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Luminescence and structure of $Eu(DBM)_3Phen$-doped vesicles composed of amphiphilic PNIPAM-b-PAzoM

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ABSTRACT

$Eu(DBM)_3Phen$-(DBM = dibenzoylmethide; Phen = 1,10-phenanthroline) doped vesicles were obtained through the self-assembly of poly (*N*-isopropylacrylamide)-b-poly{6-[4-(4-methylphenyl-azo) phenoxy] hexylacrylate} (PNIPAM-b-PAzoM) in the presence of $Eu(DBM)_3Phen$ in the H_2O/THF solution (50/50 vol.%). When the water content of the vesicle solution increased from 50 vol.% to 98 vol.%, the characteristic luminescence of $Eu(DBM)_3Phen$ at 612 nm appeared. Moreover, with the increased water content, luminescence intensity gradually increased by about 200 times from 50 vol.% to 98 vol.% of the water content. A further detailed study on this phenomenon has shown that azobenzene units and $Eu(DBM)_3Phen$ were located in the shell of the vesicle, such that when more water was added into the solution, azobenzene units aggregated to a larger extent as demonstrated by their subsequent absorption-shift. From our results, we find that it is the more hydrophobic environment within the shell that has made the fluorescence of $Eu(DBM)_3Phen$ stronger. Such an environment hinders the interactions between water molecules and the complex. In this study, a model is presented for the azobenzene-containing vesicle in order to explain this phenomenon.

1. Introduction

The emission of lanthanide organic complexes, such as $Eu(DBM)_3Phen$, usually results from the "antenna effect". This is defined as a light conversion process via an absorption-energy transfer-emission sequence involving distinct absorption by a ligand (light collector) and emission by a metal ion. In 1993, this process has been reviewed by Sabbatini et al. [1] who stated that the luminescence of lanthanide ions is determined by their local environment. This environment includes the host where they exist and the quenching molecules around them. Since then, numerous studies have been performed on the luminescence properties of lanthanide organic complexes. These are embedded into different matrixes such as sol–gel glasses [2–6], inorganic–organic hybrid materials [7–11], liquid crystals [12–14], and polymers [15–18]. The results suggest that the construction of the local environment around the lanthanide complex plays a role in controlling the luminescence properties of the material. This fact has attracted increasing interest in polymer science and technology.

Polymer vesicles and other hollow spheres have numerous potential applications in fields such as micro-reactors, microcapsules, and drug delivery systems, in which many groups have studied such structures in the past few years [19–23]. Polymer vesicles are usually obtained through the self-assembly of amphiphilic diblock copolymers, because they can offer both hydrophobic and hydrophilic chain segments. Domains formed by hydrophobic chains or hydrophilic chains can be used to incorporate organic or inorganic complexes, respectively, thereby acquiring functional vesicles directly. In the present work, the vesicle was used as a support for $Eu(DBM)_3Phen$. Enhanced luminescence of $Eu(DBM)_3Phen$ in vesicles was observed when the water content increased in the solution containing such vesicles. A model for the vesicle is presented to explain this phenomenon.

2. Experiment

2.1. Materials

$Eu(DBM)_3Phen$ [24] and poly(*N*-isopropylacrylamide)-b-poly{6-[4-(4-methylphenyl-azo)phenoxy]hexylacrylate}(PNIPAM

Abbreviations: PNIPAM-b-PAzoM, poly(*N*-isopropylacrylamide)-b-poly{6-[4-(4-methylphenyl-azo)phenoxy] hexylacrylate}; PNIPAM-SC(S)Ph, poly (*N*-isopropylacrylamide) capped with dithiobenzoate; PPDTB, 2-phenylprop-2-yl dithiobenzoate; THF, $Eu(DBM)_3Phen$ (DBM = dibenzoylmethide Phen = 1,10-phenanthroline) tetrahydrofuran.

