

## Interfacial adsorption and stripping of ions as a reason of stimuli responsive luminescence of Tb-doped silica nanoparticles

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### ABSTRACT

Herein we introduce the “on–off–on” switching of Tb-centered luminescence as a result of reversible adsorption of Fe<sup>III</sup> ions at the silica/water interface of Tb-doped silica nanoparticles and the stripping effect of anions. The interfacial adsorption of Fe<sup>III</sup> ions results in the charge neutralization and aggregation of Tb-doped silica nanoparticles, accompanied by significant quenching of Tb-centered luminescence. The analysis of the steady state and time resolved quenching measurements reveals both static and dynamic quenching mechanisms. The addition of EDTA and some phosphates, including ATP results in the deaggregation of nanoparticles due to the complex formation with Fe<sup>III</sup> ions and following stripping of Fe<sup>III</sup> ions from the silica surface. The “off–on” switching of Tb-centered luminescence resulted from the stripping effect of biorelevant phosphates is a good basis for further bioanalytical application.

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### 1. Introduction

Silica nanoparticles (SNs) have gained much attention during recent decades due to their wide use in medicine and bioanalysis [1]. The adsorption of metal ions and organic molecules onto silica, as well as the gaining of luminescent properties through the doping of luminophores into silica matrix and silica surface decoration are those advantages of silica nanoparticles, which provide their applicability as markers [2,3], sensors [4–6], drug delivery systems [7] and sorbents [8,9]. It is worth noting that despite a shielding effect of a silica coating, luminophores included in SN are still accessible to small species such as metal ions. This permeability makes SNs a very versatile platform for the design of luminescent nanosensors [10]. Lanthanide complexes have gained a great deal of attention owing to their unique spectroscopic characteristics [11,12]. Therefore lanthanide complexes are applied as dopants into SNs [13–19]. Though covalent binding of luminescent lanthanide complexes to silica matrix represents rather good alternative to doping procedure [20,21] the latter is more simple and universe. The conjugation of lanthanide complex with 3-aminopropyltriethoxysilane is the essential step of the silica surface decoration by lanthanide based luminophores. The conjugation in turn requires covalent

modification of the complex by definite anchor groups, thus resulting in multistep synthetic and purification procedure. Moreover the exposure of labile complexes onto silica surface may result in their degradation in the presence of biosubstrates due to competitive complex formation, while the silica coating tends to improve the photophysical properties of luminophores doped into SNs [10]. Due to good signal-to-noise ratio such SNs are efficient biomarkers, while their application in biosensing is more sparsely [4–6,22,23]. The works [22,23] exemplify the quenching of Eu<sup>III</sup> and Tb<sup>III</sup> centered luminescence through the ion exchange at the water/silica interface as a way to sense Cu<sup>II</sup> and H<sub>2</sub>PO<sub>4</sub><sup>−</sup>. These results are extremely interesting since they highlight lanthanide doped silica as sensor of metal ions through the quenching of lanthanide centered luminescence due to the ion exchange mechanism. Recently we introduced Tb-doped silica nanoparticles with efficient green luminescence [19]. Assuming the permeability of silica matrix to metal ions, it is rather anticipated that metal ion adsorption should affect the aggregation and luminescence behavior of the SNs.

The present work is a continuation of our previous efforts [24] to develop colloids exhibiting substrate responsive luminescence. Herein we introduce the adsorption of Fe<sup>III</sup> ions onto silica surface of Tb-doped SNs and the stripping effect of substrates, namely ethylenediaminetetraacetic acid disodium salt (Na<sub>2</sub>EDTA), KH<sub>2</sub>PO<sub>4</sub>, adenosine 5'-monophosphate (AMP), adenosine 5'-diphosphate (ADP) and adenosine 5'-triphosphate (ATP), as

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the reasons of the “on-off-on” switching of Tb-centered luminescence.

