

自极化效应对稀土掺杂 聚合物激发和发射光谱的影响*

酒红芳^{a, b}, 苏伟^b, 吉耀辉^b, 张其锦^{a, b, **}, 赵辉^b, 梁浩^b, 陈彪^b

(a. 中国科学院结构分析重点实验室; b. 中国科学技术大学高分子科学与工程系, 合肥 230026)

摘要: 合成并用 FT-IR 和元素分析方法表征了 $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$. 对不同浓度的稀土络合物溶液和掺杂聚合物的激发光谱和发射光谱进行了测定和研究. 结果发现在溶液和固体介质中都存在着溶质间的相互作用. 这种自极化相互作用影响包括两个方面: 有机配体的吸收光谱出现红移现象; 稀土离子的对称性的变化. 自极化相互作用导致分子内的电荷分布变化, 改变了激发态和基态间的能量, 激发光谱出现红移. 在低浓度时, 介质的性质对红移影响较大, 高浓度时, 介质的影响变小. 还讨论了各种因素对稀土掺杂体系的荧光性质的影响.

关键词: 自极化; 聚甲基丙烯酸甲酯; $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$; 溶剂化; 荧光

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The Effects of Self-polarization on Emission and Excitation Spectra of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ Doped in Poly(methyl methacrylate)*

Jiu Hongfang^{a, b}, Su Wei^b, Ji Yaohui^b, Zhang Qijin^{a, b, **}, Zhao Hui^b, Liang Hao^b, Chen Biao^b

(a. Structure Research Laboratory, Chinese Academy of Sciences, b. Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026)

Abstract $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ was synthesized and its structure was characterized by FT-IR and the elementary analysis. Emission and excitation spectra of rare earth complex in solution of methyl methacrylate and in solid matrix of poly(methyl methacrylate) were measured, and the experiments confirmed that an intermolecular solute-solute interaction occurred for rare earth complex in solution and solid matrix, which resulted in self-polarization. Influence of the self-polarization includes two aspects: one is the red-shift in absorption of organic ligands, and another is the symmetric changing of Eu^{3+} site in the complex. The self-polarization effect also causes a stretching of molecular bonds and shifting of charging distribution on molecules, altering the energy difference between the ground and excited states of the solute. At low concentration, the host matrix has effect on this phenomenon; but above certain concentration the difference in host matrix disappears. The other factors are also discussed impacting fluorescence property of rare earth doped systems.

Keywords Self-polarization, $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$, Poly(methyl methacrylate), Solvation, Fluorescence

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** Corresponding author, E-mail: zqjin@ustc.edu.cn Received 16 April 2003; in final form 9 July 2003.

1 Introduction

With the high fluorescence yield and the strong solubility in different solvents, organic europium complexes, such as Europium-tris(dibenzoylmethane)-1,10-phenanthroline complex ($\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$), have gained its popularity as an excellent luminophor since it was synthesized firstly in 1963^[1-5]. The high fluorescence yield is thought to be caused by energy transferring from organic ligands to Eu^{3+} as the organic ligand has higher absorption cross section. This characteristic process includes two distinguishable aspects: one is absorption by organic ligands; and the other is emission by rare earth center ions, although emission can also be obtained by exciting the ion directly. At the same time, detailed relationship between mechanism of photoluminescence and characteristic structure of rare earth complexes has also attracted much attention recently, such as narrow bandwidth of luminescence from europium complex^[6], and polarized europium emission^[7]. It has been found that there is no crystalline phase in the blend of rare earth complex and polymer within the concentration of 30%, and the emission of the material is dependent on the microstructure of rare earth complex. For example, tensile drawing can cause orienting of $\text{Eu}(\text{dbm})_3\text{phen}$ doped in polymer, and the fluorescence from the Eu complex is polarized^[7]. On the other hand, because in the complex the chelating bond is polar and relatively easy to distort and the ligand has much larger volume than the rare earth ion, self-polarization can take place easily of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in solutions or solid matrices. This effect can make the symmetry of the Eu^{3+} site change, characterizing its excitation and emission spectra.

