



The interfacial interactions of Tb-doped silica nanoparticles with surfactants and phospholipids revealed through the fluorescent response

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ABSTRACT

The quenching effect of dyes (phenol red and bromothymol blue) on Tb(III)-centered luminescence enables to sense the aggregation of cationic and anionic surfactants near the silica surface of Tb-doped silica nanoparticles (SN) in aqueous solutions. The Tb-centered luminescence of non-decorated SNs is diminished by the inner filter effect of both dyes. The decoration of the silica surface by cationic surfactants induces the quenching through the energy transfer between silica coated Tb(III) complexes and dye anions inserted into surfactant aggregates. Thus the distribution of surfactant aggregates at the silica/water interface and in the bulk of solution greatly affects dynamic quenching efficiency. The displacement of dye anions from the interfacial surfactant adlayer by anionic surfactants and phospholipids is accompanied by the “off-on” switching of Tb(III)-centered luminescence.

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1. Introduction

Fluorescent silica nanoparticles have gained a great attention during recent decades due to their bioanalytical application [1–4]. The correlation between luminescence of nanoparticles and the interfacial interactions is a top of current interest, since nanoparticles for biomarking should exhibit stable in time luminescence, which is not quenched at a binding with biotarget, while stimuli responsive luminescent nanoparticles are required for biosensing [5–13]. Lanthanide centered luminescence is of particular importance for bioanalytical and medical applications [14,15]. Thus lanthanide complexes both in the molecular form and silica coated are widely applied in bioanalysis [16–23]. The sensing of substrates is based on various mechanisms of quenching or enhancement of lanthanide centered luminescence. The energy transfer or so-called Förster mechanism is especially important for silica coated lanthanide based luminophores, since it is significant at rather long distances between luminescent and quenching molecules (1–7 nm) [24,25]. Thus the energy transfer from donors (Eu(III) chelates incorporated into nanoparticles) and proteins labeled with dyes has been successfully applied in the sensing of proteins or their

aggregation [26]. The labeling of substrates by dyes is the prerequisite step of the abovementioned route of the fluorescent recognition. The present report introduces novel approach to sense nonlabeled substrates through the fluorescent response of lanthanide doped silica nanoparticles (SNs) with the use of dye molecules as a probe. The applicability of this approach is exemplified in the interfacial interactions of SNs with cationic as well as anionic surfactants and phospholipids. It is worth noting that the development of the procedure, which can selectively probe the aggregation of surfactants at the silica/water interface of nanoparticles is rather appealing task from the viewpoint of both fundamental and practical significance. In particular the silica surface decoration is a required step for bioanalytical application of nanoparticles [27,28], while the adsorption and further aggregation of surfactants at the silica/water interface is rather convenient alternative to covalent anchoring due to the lack of multistep purification procedures [29–31]. The previously reported silica coated Tb(III) complexes with p-sulfonatocalix[4]arene (42 ± 5 nm) are used as nanoparticles with lanthanide centered luminescence [33]. Luminescence of Tb(III) complexes with p-sulfonatocalix[4]arene were used as dopants to silica nanoparticles [34]. This type of luminescent SNs can be attributed to the so-called “expanded core-shell” morphology, where luminophores are distributed both within the core and a shell, though this distribution is not homogeneous

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