Studies on the Photoluminescence of a Novel Europium (III) Complex in Solution

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Abstract— The novel ternary europium(III) complex is synthesized. The photophysical sensitization process involves an energy transfer from functional hemicyanine (aminostyrylpyridinium) cation. The sensitization mechanism follows the Förster, which is significantly different from the Dexter, the most commonly used energy transfer mechanism from ligand. When the complex is dissolved in a variety of solvents (acetone, dimethylformamide, ethanol and acetonitrile), a remarkable solvent effect is observed. The emission intensity of europium(III) complex in acetonitrile is much stronger than that in other solvents. The solvent effect on the photophysical properties is studied. The result indicates that the solvent influences the emission intensity by aid of many factors not only polarity.

1. INTRODUCTION

Lanthanide ions and their coordination complexes have been attracting considerable attention owing to their unique optical properties, such as large stokes shifts, high color purity and long luminescence lifetimes [1, 2], which gives rise to many potential applications, including biological imaging [3, 4] and medical diagnostics [5, 6]. In recent years combining the advantages of both lanthanide and two-photon scanning microscopy, two-photon sensitized luminescence of lanthanide complexes attracts great attention, which is in favor of less-harmful labeling and deep-penetrating bioimaging applications. For one- and two-photon absorption induced luminescence of lanthanide complexes, the sensitization by the so-called antenna effect is frequently used to overcome the low molar absorption coefficient of the Laporte forbidden f-f transitions ($\varepsilon < 1\,\mathrm{L\ mol^{-1}\ cm^{-1}}$). The most popular sensitization of lanthanide luminescence is via an energy transfer from the triplet excited state of ligand [7–9], and the energy transfer follows Dexter mechanism [10].

Recently, the sensitization from charge transfer (CT) excited state of organic chromophore provides an alternative process resulting in a red-shift of the excitation wavelength [11, 12]. This process due to the design of antenna with donor-accetpor charge transfer transitions. Therefore, a novel europium(III) complex [Eu(tta)$_4$·DEASPI] is synthesized by using *trans*-4-[*p*-(*NN*-Diethylamino)styryl]-*N*-methyl-pyridinium (DEASPI) as counterion to combine with a europium (III)-thenoyltrifluoroacetonato(tta) moiety. The spectra of Eu(tta)$_4$·DEASPI also demonstrate that the sensitization is through CT states of DEASPI and follows the Förster mechanism.

The europium(III) complexes as luminescent probe are extensively applied in the aqueous solution, the solvent effect on the luminescence properties of complexes has to be taken into consideration [13–15]. However, the solvent effect on energy transfer via CT excited states in lanthanide complex has rarely been reported. In this manuscript, the study of the solvent effect on the photophysical properties of Eu(tta)$_4$·DEASPI is provided. It will be helpful for the synthesis and application of europium complexes.

2. EXPERIMENTAL

2.1. Syntheses and Structures of the Molecules

Nuclear magnetic resonance spectra were measured on a FX-90Q NMR spectrometer. Element analyses were performed on a Perkin 2400(II) autoanalyser. The melting pointsand decomposition temperatures were measured on Perkin Elmer DTA 1700 differential thermal analyzer and on a Perkin Elmer TGS-2 thermogravimetric analyzer at a heating rate of 20°C min^{-1} under nitrogen atmosphere, respectively.

Synthesis of 4-methyl-N-methyl-pyridinium iodide (A): Using a three-neck flask fitted with a stirrer, thermometer, and condenser, 4-picoline (1 equiv) and methyl iodide (1.1 equiv) were mixed in toluene. The solution was stirred at room temperature for 4 h and then refluxed for 30 min. After cooling, the solution was filtered and the solid was washed with ethyl ether. The pale yellow solid was dried under vacuum, yield 21.2 g (90%). ^{l}H NMR (DMSO-*ds*) δ 2.56 (s, 3 H), 4.20 (s, 3 H), 7.0 (d, 2 H), 8.90 (d, 2 H) ppm.

Synthesis of trans-4-[p-(N,N-Diethylamino)styryl]-N-methylpyridinium iodide (B): A mixture of A (1 equiv) and 4-(*N*,*N*-dimethylamino)-benzaldehyde (1 equiv) in dried ethanol was treated with piperidine and was refluxed for 4 h. The resulting suspension was cooled. The precipitate was filtered off. Yield (82%) and T_d 264.7°C. Purified by column chromatography on silica gel using ethanol as eluent. ^{1}H NMR (DMSO-d_6) δ: 8.67 (2 H, d, J 6.84 Hz), 8.04 (2 H, d, J 6.84 Hz), 7.91 (1 H, d, J 15.61 Hz), 7.58 (2 H, d, J 8.79 Hz), 7.12 (1 H, d, J15.63 Hz), 6.75 (2 H, d, J 8.80 Hz), 4.18 (3 H, s), 3.43 (4 H, q, 6.84), 1.13 (6 H, 6.84). Anal. calcd for $C_{18}H_{23}N_2I$: C 54.83, H 5.88, N 7.10, I 32.19; found: C 54.94, H 5.92, N 7.06, I 32.08.