In a dielectric matrix, the local electric field at the position of a constituting atom or molecule is different from macroscopic one, due to the influence of surrounding atoms (molecules) that form the dielectric^[8]. This well-known difference between local and macroscopic field leads to so called " solvation effect ", which is considered as a physical polarization of the relevant molecular states of the solute due to the presence of the solvent^[9] and applied to explain emission

and absorption spectra of different systems, like laser dye in solvents of different dielectric susceptibility^[10], rare earth complexes in a series of alcohol solutions^[11] and some polar laser dyes in solid hosts^[12,13]. For solutions (liquid or solid) containing only one solute, the polarization can also take place when the concentration of solute changes, which is called self-polarization caused by a physical perturbation between solutes. However, works mentioned above mainly concerns solutes with different matrices of different polarity, no matter in solutions or solid matrices. Self-polarization of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in a solution or solid matrix has not been reported.

In this work, we determined emission and excitation spectra of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in solutions and solid matrices, respectively. Changes in the spectra were analyzed in terms of solvation effect. It is found that self-polarization took place, which could affect the symmetry of the Eu^{3+} site in the rare earth complex, and then influence the photophysical properties of the complex profoundly.

2 Experimental

2.1 The synthesis of the rare earth complex with DBM

Dibenzoylmethane was synthesized by the Claisen condensation method. The purified acetophenone (0.051 mol) and ethyl benzoate (0.41 mol) were mixed together and heated to 140°C. The sodium ethoxide solution was prepared by adding pure sodium (87 mmol) into dry ethanol and dropped into the heated mixture when stirring under vacuum. After the solution, added the reaction ended when no more ethanol backflowed. After the mixture was acidified with H_2SO_4 solution, the product was extracted with ether, dried with anhydrous Na_2SO_4 , distilled at 120°C and recrystallized twice in methanol solution. $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ was synthesized according to the procedure reported before^[11]. The final product was recrystallized in acetone/petroleum ether (2:1), and the IR spectrum of the product shown in Fig. 1. Absorptions corresponding to each functional group can be found in the spectrum, such as C=O group at 1595.1 cm^{-1} , phen

group at 1549.9 cm^{-1} and C = C group in the enol structure at 1517.9 cm^{-1} , showing the product is $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$. The composition of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ was obtained by elemental analysis as : experimental/theoretical values : C : 68.14/68.33 , H : 4.07/4.1 , N : 2.78/2.80 , which further shows the purity of the product.

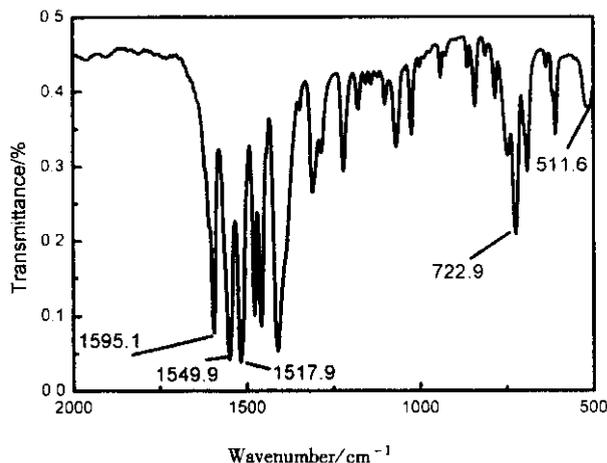


Fig. 1 The IR spectrum of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in KBr

2.2 Preparation of samples of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ doped PMMA

A certain amount of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ was dissolved in MMA solution. After the initiator AIBN (2,2'-azo-bis-iso-butyronitrile) was added into it, the MMA solution prepolymerized at 80°C and then polymerized at 40°C until solidified. The samples for measurement were made with thickness of 5 mm and the diameter of 10 mm from the polymer obtained above.