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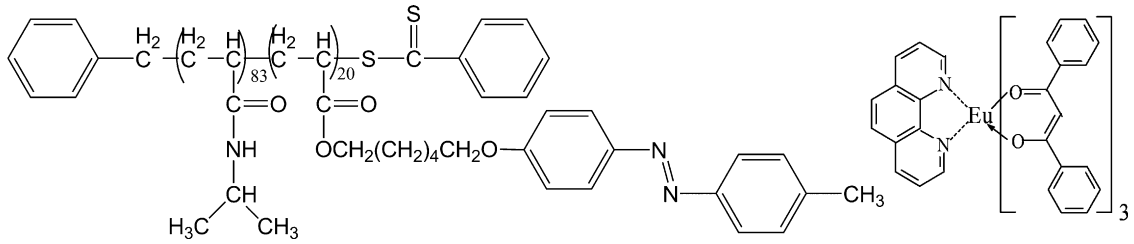

Fig. 1. Chemical structures of PNIPAM-b-PAzoM and Eu(DBM)$_3$Phen.

-b-PAzoM) were synthesized according to the procedure used in previous studies [25]. In order to obtain vesicles from the copolymer, the ratio of the two kinds of segments were controlled at 83(PNIPAM)/20 (PAzoM) (Fig. 1). Tetrahydrofuran (THF) was refluxed over sodium for 24 h, and then distilled prior to use. Other chemicals were used without further purification, unless otherwise indicated. Meanwhile, the copolymer was obtained by RAFT polymerization, in which the macro-RAFT agent, poly (*N*-isopropylacrylamide) capped with dithiobenzoate (PNIPAM-SC(S)Ph), was initially synthesized at 70 °C, using 2-phenylprop-2-yl dithiobenzoate (PPDTB) as the chain transition agent in the THF solution. Afterwards, it was reacted by using hydrophobic azobenzene monomers under the same reaction condition. In this way, by carefully controlling reaction time, PNIPAM-b-PAzoM (83(PNIPAM)/20 (PAzoM)) was obtained with M_n = 14300 and M_w/M_n = 1.06 [25]. Eu(DBM)$_3$Phen was synthesized according to the method used previously [24]. From the structure presented in Fig. 1, it can easily be seen that Eu(DBM)$_3$Phen is hydrophobic because the Eu^{3+} ion is enwrapped by non-polar groups.

2.2. Preparation of Eu(DBM)$_3$Phen-doped PNIPAM-b-PAzoM vesicles in the solution

The self-assembly process was performed in the THF solution of the diblock copolymers and Eu(DBM)$_3$Phen by adding Milli-Q water at a rate of 5 μL/s, with constant stirring. The initial concentrations were 2.0 mg/mL and 6.4 mg/mL for the copolymer and the complex, respectively. At the desired H_2O/THF ratio, the addition of water was stopped, and the mixture was left to equilibrate for 24 h. Room temperature was maintained while this process was being carried out. Eu(DBM)$_3$Phen was originally thought to be in the shell of the vesicle because Eu(DBM)$_3$Phen was hydrophobic and existed in the hydrophobic phase. In order to clarify this, a detailed analysis on its structure will be discussed in a later section.

2.3. Diluting process of the vesicle solutions

The solution of Eu(DBM)$_3$Phen-doped PNIPAM-b-PAzoM vesicles in H_2O/THF, which was left to equilibrate for 24 h, was taken out in the amount of 0.2 mL for each sample. Each sample was then diluted with mixture solutions of Milli-Q water and THF, in which the water content was progressively increased to 50 vol.%, 60 vol.%, 70 vol.%, 80 vol.%, 90 vol.%, and 100 vol.%. Through the operation mentioned above, samples of the vesicle solution were obtained with each possessing a respective final water content of 50 vol.%, 59 vol.%, 69 vol.%, 79 vol.%, 88 vol.%, and 98 vol.%.

2.4. Equipment

A modified OLYMPUS IX-70 microscope was used to observe the polymer vesicles. The irradiation beam was focused onto a sample through a 100× (UPlan Apo, 100×, NA 1.35, OLYMPUS) oil immersion objective, which was also used for microscopic observation during the manipulation process of the sample. Images were taken by a CCD camera and then recorded on a computer. Samples were made by dropping a 0.2 mL vesicle dispersion into a glass cell (1.0 cm diameter and 2.0 mm thickness), after which the cell was sealed to prevent solvent evaporation.

