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Photoacoustic and Fluorescence Spectroscopy of Metallomesogens Containing Lanthanide Ions

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Metallomesogens $Ln(bta)_3L_2$ (Ln^{3+}: La^{3+}, Eu^{3+}, and Ho^{3+}; bta: benzoyltrifluoroacetonate; L: Schiff base) were prepared. Photoacoustic (PA) spectroscopy was used to study physicochemical properties of the liquid crystalline metal complexes. In the region of ligand absorption, PA intensity increases for $Eu(bta)_3L_2$, $La(bta)_3L_2$, and $Ho(bta)_3L_2$, in that order. It is found that the PA intensity of the ligand bears a relation to the intramolecular energy transfer process. For the first time, phase transitions of $Eu(bta)_3L_2$ from glass state to smectic A (SmA) phase and SmA phase to isotropic liquid are monitored by PA and fluorescence (FL) spectroscopy from two aspects: nonradiative and radiative transitions. The results show that PA technique may serve as a new tool for investigating the spectral properties and phase transitions of liquid crystals containing metal ions.

Key words: Photoacoustic spectroscopy, Lanthanide complex, Liquid crystal, Relaxation process, Phase transition

I. INTRODUCTION

Because of the desire to combine the properties of liquid crystals and metal complexes, a substantial amount of research has been devoted during the past two decades to the design of liquid-crystalline metal complexes [1-5]. Organic luminophores have broad emission bands, and it is very difficult to obtain luminescent light with a high coloric purity when using this type of compound. On the other hand, line emission in the visible or in the near-infrared spectral region is typical for the trivalent lanthanide ions. Lanthanide-containing liquid crystals are considered as a promising class of light-emitting liquid crystal [6-10].

The main driving forces for the development of this type of advanced material are the unique physical properties of lanthanide ions. Several of the lanthanide ions show a very intense luminescence (photo- or electroluminescence). Europium(III) compounds emit in the red, terbium(III) compounds in the green, and thulium(III) compounds in the blue spectral regions. By incorporating lanthanide ions into liquid crystals, one can obtain luminescent liquid crystals, which are useful for the design of emissive LCDs. Most of the trivalent lanthanide ions are paramagnetic, due to the unfilled 4f subshell. They have a high magnetic moment, and what is more important, often they exhibit a large magnetic anisotropy. Together with a low viscos-

ity, a high magnetic anisotropy is one of the factors that reduce the threshold magnetic field for the alignment of molecules in an external magnetic field.

Photoacoustic (PA) spectroscopy has been widely used to investigate the chemical and physical properties of many samples [11-14]. PA technique can be a direct monitor of energy gaps and nonradiative relaxation channels of rare earth compounds [15-19]. Additionally, the PA effect is one of the recently introduced methods for phase transition studies in liquid crystals [20]. The direct correspondence between the light absorbed by the sample and the sound signal picked up by the microphone makes PA spectroscopy sensitive to both the optical and thermal properties of the sample. Consequently, phase transitions can be observed. However, PA technique has not been used in the study of liquid crystalline metal complexes.

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 [21-29]. The study of the physicochemical properties of liquid crystalline metal complexes is often hampered by their high transition temperatures and low thermal stability. Recently, we reported a kind of luminescent lanthanide-containing liquid crystal with low transition temperatures and high thermal stability [7]. In this work, $Ln(bta)_3L_2$ (Ln^{3+}: La^{3+}, Eu^{3+}, and Ho^{3+}, bta: benzoyltrifluoroacetonate, L: 2-hydroxy-N-octadecyloxy-4-tetradecyl-oxybenzyaldimine) liquid-crystalline complexes were prepared. The spectral properties and phase transitions of the complexes were studied by PA and fluorescence (FL) spectra.

