



Response of Tb(III) and Eu(III) centered luminescence on phase transitions in aqueous solutions of triblock copolymers



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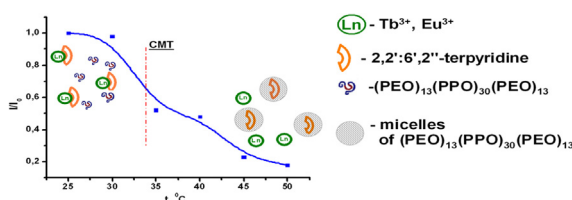
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HIGHLIGHTS

- Aggregation of triblock copolymers affects luminescence of Tb and Eu complexes.
- The luminescence quenching results from the complex formation equilibrium shift.
- The equilibrium shift depends on the aggregation mode of triblock copolymers.
- Key impact of ligand's structure in aggregation induced quenching of luminescence.

GRAPHICAL ABSTRACT



I and I_0 - the intensities of the main emission bands at 612 nm for Eu(III) (${}^6D_5 - {}^7F_2$) and 541 nm for Tb(III) (${}^6D_4 - {}^7F_3$) upon the heating and at 25 °C correspondingly

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ABSTRACT

The work introduces the temperature induced quenching of Tb(III) and Eu(III) centered luminescence sensitized by ligands 2,2':6',2''-terpyridine and difloxacin in aqueous solutions of triblock copolymers, namely $(\text{PEO})_{13}(\text{PPO})_{30}(\text{PEO})_{13}$ (L64), $(\text{PPO})_{14}(\text{PEO})_{24}(\text{PPO})_{14}$ (17R4) and $(\text{PPO})_8(\text{PEO})_{22}(\text{PPO})_8$ (10R5). The results reveal the temperature induced shifting of the complex formation equilibria in solutions of the triblock copolymers as the reason of the quenching of Eu(III) and Tb(III) centered luminescence. The correlation between the temperature induced quenching and the aggregation behavior of the triblock copolymers is revealed. Both the nature of the ligand and the architecture of the triblock copolymer affect the Tb(III) and Eu(III) centered luminescence response to the temperature induced phase transitions.

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1. Introduction

Triblock copolymers or pluronics with diverse architecture of polyethyleneoxide (PEO) and polypropyleneoxide (PPO) blocks, namely $(\text{PEO})_n(\text{PPO})_m(\text{PEO})_n$ and $(\text{PPO})_n(\text{PEO})_m(\text{PPO})_n$, designated as P-type and R-type triblock copolymers correspondingly,

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exemplify widely applied type of non-ionic surfactants with peculiar aggregation behavior [1–6]. Their wide application in development of both drug delivery and sensing or separation techniques is well documented in literature [7–9]. Their peculiar aggregation arises from the indistinct separation of hydrophilic and hydrophobic zones, which in turn can be affected by their architecture, lengths of PEO and PPO blocks and temperature [1–6]. In particular the entropy loss arising from the looping geometry of the middle PEO blocks of reverse pluronics largely reduces the driving force for micellization, which significantly restricts the experimental evidence of their aggregation [1,4,10,11]. Thus common experimental techniques including those based

on spin probes and organic luminophores or chromophores are successfully applied to detect the aggregation of P-type triblock copolymers [12–18], while fail to reveal the aggregation in aqueous solutions of reverse triblock copolymers [16]. These tendencies can be explained by either insignificant binding between probes and R-type aggregates or insignificant changes in micropolarity of organic chromophores upon their binding with these aggregates. The choice of P- and R-type triblock copolymers with middle length of PEO and PPO blocks, namely (PEO)₁₃(PPO)₃₀(PEO)₁₃ (L64), (PPO)₁₄(PEO)₂₄(PPO)₁₄ (17R4), (PPO)₈(PEO)₂₂(PPO)₈ (10R5) is affected by their peculiar aggregation behavior. In particular no aggregation is observed in their aqueous solutions under room temperature even at 10–30 mM of pluronics, while the heating to temperatures within 28–52 °C results in two phase transitions, which are the aggregation and phase separation or so-called “cloud pointing” [1,5,19,20]. Both processes result from the dehydration of PEO and PPO blocks and thus occur at definite temperatures, which are called CMT and CP correspondingly. Our previous work [16] confirms that the well developed routes, based on the application of organic spin probes or chromophores are insensitive to the aggregation behavior of 17R4 and 10R5, which prompts us to search for another probes of their aggregation behavior. Although Gd(III) ions are successfully used as paramagnetic probes [21–23] of anionic surfactants aggregation, their EPR spectra exhibit insignificant changes upon the temperature induced aggregation of L64 and 10R5 due to the poor binding of Gd(III) ions with the aggregated triblock copolymers [16]. This prompts us to search for complex organic–inorganic probes to detect the aggregation of the triblock copolymers. Luminescent lanthanide ions being in the equilibrium with organic chromophores are of particular interest from this point of view. Pattern of lanthanide centered luminescence remains invariant in diverse outer and inner sphere environment of lanthanide ions, while the intensities of the bands are greatly dependent on the nature of ligand environment, which is a reason of the application of lanthanide complexes for sensing [24–30]. Taking into account the significant difference between luminescence of lanthanide aqua ions and their complexes with organic chromophores [24–26], any shift of complex formation equilibrium should affect a lanthanide centered luminescence. Our previous work introduces Eu(III) centered luminescence, enhanced by binding with [2-(5-chloro-2-hydroxyphenyl)-2-(pent-1-yl)ethenyl]diphenyl-phosphine oxide in aqueous solutions of L64, 17R4 and 10R5 at 0.1 M of nitric acid, which is required for the complex formation [16]. The heating of all studied solutions results in the quenching of Eu(III) luminescence with the profile peculiar for each triblock copolymer and the break points at the temperatures of phase transitions. These results arise some questions concerning reasons and mechanisms of the observed effects, including the impact of the pH conditions in the quenching regularities. The present work is aimed to reveal the temperature induced changes of Eu(III) and Tb(III) centered luminescence sensitized by organic chromophores in aqueous solutions of the triblock copolymers in neutral pH conditions. Difloxacin (**1**) and 2,2':6',2''-terpyridine (**2**) are introduced as organic chromophores to sensitize Tb(III) and Eu(III) centered luminescence at pH 4.5–6.5 in aqueous solutions of the triblock copolymers. The luminescence intensity together with electronic absorption spectra of both chromophores and their lanthanide complexes at the temperatures varied within 25–50 °C are analyzed in the correlation with the temperature induced aggregation behavior of the triblock copolymers. The peculiar aggregation behavior of the triblock copolymers enables to reveal the effects of their monomers and aggregates on the luminescence of lanthanides at the same concentration level of surfactants. The revealed tendencies could shed light on main factors affecting the luminescence of lanthanide