Synthesis of trans-4-[p-(N,N-Diethylamino)styryl]-N-methylpyridinium tetrakis(α-thenoyltrifluoroacetonato) europium(III): to a mixture of B (1 equiv) and of HTTA (4 equiv) neutralized with aqueous ethanol-NaOH solution (4 equiv) was added dropwise of aqueous $Eu(NO_3)_3$ (1 equiv) under constant stirring. The resulting precipitate was filtered off. A nearly saturated solution of the precipitate in 95% ethanol was allowed to evaporate slowly, and after 24 h red powder was obtained. Anal. calcd for $C_{50}H_{43}N_2F_{12}O_8S_4Eu$: C 45.91, H 3.31, N 2.14, Eu 11.62; found: C 45.34, H 3.52, N 2.46, Eu, 11.24.

The formula of Eu(tta)$_4$·DEASPI used in this work is *trans*-4-[*p*-(*N*,*N*-Diethylamino)styryl]-*N*-methyl-pyridinium tetrakis (α-thenoyltrifluoroacetonato) europium(III). The anion $Eu(tta)_4^-$ is balanced in charge by the pyridine-cation DEASPI, which is close to europium ion through Coulombic interaction The three-dimensional structure of Eu(tta)$_4$·DEASPI is shown in Scheme 1. The anion $Eu(tta)_4^-$ whose eight ligand conjugated structure is formed by Eu^{3+} and the oxygen atoms of the four α-thenoyltrifluoroacetonato (HTTA). The cation DEASPI is used as one- and two-photon sensitizer for europium ion.

2.2. Methods and Instruments

The UV-vis absorption spectra were recorded by a UV-Vis-NIR scanning spectrophotometer (Shimadzu, model UV-3101PC). The fluorescent spectra were measured by a fluorescence spectrophotometer (Hitachi, model F-4500). The quantum-yield was measured by the standard comparison method [16], using Rhodamine 6G as the reference standard.

For the measurement of transient behavior, the excitation source is an OPA pumped by the third harmonic of a mode-locked Nd : YAG laser (Continuum, PY61C-10) with a repetition rate of 10 Hz. The tunable range of this OPA is from 760 to 1090 nm. An optical multi-channels analyzer was used as the recorder. The ultrafast laser beam passed firstly through a couple of Nicol's prisms, which were used as an attenuator to obtain a tunable excitation intensity. The laser beam was focused into the sample by a lens of $f = 5$ cm. The fluorescence was collected by a telescope system at the perpendicular direction of the pump beam. Before the input slit of optical multi-channels analyzer, a HA30 filter was inserted for cut off the excitation laser

The TPA cross section δ was determined by comparing its TPA induced up-conversion fluorescence to that of Rhodamine 6G according to Eq. (1) [17]:

$$\delta = \delta_{cal} \frac{F n c_{cal} \phi_{cal}}{F_{cal} n_{cal} c \phi} \tag{1}$$

where, ϕ is the fluorescence quantum yield, c is the concentration, n is the refractive index, and F is the intensity of up-conversed fluorescence. The cal subscript refers to the standard reference solution.

3. RESULTS

The UV-vis absorption spectra of DEASPI (in solid) and Eu(tta)$_4$·DEASPI (in dash) in acetonitrile at the concentration of 1×10^{-5} mol L^{-1} are shown in Fig. 1. In the absorption spectrum of Eu(tta)$_4$·DEASPI, two absorption bands around 340 nm and 485 nm are observed. Among them, the ultraviolet absorption band is attributed to tta [18], and the blue one results from DEASPI. In the spectral range of 600–900 nm, there is no intrinsic linear absorption for the two molecules.

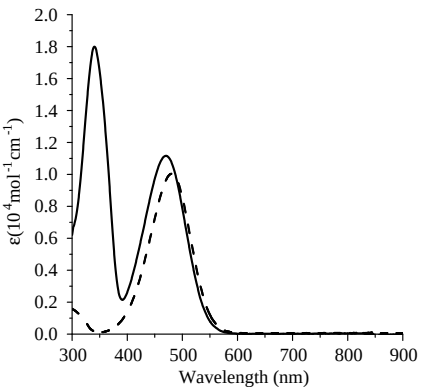

Figure 1: The UV-vis absorption spectra of $Eu(tta)_4$·DEASPI (in solid) and DEASPI (in dash) in acetonitrile (1×10^{-5} mol L^{-1}).

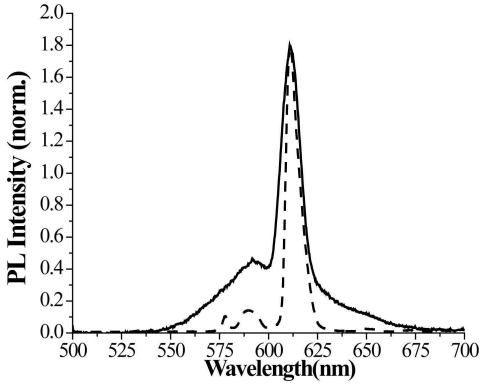

Figure 2: Fluorescent emission spectra of $Eu(tta)_4$·DEASPI, solided line: $\lambda_{ex} = 485$ nm; dashed line: $\lambda_{ex} = 340$ nm.