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II. EXPERIMENTS

A. Sample preparation

Ln(bta)$_3$L$_2$ complexes were obtained by adduct formation between L and Ln(bta)$_3$(H$_2$O)$_2$ in dry toluene at 50 °C. The synthesis of the europium(III) complex is described below, and all the other complexes were prepared by the same method. A solution of Eu(bta)$_3$(H$_2$O)$_2$ (0.1 mmol) in dry toluene was added dropwise to a solution of 2-hydroxy-N-octadecyl-4-tetradecyloxybenzaldimine (L) (0.2 mmol) in dry toluene. The reaction mixture was stirred at 50 °C for 3 h. After allowing the solution 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: 99%. Results of elemental analysis: La(bta)$_3$L$_2$: C 66.32%, H 8.23%, N 1.45%, cacl. C 66.31%, H 8.24% N, 1.43%; Eu(bta)$_3$L$_2$: C 65.89%, H 8.17%, N 1.41%, cacl. C 65.87%, H 8.19%, N 1.42%; Ho(bta)$_3$L$_2$: C 65.42%, H 8.13%, N 1.40%, cacl. C 65.44%, H 8.13%, N 1.41%.

The structure of La(bta)$_3$L$_2$ is further confirmed by IR measurement using the KBr pellet technique. The stretching vibrations of C=O of La(bta)$_3$L$_2$ hardly change compared with those of La(bta)$_3$(H$_2$O)$_2$. The stretching vibration of C=N is around 1650 cm^{-1} for Ln(bta)$_3$L$_2$, while for the free based ligand L, the stretching vibration of C=N is 1630 cm^{-1}. This indicates that L coordinates to the cental Ln^{3+} in the products.

B. Spectroscopy measurements

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. The mesophase was identified as a smectic A phase on the basis of the very typical fan-like defect texture that could be observed by polarizing optical microscopy when the isotropic liquid was cooled into the mesophase, as shown in Fig.1.

DSC traces were recorded with a Mettler-Toledo DSC-821e module. The transition temperature of glass state to SmA phase is 18 °C for all the complexes, and the transtion temperature of SmA to isotropic liquid is 50, 40, and 33 °C for La^{3+}, Eu^{3+}, and Ho^{3+} complexes, respectively. The compounds form an enantiotropic mesophase, and are thermally stable under 120 °C. *In situ* energy-dispersive X-ray diffraction experiments were performed in the Beijing Synchrotron Radiation Facility. The energy range of the synchrotron radiation in the experiment stretches from 0.728 keV to 36.028 keV, and λ=0.6199 Å. The XRD of Ln(bta)$_3$L$_2$
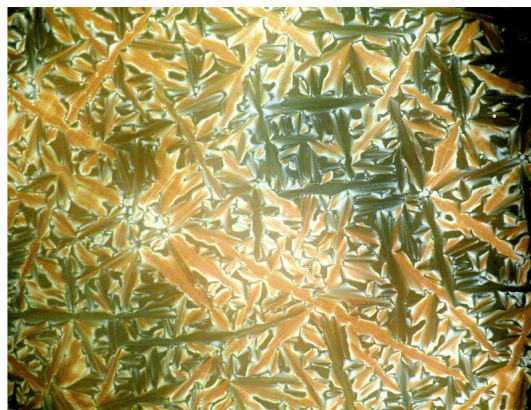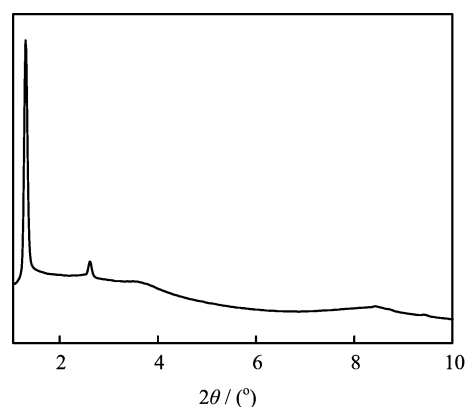

FIG. 1 Texture of Eu(bta)$_3$L$_2$ in smectic A phase ($\times$400).

FIG. 2 X-ray diffraction of Eu(bta)$_3$L$_2$ at room temperature.

at room temperature also confirms the smectic A phase, which can be seen in Fig.2. The layer structure with a periodicity d around 26 Å, which can be estimated from the diffractions in the small-angle region. The value of d for the intermolecular interferences in the direction perpendicular to the layer is about 4.5 Å, corresponding to the broad diffractions in the wide-angle region.

Fluorescence spectra were recorded on an Edinburgh Instruments FS-900 spectrofluorimeter. Fluorescence 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 lowest triplet of the organic ligand in the complex was obtained from the phosphorescence spectra of gadolinium compounds. 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 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 blanco sample in the integrating sphere). The blanco sample was a quartz measuring cell, filled with the solvent (dichloromethane).