## 2. Experimental

### 2.1. Materials

Tetraethyl orthosilicate (TEOS) 98%, ammonium hydroxide (28–30%), *n*-heptanol 98%, cyclohexane 99%, from Acros; terbium(III) nitrate hexahydrate (99.9%) from Alfa Aesar, Triton X-100 from Sigma–Aldrich are used. The synthesis of *p*-sulfonatothiacalix[4]arene (TCAS) was carried out according to the known procedure [25].  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2$ ,  $\text{Gd}(\text{NO}_3)_3$  were used as commercially available (Acros) without further purification.

Synthesis of silica coated Tb-TCAS nanoparticles has been performed according to reverse microemulsion procedure presented in the work [19]. The nanoparticles were characterized by transmission microscopy (Fig. 1S in Supplementary data).

### 2.2. Methods

The dynamic light scattering (DLS) measurements and zeta-potential values of nanoparticles in aqueous dispersions were analyzed using Malvern Mastersize 2000 particle analyzer.

All samples were prepared from the bidistilled water with prior filtering through the PVDF membrane using the Syringe Filter (0.45  $\mu\text{m}$ ).

The steady-state emission spectra were recorded on a spectrofluorometer FL3-221-NIR (Jobin Yvon) under 330 nm excitation.

The transmission spectra were recorded on a Lambda 35 spectrophotometer (Perkin-Elmer) at 0.028  $\text{g L}^{-1}$  of Tb(III)-doped silica nanoparticles at pH 5.6.

Phosphorescence 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 546 nm with 5 nm slit width for both excitation and emission.

All samples were ultrasonicated within 30 min before measurements.

All measurements have been performed triply at least.

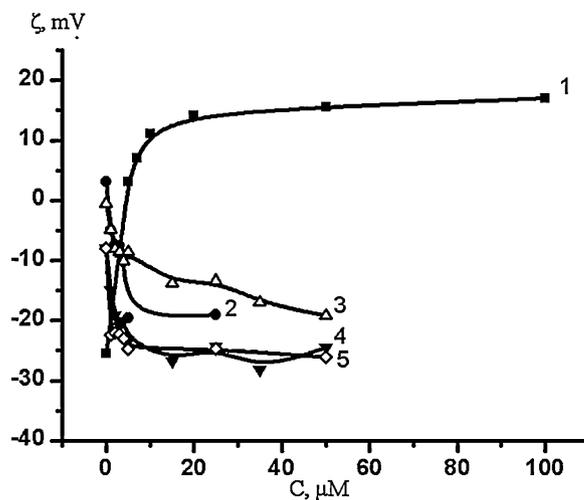
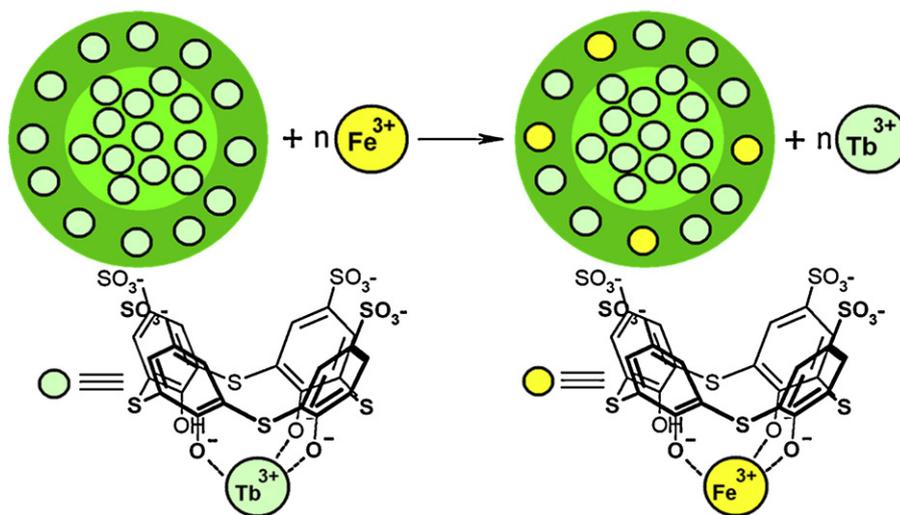