The luminescence of the solutions of each vesicle was measured using a SHIMADZU RF-5301PC fluorophotometer, while the absorption of each solution was obtained through a UV–vis spectrophotometer (SHIMADZU UV-2550PC). Luminescence lifetime was measured on a Fluorolog-3-TAU steady-state/lifetime spectrofluorimeter.

Afterwards, ultrathin sections of the frozen dispersion containing the micro-vesicles were cut using a Leica 1900 M cryostat before being collected onto glass slides. Each section had a thickness of about 10 μm. The sections were then dried at room temperature and observed directly under an optical microscope.

3. Results and discussion

3.1. Self-assembly of PNIPAM-b-PAzoM and Eu(DBM)$_3$Phen in the solution

The chemical structures of PNIPAM-b-PAzoM and Eu(DBM)$_3$-Phen are shown in Fig. 1.

Both the copolymer and the complex are soluble in THF at room temperature. When water was slowly dropped into the PNIPAM-b-PAzoM and Eu(DBM)$_3$Phen solution in THF, a self-assembly process took place, and at H_2O/THF ratio of 50 vol.%, vesicles were obtained as previously reported [25]. Images of vesicles with micrometer scale are shown in Fig. 2a, from which it can be seen that the vesicle obtained is of a diameter found in the μm scale. This makes it possible to directly observe vesicle behavior using an optical microscope. Fig. 2b shows the luminescence from such vesicles under an excitation of light at 365 nm. The measurement of the luminescence spectra of the same sample was performed. The result showed that the strongest peak in the luminescence is located at 612 nm, the typical emission of which is from the $^5D_0 \rightarrow {}^7F_2$ transition of Eu(III) ion in Eu(DBM)$_3$Phen.

Furthermore, Fig. 2b also shows that luminescence comes from the vesicles themselves and not from the solution. From this direct observation, taking into consideration the hydrophobic property of Eu(DBM)$_3$Phen, it can be estimated that the complex would exist within the shell of the vesicle formed by the hydrophobic azobenzene contained in the copolymer chains. Strong ion luminescence intensity requires a non-aqueous environment for the lanthanide complexes, and along this line, an aqueous micellar solution is considered a very efficient medium, which allows both the solubilization of the complexes and the protection of the solution against non-radiative relaxation processes [26]. As such, it can be expected that such a vesicle structure would influence the luminescence intensity of the complex.

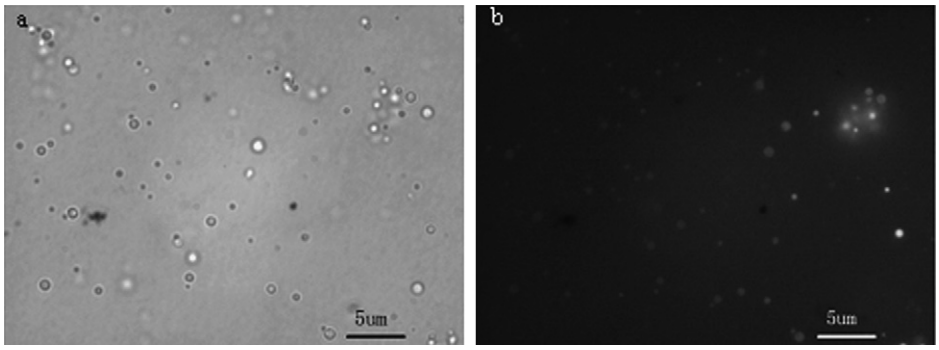

Fig. 2. (a) Direct observation of micro-vesicles composed of Eu(DBM)$_3$Phen and PNIPAM-b-PAzoM in 50 vol.% H_2O/THF solution; (b) luminescence from the vesicle excited by UV light at 365 nm under an optical microscope.

