{Eu(tta)}_2\text{phen}]\] (27.7).

The photophysical properties of scattering cells were further studied. The luminescence of the scattering cells was investigated in the off-state and the on-state (Fig. 3). Distinct differences in the luminescence intensity could be observed for the LC cell in the on-state and in the off-state, with the highest intensity for the cell in the off-state. This observation can be rationalized by the fact that the stronger light scattering of the LC cell in the off-state results in a more efficient absorption of the excitation light by the europium(III) complex \[\text{Eu(tta)}_2\text{phen}\] and thus in a higher luminescence intensity. The luminescence intensities of all the transitions in the luminescence spectrum of europium(III) are to the 7\(D_0 \rightarrow 7F_2\) transition at 613 nm and this transition is responsible for the bright red luminescence color. The luminescence spectra of the two scattering cells of \[5\text{CB}/[\text{Eu(tta)}_3\text{phen}]\] and \[5\text{CB}/[\text{Eu(tta)}_2\text{phen}]\] are very similar, so that it can be concluded that the gelator has only a minor influence on the first coordination sphere of the europium(III) ion. The contrast ratios of 2.73 and 2.15 between the off-state and on-state were observed for the scattering cells of \[5\text{CB}/[\text{Eu(tta)}_3\text{phen}]\] and \[5\text{CB}/[\text{Eu(tta)}_2\text{phen}]\], respectively. Thus, the scattering cell that showed the highest transmittance contrast ratio showed the highest luminescence intensity contrast ratio and vice versa. This experimental fact is in agreement with the above mentioned relationship between the amount of light scattering and the luminescence intensity.

4. Conclusion

In conclusion, LC physical gels which show bright, intense red luminescence light could be easily prepared by doping LC gels with the europium(III) complex \[\text{Eu(tta)}_2\text{phen}\]. Scattering cells on the basis of these LC gels could be switched between a non-transparent off-state and a transparent on-state, and produced intense red light when irradiated with UV-light.

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References