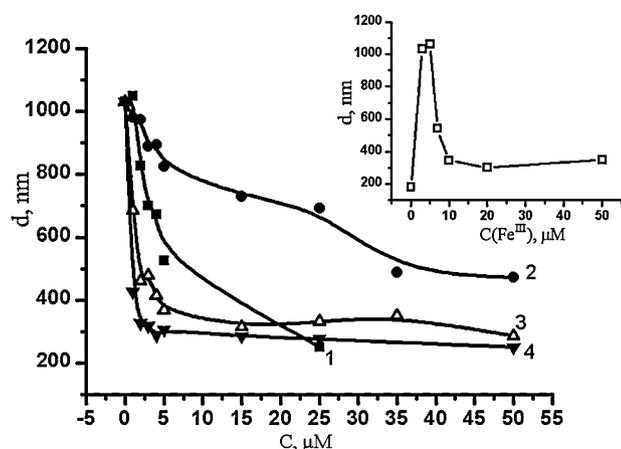
Fig. 1. Electrokinetic potential ( $\xi$ , mV) of Tb-doped NSs ( $0.028 \text{ g L}^{-1}$ ) versus concentrations of  $\text{FeCl}_3$  (1),  $\text{Na}_2\text{EDTA}$  (2), AMP (3), ADP (4), ATP (5) at  $C_{\text{Fe}} = 5 \mu\text{mol L}^{-1}$ , pH 5.5.

## 3. Results and discussion

The doping of  $\text{Tb}^{\text{III}}$  complex with *p*-sulfonatothiacalix[4]arene (the structure of this complex is represented in Scheme 1) into SNs has been performed through the water-in-oil microemulsion procedure [19]. These nanoparticles are 40 nm sized according to TEM images (Fig. 1S in Supplementary data), negatively charged (electrokinetic potential ( $\xi$ ) is about  $-24$  at pH 5.5) and highly luminescent [19]. Since the negative charge arises from the partial deprotonation of SiOH groups at the surface of SNs [26] their aggregation behavior is pH-dependent, coming to 200 nm sized aggregates at pH 5.6 (the pH 5.6 was maintained by adding small amounts of NaOH or HCl without buffer to avoid undesirable competitive interactions). The adsorption of metal ions onto negatively charged silica surface results in the surface charge neutralization, which in turn may induce the aggregation of nanoparticles [27]. Thus dynamic light scattering (DLS) and electrokinetic measurements are most convenient to reveal the metal ion adsorption at the silica/water interface. The peculiar effect of micromolar concentrations of  $\text{FeCl}_3$  on the aggregation and  $\xi$ -value of Tb-doped silica nanoparticles has been revealed (Figs. 1 and 2), while  $\text{Gd}(\text{NO}_3)_3$  or  $\text{FeCl}_2$  do not affect the electrokinetic and aggregation behavior



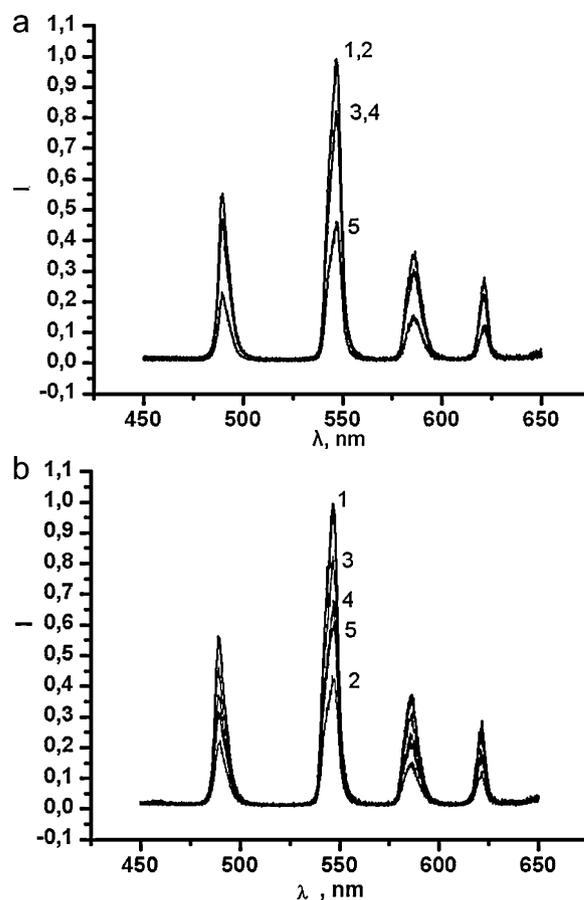
Scheme 1. Schematic representation of the ion exchange at the interface of Tb-doped SNs.