2.3 Measurements

The IR spectra of pure $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ was measured on a 170 SX Nicolet fourier transform infrared spectrophotometer using the KBr pellet technique. The elementary analysis of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ was carried out with an Elementar Vario EL-III elementary analyzer. The emission spectra of the samples were obtained on an RF-5301PC spectrofluorophotometer with the excitation and emission slit at 0.2 nm. The excitation spectra were obtained with the same equipment by monitoring emission at 613 nm. All the spectra were measured at the room temperature and in the range of 300 ~ 700 nm.

3 Results and discussion

It is well known that^[14,15] transitions between different energy levels are governed by the parity selection rule, which forbids electronic (electric-dipole) transitions between levels with the same parity, such as 4f-4f transitions of rare earth ions. That is to say, if the site which a rare-earth ion occupies has inversion symmetry (the components of the ligand-field it is in are even), electric-dipole transitions between its 4f energy levels are strictly forbidden as the parity selection rule states. In the case, only magnetic-dipole transitions which obey the selection rule $\Delta J = 0, \pm 1$ ($J = 0$ to $J = 0$ forbidden) occur. However, when the rare-earth ion occupies a site without inversion symmetry, the uneven ligand-field components mix a certain amount of opposite-parity wave functions into 4f wave functions. Then, the intraconfigurational electric-dipole 4f transitions are no longer forbidden, called the forced electric-dipole transitions. Fig. 2 shows fluorescence spectra of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in solution of methyl methacrylate (MMA) and doped in poly(methyl methacrylate) (PMMA) under excitation of light at 466 nm, respectively. Corresponding emission of the forced electric-dipole transition is located at 613 nm. From the fluorescence spectra shown in Fig. 2 of the liquid and the solid states it can be seen that there is no change in positions of emission peaks. It can be known from this result that the interior energy levels of Eu^{3+} in the complex does not change. This is due to 4f electrons of rare earth ions which are well shielded from external charge in 5s and 5p shells. Different phenomena are observed for organic dyes, in which peak shifts are found^[16]. On the other hand, the strength of those transitions with $\Delta J = 0, \pm 2$ is also dramatically influenced by the ligand-field effect. The lower symmetry the ligand-field has, the stronger the electric-dipole transitions are influenced and the fluorescent intensities of the emissions originating from them. In order to find out the difference in effect of ligand-field between the liquid and the solid system, it is no use comparing the fluorescence strength at 613 nm in Fig. 2 with each other directly because the unit of vertical axe is relative.

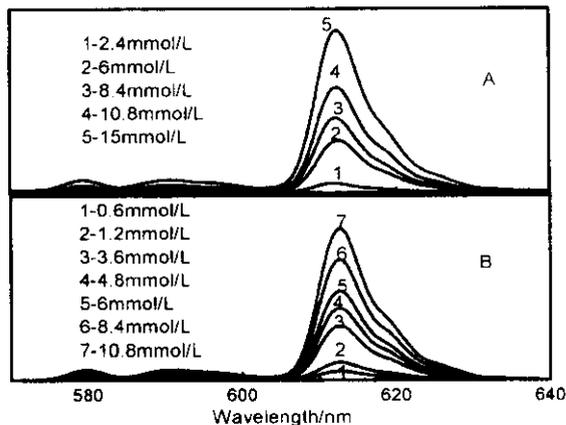


Fig. 2 The fluorescence spectra of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ with different concentration in PMMA (A) and in MMA solution (B) excited by light at 466 nm

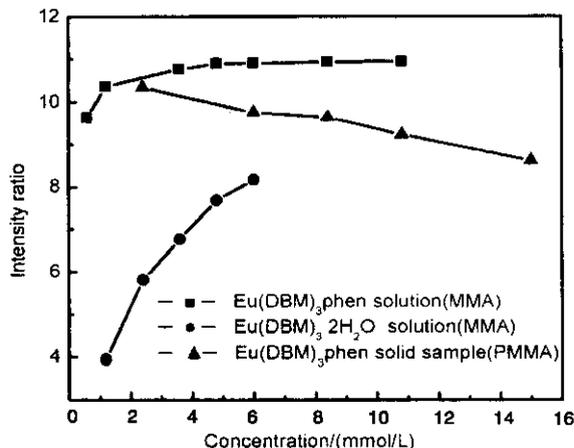


Fig. 3 Relationship between the intensity ratio (613/591 nm) and the concentration of Eu^{3+} in various systems

