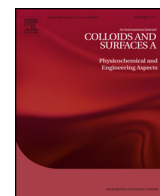




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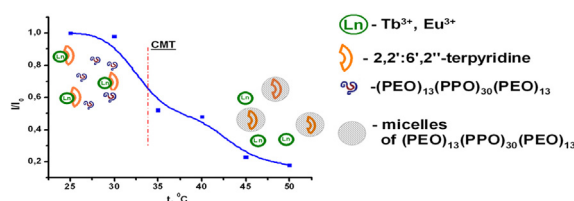
Response of Tb(III) and Eu(III) centered luminescence on phase transitions in aqueous solutions of triblock copolymers

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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) (${}^5D_0 - {}^7F_2$) and 541 nm for Tb(III) (${}^5D_4 - {}^7F_3$) 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 $(PEO)_{13}(PPO)_{30}(PEO)_{13}$ (L64), $(PPO)_{14}(PEO)_{24}(PPO)_{14}$ (17R4) and $(PPO)_8(PEO)_{22}(PPO)_8$ (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 $(PEO)_n(PPO)_m(PEO)_n$ and $(PPO)_n(PEO)_m(PPO)_n$, designated as P-type and R-type triblock copolymers correspondingly,

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

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