**Fig. 2.** The averaged hydrodynamic diameter ( $d$ ) for Tb-doped SNs ( $0.028 \text{ g L}^{-1}$ ) at various concentrations of  $\text{Na}_2\text{EDTA}$  (1), AMP (2), ADP (3), ATP (4) at  $C_{\text{Fe}} = 5 \text{ } \mu\text{mol L}^{-1}$ . The inset shows  $d$  versus  $C_{\text{Fe}}$  at pH 5.5.

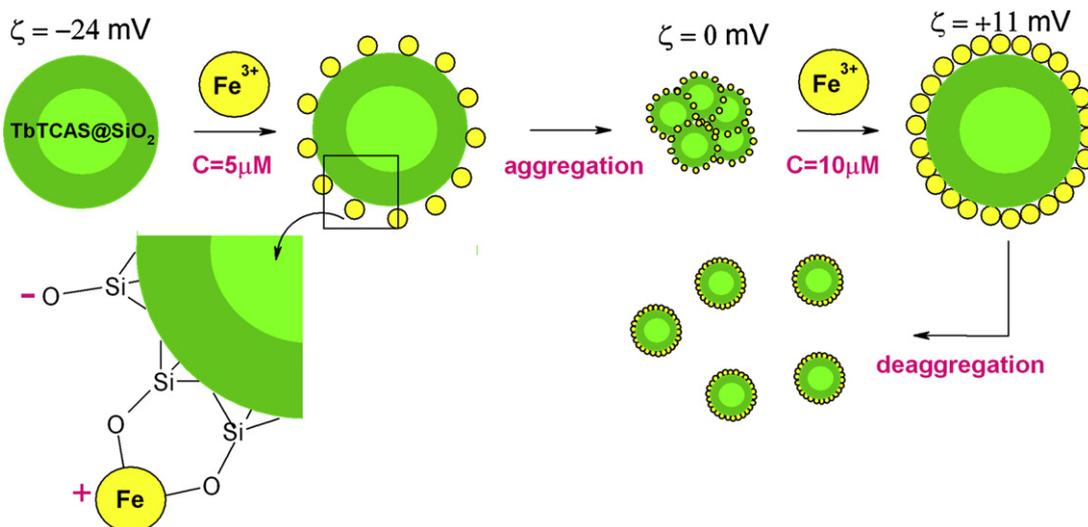
of SNs at these concentration conditions (Table 1S in Supplementary data). The analysis of the data represented in Figs. 1 and 2 reveals that the charge neutralization and the aggregation of nanoparticles are observed at 3–5  $\mu\text{M}$  of  $\text{FeCl}_3$ , while further increase of its concentration results in the recharging of silica surface and the de-aggregation of silica nanoparticles. The pronounced specific binding of  $\text{Fe}^{\text{III}}$  ions with hydroxy-groups and the enhanced adsorption in the diffuse layer should be noted as the reasons of the peculiar effect of  $\text{FeCl}_3$  on electrokinetic and aggregation behavior of SNs (Scheme 2). Though adsorption of metal ions onto silica surface is time dependent the changes in averaged hydrodynamic diameter ( $d$ ) and  $\xi$ -potential are observed at once (within few minutes) after the addition of metal salts, maintaining at the similar level within 1 h at least. The more or less significant changes occur only after 24 h (Table 1S in Supplementary data). Thus both the  $d$  and  $\xi$ -values represented in Figs. 1 and 2 are measured within a quarter of an hour after the sample preparation.