The fluorescent spectra of $Eu(tta)_4$·DEASPI under 485 nm excitation are measured (as shown in Fig. 2). In the fluorescent spectra of $Eu(tta)_4$·DEASPI (dashed line for $\lambda_{ex} = 340$ nm, solided line for $\lambda_{ex} = 485$ nm), the distinct emission peak of 611 nm corresponds to the hypersensitive transition $^5D_0 \rightarrow ^7F_2$ of Eu^{3+} [19]. Under 340 nm excitation, there are only emission peaks of Eu^{3+} in the emission spectrum. Under 485 nm excitation, the emission spectrum of $Eu(tta)_4$·DEASPI consists of not only emission band of DEASPI but also the characteristic emission peak $^5D_0 \rightarrow ^7F_2$ of Eu^{3+}. 485 nm corresponding to the absorption peak of DEASPI, therefore, it can be concluded that the fluorescence of Eu^{3+} in $Eu(tta)_4$·DEASPI under 485 nm excitation is sensitized by CT states of DEASPI rather than *f-f* transitions of Eu(III).

$Eu(tta)_4$·DEASPI is dissolved in acetone, DMF, ethanol and acetonitrile, respectively. The complex exhibits effective europium(III) luminescence in acetonitrile, however in other solutions the fluorescence intensity decreases obviously. For dissolved in different solvents, the emission intensity of $Eu(tta)_4$·DEASPI is in the order of acetonitrile>DMF>acetone>ethanol. This ordering is not in accordance with polarity of solvent, indicate that solvent influence the fluorescence not only by polarity. Furthermore, the emission peak of DEASPI shift with different solvents, indicate that the solvent influence the CT states of DEASPI. Detailed analysis of solvent effect is provided in following Discussion.

4. DISCUSSION

DEASPI is a stilbene-type chromophore with high thermal stability and photostability, and it has donor-π-bridge-acceptor (D-π-A) character [20]. The D-π-A structure is a typical charge-transfer structure. In DEASPI, the nitrogen of the pyridinium group loses an electron and makes the group prone to attract electrons from the amino group on another end of the DEASPI. i.e., pyridinium group plays as an acceptor and the amino group plays as a donor. The inherent electrical dipole moment appears in DEASPI. A solvent cage is formed when solvent molecules cover the outermost layer of DEASPI, which increases the geometrical distance between the cation and anion. The electronegativity in DMF and acetone is stronger than acetonitrile, which gives rise to more prominent solvent cage effect and decreases the fluorescence.

In addition, it is well known that 'hypersensitive transitions' is a unique property for lanthanide ions, which is very sensitive to the surrounding environment. These transitions are described by the term 'pseudo-quadrupole transitions', they obey the selection rule $|\Delta J| \leq 2$, $|\Delta L| \leq 2$, $\Delta S = 0$ [21]. According to Binnemans [22], the hypersensitive transitions are evidently influenced by Judd-Ofelt intensity parameter Ω_2, which is determined by the asymmetry of the coordination environment of the lanthanide ion. Our previous study indicates that the increase of the asymmetry leads to the enhancement of hypersensitive transitions [23]. In this manuscript, the hypersensitive transition $^5D \rightarrow ^7F_2$ (612 nm) was significantly affected by the solution medium. It is because Eu(III) can provide nine coordination bonds, there are unsaturated for Eu(III) in $Eu(tta)_4$·DEASPI, as illustrated in Fig. 3. In this case, solvent molecules can take part in the coordination to the Eu^{3+}, such as water molecule can take part in the coordination to the Eu^{3+} ions [24]. Compared with other organic solutions, acetonitrile provides more asymmetry of the coordination environment of

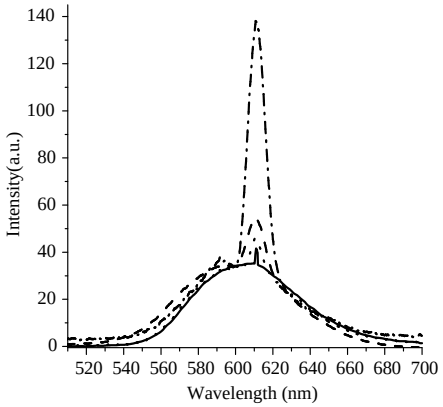

Figure 3: The emission spectra of $Eu(tta)_4$·DEASPI in acetone (in dot), DMF (in dash), ethanol (in solid) and acetonitrile (in dash-dot) at 485 nm excitation.

Eu(III) ion. Therefore, the emission intensity of transition $^5D \rightarrow ^7F_2$ is much higher than in other solutions.

5. CONCLUSION

In conclusion, the prominent solvent effect on the optical properties of $Eu(tta)_4$·DEASPI is analyzed: Firstly, the formation of solvent cage changes the geometrical distance between the donor and the acceptor; Secondly, the solvent molecules take part in the coordination environment of Eu(III) ion, which changes the emission intensity of hypersensitive transition $^5D \rightarrow ^7F_2$. All of factors lead to the solvent effect is remarkable in this kind of europium complex.

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