PA spectra were measured on a single-beam spectrometer constructed in our laboratory [17]. The excitation source was a 500 W xenon lamp. The optical system was a monochromator and a variable speed mechanical chopper at a frequency of 33 Hz. The acoustic signal was monitored with the sample placed in an indigenous photoacoustic cell fitted with an electric microphone. The output signal from the microphone was amplified by a preamplifier and then fed to a lock-in-amplifier. The final signal was normalized for the changes in lamp intensity using carbon black. The PA cell temperature can be changed continuously in order to monitor the phase transition. The PA spectra of all the complexes were recorded in the region of 320-800 nm.

III. RESULTS AND DISCUSSION

A. PA and FL spectra of lanthanide complexes

The PA signal is obtained by detecting the heat generated through nonradiative transitions by the sample after absorbing a periodically varying incident light. PA amplitude A can be expressed as Eq.(1) for the complexes [14],

$$A = KP_{abs}\gamma \qquad (1)$$

where P_{abs} is the radiant power absorbed by the sample, γ is the probability of nonradiative transitions after excitation, and K is a coefficient determined by the thermal properties of the sample and by the spectrometer.

PA spectra of lanthanide complexes are shown in Fig.3. The broad absorption band around 400 nm is assigned to the π-π^* transition of the ligand. La^{3+} has no absorption in the UV-Vis region. PA absorption of f-f transitions of Ho^{3+} is clearly observed. However, PA absorptions of Eu^{3+} are quite weak. The PA spectrum only responds to the nonradiative relaxation process, whereas the PA signal of fluorescence energy levels which relax by radiative process will be very weak or vanish. Among the energy levels of Eu^{3+}, the longest-lived energy level is $^5D_0$ and it is also a strong fluo-
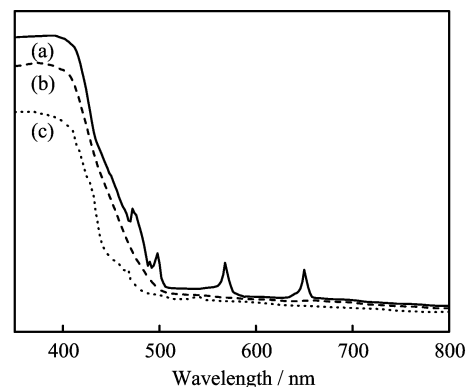

FIG. 3 PA spectra of (a) Ho(bta)$_3$L$_2$, (b) La(bta)$_3$L$_2$, and (c) Eu(bta)$_3$L$_2$ complexes.

rescence energy level. The electron in the excited level $^5D_0$ has a high probability to take a radiative relaxation process. When the electrons are excited to higher energy levels such as $^5D_2$, $^5D_1$, usually they will relax to $^5D_0$ by a nonradiative process, and then relax by radiative process (fluorescence). For Eu^{3+}, its PA signals at 470 nm ($^5D_2$) and 538 nm ($^5D_1$) are quite weak, and that at $^5D_0$ of Eu^{3+} can not be monitored.

PA intensity of the ligand increases in the order of Eu(bta)$_3$L$_2$<La(bta)$_3$L$_2$<Ho(bta)$_3$L$_2$. In the region of ligand absorption, we measured PA amplitude A as a function of modulation frequency ω, and found that A was proportional to ω^{-1}. This indicates that photoacoustic saturation occurs, and P_{abs} in Eq.(1) becomes a constant instrumental parameter for the complexes, so A will be independent of the absorption coefficients of the samples [30]. This is because the complexes have high absorption coefficients due to the conjugated π-π^* systems. In Eq.(1), A is independent of the absorption coefficient of lanthanide complexes, but depends on the sample's thermal and nonradiative relaxation probability directly. As the thermal property of Ln(bta)$_3$L$_2$ is basically the same at room temperature, PA spectra indicate that the probability of nonradiative transition γ is the lowest for Eu(bta)$_3$L$_2$, and the largest for Ho(bta)$_3$L$_2$.