To reveal the correlation of photophysical properties of Tb-doped SNs with the adsorption of metal ions onto silica both the steady state and time resolved emission measurements have been performed at various concentrations of  $\text{FeCl}_2$ ,  $\text{Gd}(\text{NO}_3)_3$  and  $\text{FeCl}_3$ . The emission spectrum of nanoparticles reveals four bands, peculiar to the Tb-centered luminescence with the main peak at 541 nm, assigned as the  $^5\text{D}_4\text{--}^7\text{F}_5$  transition [11,12] (Fig. 3a). Though



**Fig. 3.** Normalized emission spectra of Tb-doped SNs in aqueous solution (1), with various additives: (a): 5  $\mu\text{M}$  of  $\text{FeCl}_2$  or 5  $\mu\text{M}$  of  $\text{Gd}(\text{NO}_3)_3$  (2); 10  $\mu\text{M}$  of  $\text{FeCl}_2$  (3), 20  $\mu\text{M}$  of  $\text{FeCl}_2$  (4); 5  $\mu\text{M}$  of  $\text{FeCl}_3$  before and after addition of 5–50  $\mu\text{M}$  of  $\text{NaNO}_3$  or  $\text{NaCl}$  (5); (b): 5  $\mu\text{M}$  of  $\text{FeCl}_3$  (2), 5  $\mu\text{M}$  of  $\text{FeCl}_3$  and 5  $\mu\text{M}$  of  $\text{Na}_2\text{EDTA}$ , where  $\text{Na}_2\text{EDTA}$  added after 3 min (3); 15 min (4); 90 min (5).

Ln-centered luminescence is highly sensitive to various environmental changes, the silica coating of Tb-complexes minimizes the environmental effects [19]. The difference between lifetimes for silica coated Tb<sup>III</sup> complex (0.9 ms) and this complex in solution [28] (0.7 ms) confirms this assumption. Thus, no changes in luminescence are observed at the addition of  $\text{Gd}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$  in the



**Scheme 2.** Aggregation behavior of Tb-doped SNs following the adsorption of  $\text{Fe}^{\text{III}}$  ions at the silica/water interface.

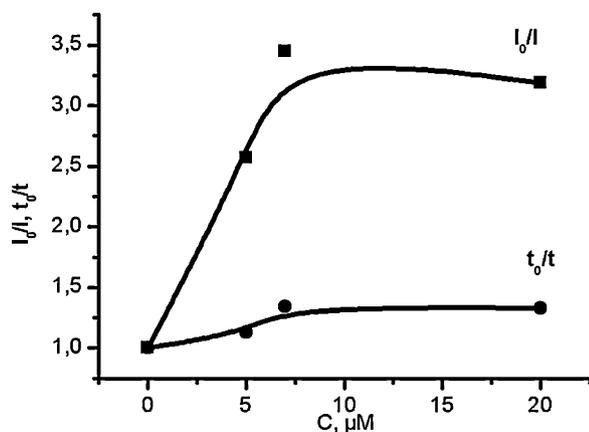


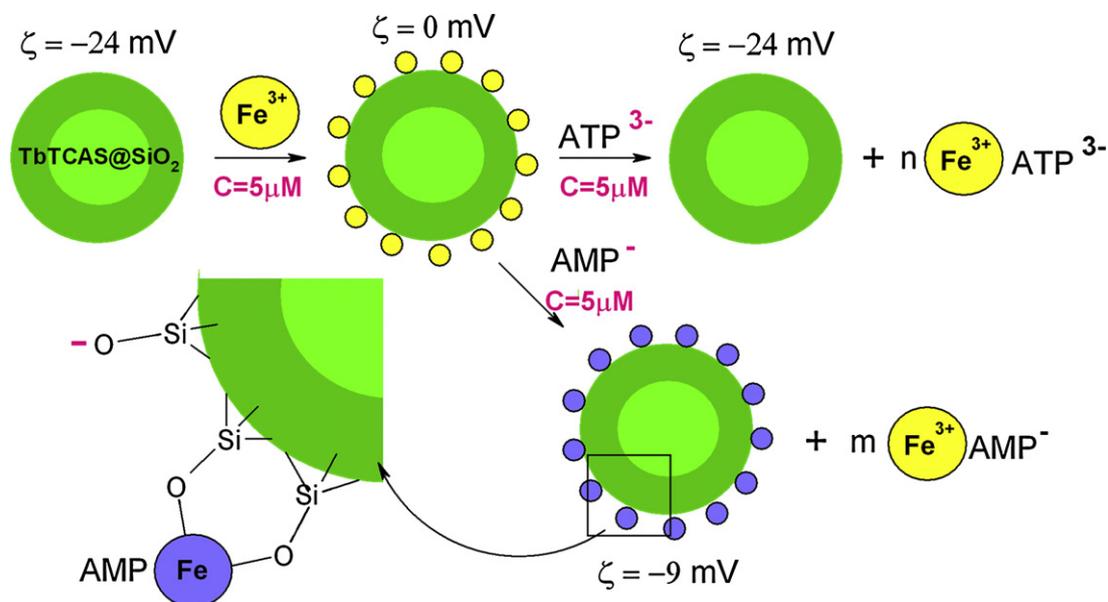
Fig. 4.  $I_0/I$  at 541 nm and  $\tau_0/\tau$  versus concentration of  $\text{FeCl}_3$ .