For $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$, the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition (corresponding to 591 nm in the emission spectrum), which is categorized to the magnetic-dipole transition ($\Delta J = \pm 1$), is independent of the surrounding environment around Eu^{3+} given by the ligand-field of the complex; the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition (613 nm in the emission spectrum), which is categorized to the electric-dipole transition ($\Delta J = \pm 2$), is connected mainly with the environment. Therefore, the ratio of R (R is the ratio value of fluorescence intensities: ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$) can give valuable information about environment changes around Eu^{3+} [17]. When R -value is larger, Eu^{3+} occupies a site of lower symmetry, while R -value is smaller, Eu^{3+} occupies a site of high symmetry. Fig. 3 shows relationship between R -value and concentration of Eu^{3+} in the solutions and the solid matrices. It can be seen from Fig. 3 that R values for $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in solution of MMA increases along with increasing of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ concentration, and at lower concentration, the site of Eu^{3+} occupied is of higher symmetry. In order to further investigate this self-polarization effect, $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$ is synthesized and used to substitute $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in the experiment. The result is shown also in Fig. 3. The absolute R -value for $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$ is lower than that for $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$. There are several reasons accounting for this, such as fluorescence quenching-caused by H_2O existing molecules in the complex, and

more symmetry Eu^{3+} sites in $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$ (D4) than those in $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ (D2) because $\text{Eu}(\text{DBM})_3 \cdot 2\text{H}_2\text{O}$ has two H_2O molecules coordinated to Eu^{3+} in two directions of both sides of the plane composed of three classic bidentate coordinating ring structure. However, there is a same changing tendency in the relationship between R -values and concentrations observed in Fig. 2 for two solution systems.

Different from the solution system, for the emission of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ doped in PMMA, a contrast tendency can be observed: R -value decreases along with the increasing of the concentration, although similar R exists for $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ solutions in MMA and in PMMA, respectively, at low concentration. This means the symmetry of the site of Eu^{3+} increases in PMMA matrix with increasing of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ concentration. Polymer matrix is of soft elastoplasticity, and the polymer chains will enforce the molecules doped in it. This phenomenon has been observed in recent work about Eu^{3+} complex doped in polyethylene under tensile drawing [7]. Under drawing polymer chains tend to align along the direction of the drawing, forming a part ordering morphology, which would enforce molecules doped in it with an asymmetric way. Without drawing and because of the homogenous amorphous structure of PMMA, the enforcement from polymer chains is symmetric, which can balance the asymmetric effect of self-polarization and make R -value decrease when $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ concentration

increases.

Besides effect of self-polarization on the symmetry of Eu^{3+} site, electric energy levels of organic ligands will be also affected by the self-polarization because each organic ligand is composed of aryl group, which contains conjugated double bonds and is easily polarized. Fig. 4 shows excitation spectra of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in solutions of MMA and doped in PMMA. The red shift of absorption peak for ligands can be seen for each sample when Eu^{3+} concentration increases. It is worthy to note that the peak at 466 nm, which corresponds to the absorption of $\text{Eu}^{3+} ({}^7\text{F}_0 \rightarrow {}^5\text{D}_2)$, is not changed, and this result is identical with one described above: the self-polarization will not affect interior energy levels of Eu^{3+} .

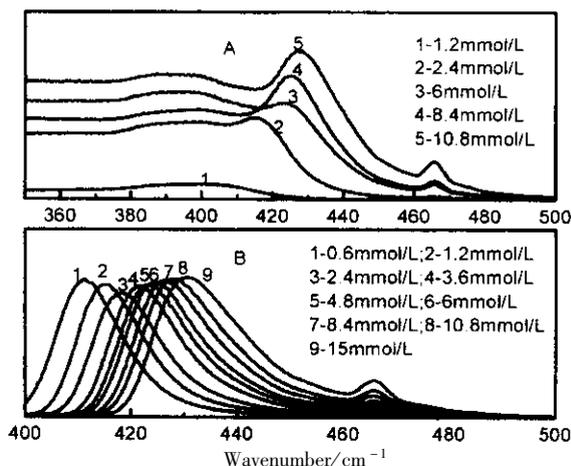


Fig. 4 The excitation spectra of the PMMA sample doped with $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ (A) and the solutions (B) of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in MMA with different Eu^{3+} concentration under monitoring emission at 613 nm