Fluorescence spectra of the complexes are shown in Fig.4. For Eu(bta)$_3$L$_2$, There are strong and sharp emission bands from $^5D_0$ of Eu^{3+} at 580, 591, 615, and 652 nm. For La(bta)$_3$L$_2$, there is a weak and broad emission band in the region of 450-600 nm, which is attributed to fluorescence of the ligand. As for Ho(bta)$_3$L$_2$, its fluorescence is too weak to be detected in the visible and near infrared region.

It is generally accepted that the intramolecular energy transfer from the ligand to lanthanide ion occurs from the lowest triplet state energy level of the ligand to the resonance energy level of lanthanide ion, which explains the excellent fluorescence property of lanthanide chelates. The energy transfer efficiency of lanthanide complexes depends mainly on the two energy transfer
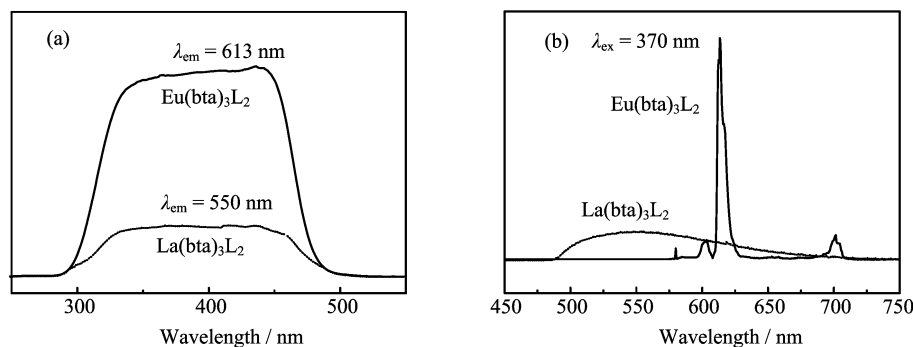
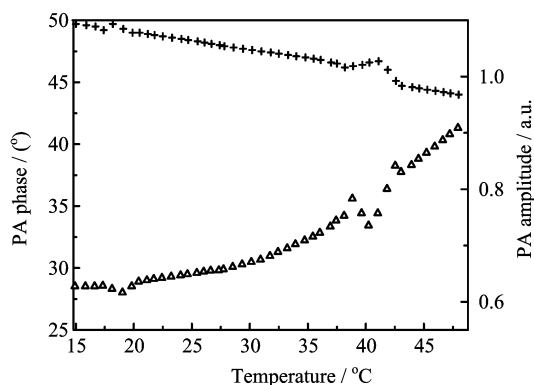FIG. 4 Excitation (a) and emission (b) spectra of Eu(bta)$_3$L$_2$ and La(bta)$_3$L$_2$.

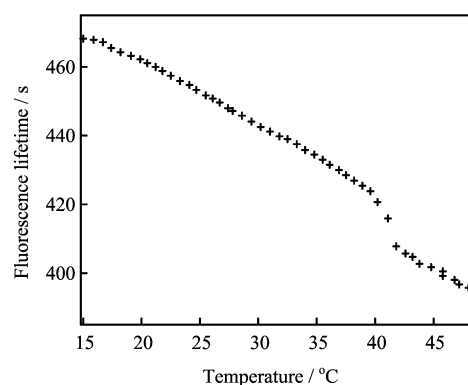FIG. 5 Dependence of PA phase and PA amplitude on the temperature for Eu(bta)$_3$L$_2$.

FIG. 6 Dependence of fluorescence lifetime on the temperature for Eu(bta)$_3$L$_2$.

processes, one of which is from the lowest triplet state of organic ligand to the resonant level of lanthanide ion through the resonant exchange interaction. The other process is the inverse energy transfer by the thermal de-excitation mechanism.

For Eu(bta)$_3$L$_2$ the excitation spectrum is in the region of the ligand absorption, which confirms that there is an efficient energy transfer process from the ligand to Eu^{3+}. Because of the intramolecular energy transfer process from the ligand to Eu^{3+}, following by radiative transitions to the ground state, Eu(bta)$_3$L$_2$ complex has the lowest probability of nonradiative transition γ [31]. For Ho(bta)$_3$L$_2$, all the energy absorbed by the ligand relaxes through nonradiative transitions, so Ho(bta)$_3$L$_2$ has the largest probability of nonradiative transition. For La(bta)$_3$L$_2$, La^{3+} has no excited states below the lowest triplet state of ligand (21600 cm^{-1}). The energy absorbed by the ligand can not transfer to La^{3+}, but relaxes through its own lower energy levels, which results the weak ligand emission. The result of fluorescence spectra is coincident with PA spectra.