concentration range, where no adsorption occurs (Fig. 3a). The experimentally observed dramatic decrease of Tb-centered emission intensity at the addition of  $\text{Fe}^{\text{III}}$  in micromolar concentration range (Fig. 3a) is in good agreement with its adsorption onto silica revealed from DLS and electrokinetic measurements (Figs. 1 and 2). The quenching of Tb-centered luminescence can arise from both the static and dynamic quenching mechanisms [29,30]. Thus the steady state and time resolved quenching measurements have been analyzed in Stern–Volmer coordinates (Fig. 4). The comparison of the intensity-based ( $I_0/I$ ) and lifetime-based ( $\tau_0/\tau$ ) Stern–Volmer analysis at various  $\text{Fe}^{\text{III}}$  concentrations reveals both dynamic and static quenching mechanisms, though the latter is predominant (Fig. 4).

The quenching of Tb-centered luminescence by transition metal complexes is known to be driven by the energy transfer mechanism, which explains the contribution of the dynamic quenching through the energy transfer in this case [31]. The dependence of  $\tau_0/\tau$  on the concentration of  $\text{FeCl}_3$  is more or less linear within 0–5  $\mu\text{M}$ , coming to plateau with the further addition of  $\text{FeCl}_3$  (Fig. 4). The contribution of the energy transfer mechanism is in good agreement with the observed mode of quenching, which is rather common for proteins and luminophore-doped nanoparticles [19,29,30]. In particular the linear increase of  $\tau_0/\tau$  results from the efficient

quenching of the luminophores located close to silica/water interface, while those emitting molecules, which are within the core of nanoparticles are poorly quenched by interfacial interactions with quenching ions.

The static quenching mechanism is predominant, thus it should be discussed in detail. Several possible reasons can be responsible for the decrease of the emission intensity. The replacement of  $\text{Tb}^{\text{III}}$  by  $\text{Fe}^{\text{III}}$  according to Scheme 1 should be mentioned as the probable reason. The contribution of the ion substitution into the quenching can be revealed, if the stripping of  $\text{Fe}^{\text{III}}$  ions from the silica surface would be done. It is anticipated that anions, which are able to form stable complexes with  $\text{Fe}^{\text{III}}$ , should strip  $\text{Fe}^{\text{III}}$  ions from the silica surface (Scheme 3). Indeed, the addition of  $\text{Na}_2\text{EDTA}$  (5  $\mu\text{M}$  and more) to SNs pretreated by 5  $\mu\text{M}$  of  $\text{FeCl}_3$  results in the recharging and the deaggregation of nanoparticles (Figs. 1 and 2). The addition of  $\text{KH}_2\text{PO}_4$ , AMP, ADP and ATP also leads to the stripping effect, which is evident from the recharging and the deaggregation of SNs (Figs. 1 and 2, more details are represented in Table 2S in Supplementary material). The amounts of the added phosphates, which are required for the similar stripping effect, reveal good correlation with their complex ability with metal ions [33]. The stripping of  $\text{Fe}^{\text{III}}$  ions from the silica by EDTA and phosphates should induce the luminescent response. Indeed, 5  $\mu\text{M}$  of EDTA is enough to switch on the Tb-centered luminescence of nanoparticles, which has been switched off by 5  $\mu\text{M}$  of  $\text{FeCl}_3$  (Fig. 5). This result confirms well with  $\zeta$ -potential data (Fig. 1), indicating the correlation between the reestablished luminescence and the stripping effect of EDTA. Analogously to EDTA the addition of phosphates results in the reestablished emission intensity, while no luminescent response is observed at the addition of similar amounts of  $\text{NaCl}$  and  $\text{NaNO}_3$  (Figs. 3b and 5). These data confirm that the stripping effect of anions, which is in good correlation with their complex ability towards  $\text{Fe}^{\text{III}}$ , is the reason of the reestablished luminescence. The reestablishment of  $\tau$  is exemplified for ATP ( $\tau$  is equal to 0.9 ms at the addition 15  $\mu\text{M}$  of ATP to SNs pretreated by 5  $\mu\text{M}$  of  $\text{FeCl}_3$ ). The stripping effect of the anions forming complexes with  $\text{Fe}^{\text{III}}$  indicates that the ion exchange (Scheme 1) is not the only reason of the Tb-centered luminescence quenching at the addition of  $\text{FeCl}_3$ . Thus the reversible aggregation of SNs resulting from the adsorption of  $\text{Fe}^{\text{III}}$  ions (Scheme 2) is another probable reason of the quenching