3.2. Enhancement in the luminescence of Eu(DBM)$_3$Phen-doped vesicle

During the self-assembling process of PNIPAM-b-PAzoM and Eu(DBM)$_3$Phen in the THF solution, a hydrophobic vesicle shell composed of PAzoM segments and Eu(DBM)$_3$Phen formed through the gradual addition of water. The more water is added, the less solvent is left in the shell and the more likely that the hydrophobic shell would form within the shell. The question on whether or not this environment change around Eu(III) ions could affect the luminescence property of the complex was examined in detail. Fig. 3a and b shows experimental results on luminescence and its lifetime. Fig. 3a shows that the increase in water content in the vesicle solution results in an accompanying increase of luminescence at about 612 nm. This level reaches its maximum as the water content is at its highest (98 vol.%). Correspondingly, the same result was also obtained from the measurement of the lifetime of the luminescence as shown in Fig. 3b. From the figure, we can also see that the critical level of water content is at about 80 vol.% for luminescence enhancement. Under this critical level, the luminescence lifetime is kept relatively short, while above this level, it rapidly increases to a high value. At the water content of 98 vol.%, the lifetime reached the longest value of about 0.5 ms. Some other systems containing Eu(DBM)$_3$Phen and other kinds of host showed nearly the same lifetime. For example, the lifetime of Eu(DBM)$_3$Phen in PMMA film [27,28] is about 0.5 ms.

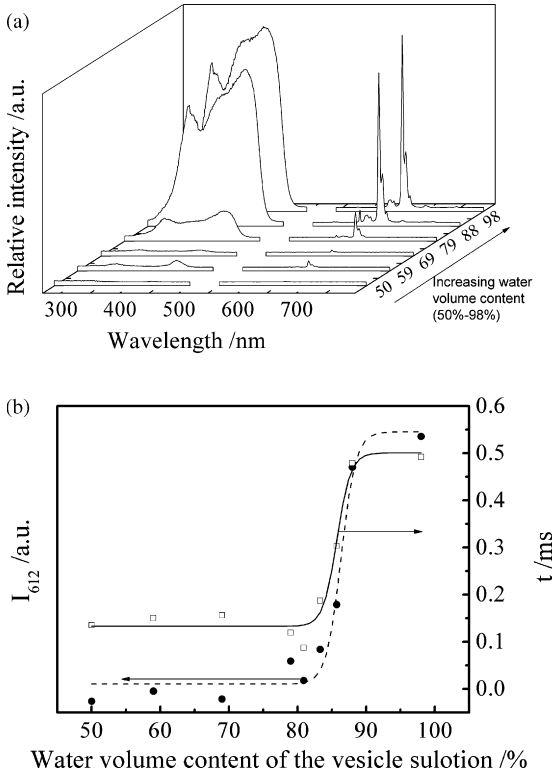

Fig. 3. (a) Excitation and emission spectra of Eu(DBM)$_3$Phen-doped PNIPAM-b-PAzoM vesicles in H_2O/THF solution with different water content; (b) luminescence intensity at 612 nm ($^5D_0 \rightarrow {}^7F_2$) (●) and the corresponding lifetime(□). The concentration of Eu(DBM)$_3$Phen is 1.5×10^{-4} M in all solutions containing Eu(DBM)$_3$Phen.

It is worth noting that a more hydrophobic environment within the shell of the vesicle is obtained when more water is added into the solution as described above. Moreover, the respective lifetimes of the Eu(III) complexes depend strongly on the vibrations of its nearest ligands. In other words, the excitation energy of Eu(III) can be absorbed by the vibration of the ligands, thereby decreasing the lifetime of Eu(III). Under these preconditions, when water concentration in the solution is low, some water molecules surrounding the Eu(III) ion absorb part of the excitation energy, resulting in a decreased lifetime. When the water concentration increases, Eu(DBM)$_3$Phen becomes situated in a more compact organic environment with less water. This more hydrophobic environment inhibits luminescence quenching from water molecules. This phenomenon is similar to that observed in the micelle system, in which micelle formation results in the decrease of collision-induced non-radiative decay and subsequent luminescence enhancement [26,29].

