



## Interfacial interactions of hard polyelectrolyte-stabilized luminescent colloids with substrates



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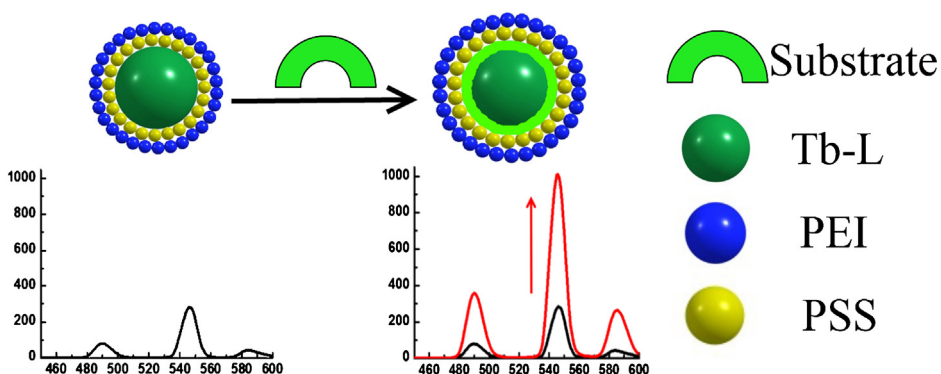
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### HIGHLIGHTS

- Tb(III) complexes at molecular and colloidal organization levels are compared.
- Interfacial complex formation with substrates differs from that in solution.
- Precipitated Tb(III) complexes form hard templates of polyelectrolyte-coated colloids.
- The colloids exhibit high stability of luminescence at pH 3–9.
- Luminescent response of Tb(III) colloids on substrates results from interfacial complex formation.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 6 April 2015

Received in revised form 14 May 2015

Accepted 19 May 2015

Available online 24 May 2015

#### Keywords:

Lanthanide complexes

Luminescence

Sensing

Antibiotics

Interface

Colloids

Fluoroquinolones

Tetracyclines

### ABSTRACT

The present work introduces an origin of sensing function of polyelectrolyte-coated colloids based on Tb(III) complexes with calix[4]resorcinarene cavitand bearing four 1,3-diketone groups at the upper rim. The Tb(III)-centered luminescence of the colloids remains unchanged at pH 3–9, although the Tb(III) complexes are highly pH-dependent in DMF solutions. Both colloidal and luminescent properties of the colloids are stable within one month at least, which reveals stability of complex-based hard nanotemplates and soft polyelectrolyte deposition. The chelating substrates (catechol, tetracycline and fluoroquinolone derivatives) induce quick and reproducible luminescent response of the complex-based colloids without any detectable changes of their colloidal properties. The ternary complex formation at the interface of the colloids is the reason for their luminescent response on the substrates in aqueous solutions. Both the insolubility of the Tb(III)-containing cores and the shielding and/or buffer effect of the polyelectrolyte coating affect the interfacial complex formation, which results in more selective luminescent response of the colloids on the tetracycline and fluoroquinolone antibiotics in comparison with the complexes in solutions.

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**Abbreviations:** TEA, triethylamine; PSS, poly(sodium 4-styrenesulfonate); PEI, polyethyleneimine; Tiron, H<sub>2</sub>T<sub>2</sub>-, 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate; DF, difloxacin hydrochloride; MF, moxifloxacin hydrochloride; H2TC, tetracycline hydrochloride; H2CTC, chlortetracycline hydrochloride; H2MC, minocycline hydrochloride; L, 7,11,15,28-tetrakis[(acetylaceton-3-yl)methyl] calix[4]resorcinarene; H2B, 1,2-dihydroxybenzene.

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<http://dx.doi.org/10.1016/j.colsurfa.2015.05.013>

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## 1. Introduction

Luminescent nanoparticles have gained great attention during recent decades due to their applicability in sensing and imaging [1–4]. Core-shell morphology of luminescent nanoparticles is of great impact in their sensing function and biocompatibility [3–6].

An ability of nanoparticles to give an active response on specific external stimuli is a key point in a development of nanosensors. From this point of view a use of luminescent lanthanide complexes as luminescent component of nanoparticles is of particular importance. It derives from unique photophysical properties of lanthanide-centered luminescence and stimuli response ability of lanthanide complexes, which have been widely applied in a development of sensing procedures [7–10]. Commonly, luminescent lanthanide assays are based on ligand or ion exchange. A plenty of biorelevant substrates are chelating ligands able to complex with lanthanides [8–10]. Literature data represent fine examples of luminescent sensing of phosphates [10] and antibiotics [11–15] through a sensitization of lanthanide-centered luminescence in aqueous solutions.

It is well understood that ancillary ligands bound with lanthanide ion facilitate a sensing of chelating substrates through lanthanide-centered luminescence response [16,17]. Thus lanthanide complexes are preferably applied instead of lanthanide ions in sensing. The particular importance of the lanthanide complexes with  $\beta$ -diketonates as ancillary ligands for sensing arises from their well-known sensitizing effect on lanthanide-centered luminescence or so-called “antennae effect” arisen from a ligand-to-metal energy transfer [15,18–24]. These complexes exhibit high binding capacity towards additional ligands, which results from an incomplete coordination sphere of lanthanide ions due to their high coordination numbers [18–24]. Unfortunately, a majority of luminescent lanthanide complexes are poor soluble in water, which restricts their application in sensing. Moreover, a kinetic lability of lanthanide complexes results in their degradation in alkaline/acidic media or in buffer solutions, which also restricts their applicability in sensing.