B. Study of phase transitions of europium complex by PA and FL spectra

It is interesting to study the change of physical and chemical properties upon phase transions for liquid

crystalline lanthanide complexes, a promising class of photoelectric functional materials. For Eu(bta)$_3$L$_2$, its PA amplitude and phase variations with temperature are shown in Fig.5, together with the fluorescence lifetime of Eu^{3+} in Fig.6 for comparison.

The fluorescence lifetime decreases continuously as temperature increases. The deviation of lifetime at phase transition around 40 °C is due to a less efficient quenching of the excited states of Eu^{3+} in SmA phase compared to in liquid phase. It was shown earlier by Bünzli and coworkers that the melting point can be detected by luminescence lifetime measurements [8]. However, our work indicates that the clearing temperature can also be detected by this method. 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 Fig.5, the PA phase shows a gradual decrease, while PA amplitude shows an increase as the temperature increases. The increase of PA amplitude is attributed to both the increase of probability of nonradiative transition γ (thermal quenching of fluorescence of Eu^{3+}) and the change of thermal property of the sample. PA phase can be expressed as follows for lanthanide

complexes [32],

$$\phi = \tan^{-1}(\omega\tau) + \tan^{-1}\left(1 + \frac{2}{\beta\mu_s}\right) \qquad (2)$$

where ω is the modulated frequency, τ is the relaxation time, and β is the absorption coefficient of the sample. For $Eu(bta)_3L_2$ with the conjugated π electron ligand, $\beta > 10^5$ cm^{-1} and $1/\beta\mu_s \to 0$, PA phase then has the form,

$$\phi = \frac{\pi}{4} + \tan^{-1}(\omega\tau) \qquad (3)$$

Because the efficient energy transfer from the ligand to Eu^{3+} makes the lifetime of ligand shorter, the relaxation time τ is mainly determined by the lifetime of Eu^{3+} (in the order of milliseconds). The PA phase variation is consistent with the change of lifetime of Eu^{3+}. As the lifetime of Eu^{3+} decreases, PA phase shows a corresponding decrease. Upon phase transitions from glass state to SmA phase to at 18 °C and SmA phase to liquid to at 40 °C, a marked increase of PA phase and decrease of PA amplitude are observed. The sudden variations are coincident with the theoretical prediction of PA signal change during a reversible first-order phase transition, when the latent heat involved should be taken into consideration [33].

For $Eu(bta)_3L_2$, one phase transition from SmA to liquid state is observed by fluorescence lifetime measurement, but no deviation of the lifetime can be seen at the other transition from glass state to SmA phase. However, both the two phase transitions can be clearly monitored by nonradiative transitions through PA phase or amplitude technique. Additionally, in the case of photoacoustic saturation, PA amplitude has the advantage that it is independent of the optical absorption change of the sample, thus can avoid the influence of sample fluidity during heating or cooling, which limits the application of fluorescence intensity measurement in phase transition characterization.

IV. CONCLUSION

$Ln(bta)_3L_2$ (Ln^{3+}: La^{3+}, Eu^{3+}, and Ho^{3+}; bta: benzoyltrifluoroacetonate; L: Schiff base) liquid crystalline complexes were synthesized. Photoacoustic (PA) spectroscopy is used to study physicochemical properties of the liquid crystalline metal complexes. It was found that PA saturation effect occurs in the region of ligand absorption. PA spectra indicate that the probability of nonradiative transition γ is the lowest for $Eu(bta)_3L_2$, and the largest for $Ho(bta)_3L_2$. Fluorescence measurement turns out to be complementary to the PA spectra. The results are interpreted based on energy structures of the complexes. For $Eu(bta)_3L_2$, one phase transition from SmA to liquid state is observed by fluorescence lifetime measurement, while two phase transitions can

be clearly monitored by both PA phase and amplitude techniques. In the case of photoacoustic saturation, PA amplitude has the advantage that it is independent of the optical absorption change of the sample, thus can avoid the influence of sample fluidity during heating or cooling. The results show that PA technique may serve as a new tool for investigating the spectral properties and phase transitions of liquid crystals containing metal ions.

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