complexes within their supramolecular assemblies with surfactants or become the basis of novel aggregation sensitive fluorescent techniques.

2. Experimental

2.1. Materials

Pluronics (PEO)₁₃(PPO)₃₀(PEO)₁₃ (L64), (PPO)₁₄(PEO)₂₄(PPO)₁₄ (17R4), (PPO)₈(PEO)₂₂(PPO)₈ (10R5), 2,2':6',2''-terpyridine, difloxacin hydrochloride were used as commercially available (Sigma-Aldrich) without further purification. Ln(NO₃)₃·6H₂O (Ln = Eu and Tb), 2-(N-morpholino)ethanesulfonic acid (MES) were used as purchased from Acros.

Stock solutions of Ln(NO₃)₃ (Ln = Eu and Tb) were prepared by dissolving the appropriate amounts of their salts Ln(NO₃)₃·nH₂O in doubly distilled water with further standardization with EDTA at pH 6, using Xylenol orange as indicator [31]. Some amounts of nitric acid up to pH 2 were added to stock solutions of lanthanide salts to prevent the formation of hydroxy-complexes.

2.2. Methods

The steady-state emission spectra were recorded on a spectrofluorometer FL3-221-NIR (Jobin Yvon) under the excitation at 330 nm for both difloxacin and 2,2':6',2''-terpyridine. Luminescence decay measurements were performed using a Horiba Jobin Yvon Fluorolog-3-221 spectrofluorometer with SPEX FL-1042 phosphorimeter accessory using a xenon flash lamp as the photon source with following parameters: time per flash—50.00 ms, flash count—200 ms, initial delay—0.05 ms and sample window—2 ms. Excitation of samples was performed at 330 nm, and emission detected at 541 and 612 nm with 5 nm slit width for both excitation and emission.

UV–vis spectra were recorded on a Lambda 35 spectrophotometer (Perkin-Elmer).

All samples were prepared from the bidistilled water. All spectra were recorded at least three times for each sample.

The dynamic light scattering (DLS) measurements in aqueous solutions of the triblock copolymers were performed using Malvern Mastersize 2000 particle analyzer. The measured autocorrelation functions were analyzed by Malvern DTS software and the second-order cumulant expansion methods. All samples were prepared from the bidistilled water or aqueous buffer solutions. The latter were filtered through the poly(vinylidene fluoride) (PVDF) membrane using the syringe filter (0.45 μm). The diffusion coefficient values were measured at least three times for each sample. The average error in these experiments was approximately 4%.

3. Results and discussion

The lanthanide centered luminescence is greatly enhanced by a ligand-to-metal energy transfer, which in turn requires organic chromophores with a large absorption cross section and suitable triplet state energy. Radiationless decay of lanthanide centered excited state arisen from an energy transfer to vibrational levels of water molecules is another factor affecting luminescence of lanthanide complexes, which can be brought to nothing by displacement of water molecules by organic chromophores from the inner sphere of lanthanides [26]. The optimal conditions for the complex formation of chromophores **1** and **2** with lanthanides are well documented in literature [32–35]. It is known that the complex formation of Tb(III) and Eu(III) with the chromophores can be revealed from the appearance of the spectrum patterns peculiar for Eu(III) and Tb(III) centered luminescence arisen from ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₃, ⁵D₀ → ⁷F₄,

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