3.3. A model of vesicles composed of PNIPAM-b-PAzoM and Eu(DBM)$_3$Phen

From the description above, it can be concluded that it is the structure of the vesicles that affects the luminescence behavior of Eu(DBM)$_3$Phen, thereby necessitating further investigation on its structure. Fig. 4 shows a comparison of the UV–vis spectra of two series samples with and without Eu(DBM)$_3$Phen. Before self-assembling in the THF solution, the shapes of the absorption spectra were nearly the same, with a main peak of about 350 nm. However, the extinction coefficient measured for Eu(DBM)$_3$Phen and azobenzene groups are 5.5×10^4 L mol^{-1} cm^{-1} and 5.1×10^4 L mol^{-1} cm^{-1}, respectively. The concentration of Eu(DBM)$_3$Phen (1.5×10^{-4} mol L^{-1}) is also higher than that of the azobenzene groups (0.7×10^{-4} mol L^{-1}) in the vesicle solution. At this point, it is important to find out what happens in the vesicle's structure when water content is increased. Fig. 4b presents the spectrum for vesicles without Eu(DBM)$_3$Phen. As can be seen, when water content increases, there is an apparent widening different from that of vesicles with Eu(DBM)$_3$Phen which show a red shift (see Fig. 4a).

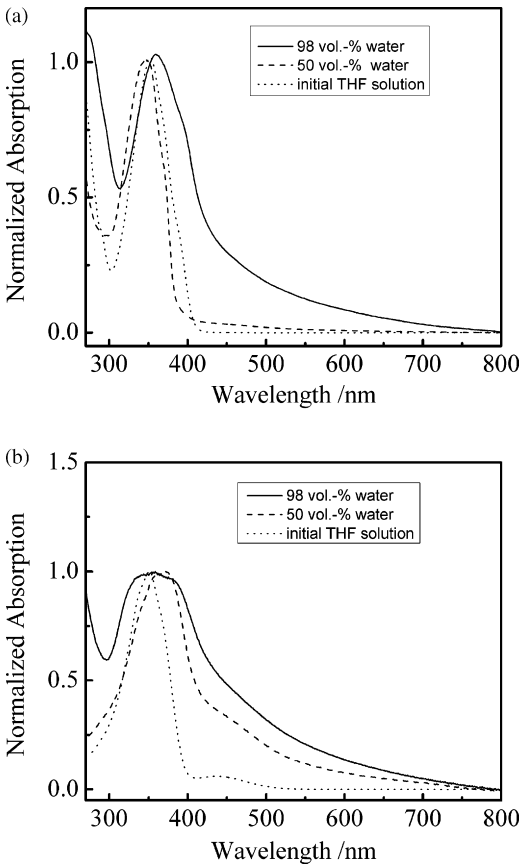

Fig. 4. (a) UV–vis spectra of the diluted solution of vesicles composed of $Eu(DBM)_3Phen$ and PNIPAM-b-PAzoM; (b) UV–vis spectra of the diluted solution of PNIPAM-b-PAzoM vesicles.

The strong aggregation of azobenzene chromophores was often observed on the basis of the spectral shift of the maximum band. The blue shift of the maximum absorption band for azobenzene moiety is usually assigned to the parallel head-to-head alignment of the azobenzene chromophores, which is called H-aggregation. In contrast, the red shift is normally observed as the azobenzene chromophores being aggregated in a head-to-tail manner, which is called J-aggregation. The self-assembly process of amphiphilic copolymer causes the aggregation of azobenzene moieties [30]. From such observation, it is safe to assume that the aggregation state of the azobenzene groups can greatly influence the morphologies of the formed vesicles. Therefore, the widening of the maximum band of the vesicle without $Eu(DBM)_3Phen$ can be attributed to both the H- and J-aggregations of azobenzene moieties in the amphiphilic copolymer. Moreover, with the addition of $Eu(DBM)_3Phen$, there is still a trend in the widening of the absorption peak, although it is not as obvious as that of the vesicle of the copolymer without $Eu(DBM)_3Phen$.

Based on the analysis above, a model for the vesicle's formation and subsequent change in structure is presented in Fig. 5. It shows a photomicrograph of an ultrathin section cut from a vesicle, from which a visible cross-section of the micro-vesicle can be observed. The cross-section of the shell can also be directly observed by the naked eye as a yellow band (fuscous band), due to the composition of the azobenzene chromophore.