Our previous reports introduce rather simple and convenient synthetic route of getting luminescent aqueous colloids based on lanthanide complexes [25–28]. The basis of the introduced approach is the precipitation of the luminescent lanthanide complexes from organic to aqueous solutions followed by a stabilization of the obtained colloids through an adsorption of polyelectrolytes onto hard templates [25–28]. A water insolubility of the lanthanide complexes is a key factor affecting both colloid and luminescent stability of the colloids.

The sensing function of the complex-based colloids arises from their ability to generate the substrate-induced response in aqueous solutions. Our previous report [15] revealed the ternary complex formation at the colloid/solution interface as the key reason for the sensing function of the complex-based luminescent colloids. The lanthanide complexes at the colloid/solution interface tend to form ternary complexes with substrates in the similar way with the complexes in solutions, although the ternary complex formation is greatly affected by the nature of the coating of the complex-based colloids [15,27]. Thus, a correlation between an interfacial complex formation and a luminescence of the complex-based colloids is of great importance in a development of nanosized sensors with lanthanide-centered luminescence.

The recently published results [25] represent the luminescent colloids based on Tb(III) complexes with tetra- $\beta$ -diketone calix[4]resorcinarene, where the hard nanosized complex-based species are coated by the soft polyelectrolyte multilayers. The present work is aimed at highlighting the impact of interfacial processes, including the degradation of the hard templates, in a generation of the substrate-induced luminescent response of

the colloids. The luminescent response of the colloids on pH and biorelevant chelating substrates (catechol derivatives and some representatives of tetracycline and fluoroquinolone antibiotics) is presented herein in the correlation with the processes taking part at the colloid/solution interface.

## 2. Experimental

### 2.1. Chemicals

Terbium(III) nitrate hydrate ( $\text{Tb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ ) (Alfa Aesar), triethylamine (TEA) (Acros Organics), poly(sodium 4-styrenesulfonate) (PSS) ( $MW_{\text{average}} = 70,000$ ) (Acros Organics), polyethyleneimine (PEI) branched ( $MW_{\text{average}} = 25,000$ ) (Aldrich Chemistry), sodium chloride (Sigma-Aldrich), sodium hydroxide (Sigma-Aldrich), hydrochloric acid concentrate (Fluka), tris-(hydroxymethyl)aminomethane (Tris) (Acros Organics), 4,5-dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate (Tiron) (Aldrich), 1,2-dihydroxybenzene (Sigma-Aldrich), difloxacin hydrochloride (DF) (Sigma), moxifloxacin hydrochloride (MF) (Fluka), tetracycline hydrochloride ( $\text{H}_2\text{TC}$ ) (Sigma-Aldrich), chlortetracycline hydrochloride ( $\text{H}_2\text{CTC}$ ) (Sigma), minocycline hydrochloride ( $\text{H}_2\text{MC}$ ) (Sigma) were used as commercially received without further purification. N,N-Dimethylformamide (DMF) (Acros Organics) was twice distilled over  $\text{P}_2\text{O}_5$ .

The cavitand 7,11,15,28-tetrakis[(acetylaceton-3-yl)methyl]calix[4]resorcinarene (L) was synthesized according to the previously reported procedure [25].

### 2.2. Synthesis of the colloids

DMF solution of Tb(III) (4.5 mM) and L (4.5 mM) was alkalinized by TEA (18 mM) to induce the complex formation. This solution was added dropwise to aqueous solution of PSS ( $1 \text{ g L}^{-1}$ ) and NaCl (0.5 M) at pH 6.0 under intensive stirring (2200 rpm). The volume ratio of the DMF to aqueous solutions was 1:5. Afterwards the obtained dispersion was exposed to ultrasonication for 30 min.

To synthesize PEI-PSS-Tb(III) colloids, the dispersion of PSS-coated nanoparticles was centrifuged (11,000 rpm, 15 min). The supernatant was poured out. Afterwards, the solution of PEI ( $1 \text{ g L}^{-1}$ ) and NaCl (0.5 M) at pH 7.0 was added to the precipitate. Then the dispersion was sonicated for 30 min.

The synthesis of the PSS-PEI-PSS-coated colloids was performed through the precipitation and further addition of the PSS aqueous solution.

In order to eliminate the excess amounts of polyelectrolytes and sodium chloride the next procedure was performed. After the last polyelectrolyte layer deposition the PSS-Tb(III), PEI-PSS-Tb(III) and PSS-PEI-PSS-Tb(III) colloids were centrifuged (11,000 rpm, 15 min). The supernatant was poured out. The obtained precipitate was redispersed in water *via* sonication for 30 min.

The PSS-Tb(III), PEI-PSS-Tb(III) and PSS-PEI-PSS-Tb(III) colloids were diluted to adjust the 0.075 mM concentration of Tb(III) ions in the colloidal form. A twice distilled water filtered through Nylon membrane using a Syringe Filter (0.45  $\mu\text{m}$ ) was applied for the colloids redispersion and dissolution.

The colloids were ultrasonicated for 30 min before measurements. All measurements have been performed at least three times.

### 2.3. Characterization

The dynamic light scattering (DLS) measurements have been performed by means of the Malvern Mastersize 2000 particle analyzer. A He-Ne laser operating at 633 nm wavelength and emitting vertically polarized light has been used as a light source. The measured autocorrelation functions have been analyzed by Malvern

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