



The discrimination between phospholipids of diverse structure and phosphacoumarins of various hydrophobicity through fluorescent response of Tb-doped silica nanoparticles decorated by cationic surfactant

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ABSTRACT

The work represents colloids of silica nanoparticles displaying fluorescent response on biorelevant compounds exemplified by phosphacoumarins and phospholipids. The luminescent properties of the colloids arise from Tb(III) complexes doped into silica nanoparticles (SNs). The noncovalent decoration of SNs by dicationic surfactant with further interfacial binding of dye anions enables to develop colloids programmed to display a substrate induced fluorescent response. The latter results from the quenching of Tb(III) centered luminescence by dye anions through dynamic mechanism and subsequent displacement of quenching anions by the non-quenching substrates from the interface of SNs. Both negative charge and hydrophobicity of substrates are the key factors affecting the selectivity of the substrate induced fluorescent response. The peculiar effects of zwitter-ionic and anionic phospholipids on the fluorescent response have been revealed. The applicability of the fluorescent procedure in the sensing of impurities in commercial phosphatidylcholine is also introduced.

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1. Introduction

The recognition of biorelevant anions through the fluorescent response is a top of current interest [1–8]. Lanthanide-centered luminescence is of particular importance for these purposes due to narrow bands in emission spectra and long lifetimes of the excited states, which enables to get good signal-to-noise ratio [9,10]. Though literature data introduce a plenty of excellent works concerning the recognition of biorelevant anions with the use of lanthanide complexes [1–8], many problems are still unresolved. For example the lack of kinetic and thermodynamic stability of lanthanide complexes significantly restricts biocompatibility and reusability of lanthanide based molecular sensors. The encapsulation of lanthanide containing luminophores into silica nanoparticles (SNs) is a route to protect lanthanide complexes from the degradation in bio-environment [11–17]. The easy modification of SNs provides the opportunity to increase the affinity towards biotargets and biocompatibility of SNs [18,19]. The reusability of nanomaterial should be noted as an additional advantage of SNs in a bioanalytical application.

The development of nanomaterial exhibiting substrate induced fluorescent response is commonly based on the energy transfer between luminophores fixed on the silica surface or inserted into SNs and quenching molecules or ions located at the silica/water interface. The fluorescent properties of dyes are widely applied in the development of nanosized biosensors, which is well documented in the articles [20–25]. The energy transfer was successfully applied to reveal biotin–avidin binding or to detect some biotargets [25–27]. Though there are some fine examples of the application of lanthanide centered luminescence in the development of colloids with sensing functions [28–30,31,32], such publications are not enough. The peculiarity of the introduced herein approach is the discrimination between non-labeled substrates through the luminescent response with the use of cationic molecules as a probe. This approach is based on the quenching of nanoparticles luminescence by some quenching ions (probes) with their further displacement by substrates, which in turn reestablishes the initial emission of nanoparticles. The previously reported use of copper or iron ions to quench the nanoparticles luminescence with further stripping of metal ions from the interface of some chelating anions should be also noted as a similar route to get substrate responsive luminescent colloids [31–33].

The present work is a continuation of our previous report on synthesis of highly luminescent Tb(III) doped SNs [17] and

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