According to this model, the relationship between the structure and the luminescence of vesicles composed of $Eu(DBM)_3Phen$ and PNIPAM-b-PAzoM can be vividly presented as follows: initially, the $Eu(DBM)_3Phen$ and the PNIPAM-b-PAzoM in a THF solution are self-assembled into vesicles by adding water up to H_2O/THF of 50 vol.% (the initial one). At this stage, the $Eu(DBM)_3Phen$ is dispersed in the area of the hydrophobic PAzoM blocks and is still surrounded by the H_2O/THF mixture solvent. Under this circumstance, the luminescence of the $Eu(DBM)_3Phen$ is quenched by water molecules. Afterwards, when the vesicles solution is further diluted by water, the hydrophilic PNIPAM blocks stretches out from the PAzoM blocks, which aggregate to form tighter domains.

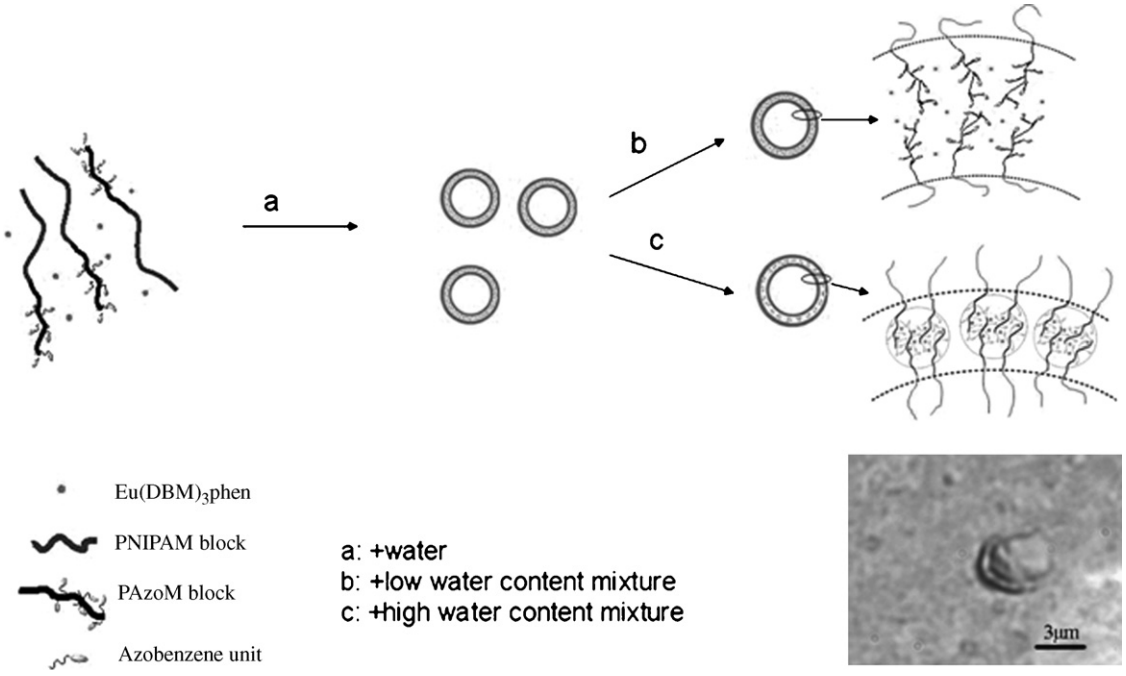

Fig. 5. Schematic model of the self-assembly process of $Eu(DBM)_3Phen$-doped PNIPAM-b-PAzoM vesicles and their structural changes brought about by increasing water content.

These more hydrophobic domains protect the $Eu(DBM)_3Phen$ from the water, thereby reducing the quenching effect and enhancing luminescence.

4. Conclusion

Micro-vesicles composed of $Eu(DBM)_3Phen$ and PNIPAM-b-PAzoM were prepared through the self-assembling process. Luminescence from the vesicle exhibited a tendency to increase along with increased water content in the mixture solvent. This characteristic property was found to be highly correlated with the structure of vesicles composed of $Eu(DBM)_3Phen$ and PNIPAM-b-PAzoM. A qualitative model was presented to explain this relationship. Furthermore, results showed that the enhancement in luminescence intensity is brought about by the change in the hydrophobic environment within the shell of the vesicles.

Acknowledgements

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