For absorptions of the ligand at about 411 nm, the similarity of spectral widths and magnitudes of the peak shifts in solution system (Fig. 4B) suggest that $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ suspended in the matrix undergoes an energy shift due to self-polarization. That is, as concentration of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ increases, the distance between nearest neighbor $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ molecules decreases, thereby increasing the local electric field. This field perturbation tends to disperse the charge of the ligands, and to red-shift the $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ excitation spectrum. For the sample of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$

doped in PMMA, the same red-shift tendency can be found in Fig. 3A, although the absorption of the ligand is not very clear at the concentration of 1.2 mmol/L Eu^{3+} .

At the low concentration range, the self-polarization is related with the host materials. In Fig. 5, it can be seen that absorptions of organic ligands in MMA solution are in longer wavelength and less affected by the self-polarization than absorptions of the ligands in PMMA. In addition, at the low concentration range absorption from the solution is always red-shifted from that of the solid sample since the local field is largely determined by the host. However, for Eu^{3+} concentration above 9 mmol/L (corresponding to about 1% of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$), and for absorptions, both of the liquid and the solid systems, the red-shift is independent of the host material as the local field is overwhelmingly determined by the highly polarized $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ molecules.

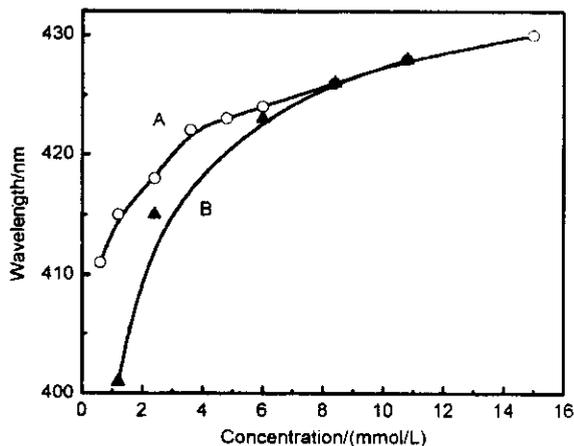


Fig. 5 Relationship between absorption wavelength and concentration of Eu^{3+} in the solutions of MMA (A) and in the PMMA (B) sample

In the solid sample and over a large volume, the net $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ dipole moment averages to zero since the molecules in the solid solution should be randomly distributed. However, considering that the dipole field decreases as $1/r^3$ where r is the distance between dipoles, only those molecules nearest to the center molecule contribute to the local electric field and hence influence the absorption spectrum. It can be de-

duced from this that polar dopants of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ tend to aggregate in PMMA that minimize the overall energy of the system, causing the spectra red-shift.

4 Conclusion

In summary, self-polarization has been observed in both of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ solution in MMA and $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ in the solid solution of PMMA. Influence of the self-polarization on photophysical properties of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ includes two aspects: one is the red-shift in absorption of organic ligands, and the other is the symmetric changing of Eu^{3+} site in the complex. For the solid sample, more symmetric sites can be observed as the concentration increasing since polymer chain can give the complex a symmetric force. At low concentration range, the red-shift caused by the self-polarization in absorption is dependent on the host material. However, for Eu^{3+} concentration above 9 mmol/L (corresponding to about 1% of $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$) the red-shift of absorptions is independent of the host material as the local field is overwhelmingly determined by the highly polarized $\text{Eu}(\text{DBM})_3 \cdot \text{Phen}$ molecules. The self-polarization does not affect the interior energy levels of Eu^{3+} because those energy levels are well shielded from external charge in 5s and 5p shells. The only changes in symmetry of Eu^{3+} site can be attributed to the asymmetric interactions caused by the self-polarization.

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