Scheme 3. Stripping of  $\text{Fe}^{\text{III}}$  ions by ATP (upper scheme) and by AMP (lower scheme). The blue balls at the lower scheme represent the  $\text{Fe}^{\text{III}}$  complexes with AMP readsorbed onto silica surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

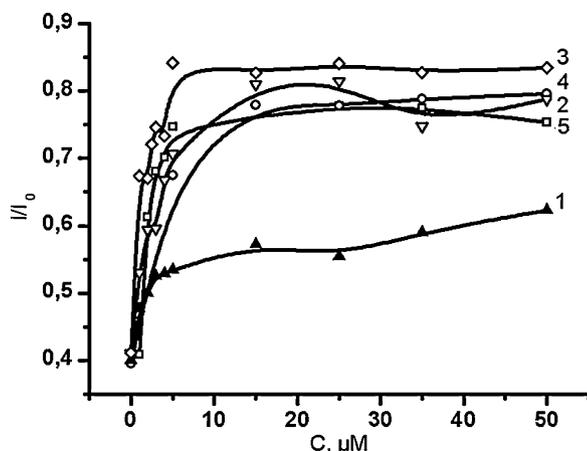


Fig. 5. The  $I/I_0$  versus concentrations of AMP (1), ADP (2), ATP (3),  $\text{KH}_2\text{PO}_4$  (4),  $\text{Na}_2\text{EDTA}$  (5), at pH 5.6, the addition of anions have been performed within 5 min after the pretreatment by  $\text{FeCl}_3$ .

through the static mechanism. The stirring of SNs in  $\text{FeCl}_3$  solution provides no effect on the emission intensity. Thus the emission intensity is not affected by the sedimentation of SNs aggregates. It is also worth noting that the aggregation of SNs can change the transmittance of the excited light in colloids of SNs in the presence of  $\text{Fe}^{\text{III}}$  ions due to the light scattering effect, which in turn depends on the size of the aggregates [32]. No significant changes of the transmittance at 330 nm have been revealed at  $5 \mu\text{M}$  of  $\text{FeCl}_3$  (Fig. 2S in Supplementary material), where the aggregation of SNs is the most (Fig. 2).

It is worth noting that the reestablishment of Tb-centered luminescence resulted from the stripping effect of anions is incomplete. Indeed the  $I/I_0$ -value does not exceed 0.85, depending on the nature of stripping ions (Fig. 5). The reasons of the incomplete reestablishment are worth discussing. The replacement of  $\text{Tb}^{\text{III}}$  by  $\text{Fe}^{\text{III}}$  (Scheme 1) should be mentioned as the first probable reason. The penetration of the ions into the silica matrix is diffusion controlled and time dependent [34]. Thus the stripping effect of EDTA at various space of time after the addition of  $\text{Fe}^{\text{III}}$  has been evaluated. Indeed, the reestablishment is practically complete when EDTA is added within 3 min after the addition of  $\text{FeCl}_3$ , while about 20% of Tb-centered emission intensity is lost after 15 min (Fig. 3b). No reestablishment of luminescence is observed within 1.5 h after the addition of  $\text{FeCl}_3$ . These results show that more time is required for the significant quenching through the ion exchange (Scheme 1), while some effect of the ion exchange is observed within 15 min. As it has been above mentioned the saturated value of  $I/I_0$  depends on the nature of stripping anions, being less for AMP, increasing for  $\text{H}_2\text{PO}_4^-$ , ADP and EDTA and being the most for ATP ( $I/I_0$  increases from 0.65 to 0.85) (Fig. 5), while kinetic conditions are the same. The reasons of this dependence should be discussed. Silica surface tend to adsorb both organic substrates and metal complexes [35,36], thus the adsorption of  $\text{Fe}^{\text{III}}$  complexes with stripping anions onto silica is rather probable. It means that the stripping effect of EDTA and phosphates is accompanied by some readsorption of  $\text{Fe}^{\text{III}}$  complexes onto silica, which is another probable reason of the incomplete reestablishment of emission intensity. The DLS measurements bring the confirmation of this assumption. Indeed the addition of AMP induces less significant recharging from plus to minus in the comparison with  $\text{Na}_2\text{EDTA}$ ,  $\text{KH}_2\text{PO}_4$ , ADP, ATP (Fig. 1). It is worth noting that the adsorption of  $\text{Fe}^{\text{III}}$ -AMP complex being more significant than others is in good agreement with the well-known tendency that the positive charge and hydrophobicity of substrates enhance their adsorption onto silica. The readsorption of  $\text{Fe}^{\text{III}}$  complexes with stripping anions schematically represented

in Scheme 3 can be regarded as the second reason of the incomplete reestablishment, which restricts the stripping effect of anions. Thus both high complex ability and hydrophilicity are the main reasons of the enhanced stripping effect of ATP versus other phosphates. The simplified illustration of the enhanced stripping effect of ATP versus AMP is shown in Scheme 3. The stripping effect of phosphates being most enhanced for ATP results in the “off-on” switching of Tb-luminescence, which in turn enables to sense ATP in micromolar concentration range.

#### 4. Conclusions

The represented results reveal the reversible adsorption of  $\text{Fe}^{\text{III}}$  ions onto surface of Tb-doped SNs as the reason of the Tb-centered luminescence quenching through the dynamic and static mechanisms. The latter quenching mechanism is predominant and arises from the reversible aggregation of SNs and the ion exchange. The contribution of the dynamic quenching mechanism reveals that the permeability of silica matrix is enough for the energy transfer between luminophores inside SNs and outside quenching ions, though only part of luminophores are accessible for quenching through the energy transfer. The stripping of  $\text{Fe}^{\text{III}}$  ions from the silica surface results in “off-on” switching of Tb-luminescence. The luminescent response on the addition of various anions depends on the space of time after the pretreating of SNs by  $\text{FeCl}_3$ , which reveals the contribution of the ion exchange into the quenching through the static mechanism. The quenching through the ion exchange is also limited, indicating that some luminophores within the core of SNs are enaccessible for the ion exchange. The analysis of the stripping effect of EDTA and various phosphates reveals both high complex ability and hydrophilicity as the main reasons of the enhanced stripping effect of ATP versus other phosphates.

The present report highlights the interfacial adsorption and further stripping of metal ions as the reasons of “on-off-on” switching of Tb-centered luminescence, while the displacements in the inner coordination sphere of lanthanides is more common approach to sense metal ions and phosphates through luminescent response [23,25,37,38]. It is also worth noting that the adsorption of metal ions is an easy and convenient way of a silica surface decoration, while the stripping effect of phosphates is detectable even in micromolar concentration of the latter. Thus Tb-doped SNs pretreated by  $\text{Fe}^{\text{III}}$  ions exemplify a convenient basis of substrate sensitive nanomaterial for further application in bioanalytical purposes.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matchemphys.2011.11.058.

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