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Effect of silica coating and further silica surface decoration by phospholipid bilayer on quenching of Tb(III) complexes by adrenochrome

Alsu Mukhametshina [b,*], Asiya Mustafina [a], Victor Syakaev [a], Rustem Amirov [b], Konstantin Petrov [a,b], Alexander Konovalov [a]

[a] A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Arbuzov str. 8, 42088 Kazan, Russian Federation
[b] Kazan Federal University, Kremlyovskaya str. 18, 420008 Kazan, Russian Federation

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ABSTRACT

The present report introduces regularities and mechanisms of Tb(III)-centered luminescence quenching by adrenochrome for Tb(III)-p-sulfonatothiacalix[4]arene complexes in the aqueous solutions and the same complexes doped into silica nanoparticles. The choice of adrenochrome (the oxidized form of adrenaline) as quencher originates from its quenching effect on the Tb(III)-centered luminescence, which discriminates it from adrenaline and dopamine. The quenching through dynamic mechanism of the Tb(III) complexes in the solutions results from their concentration induced collision with adrenochrome molecules. The quenching of the Tb(III)-doped silica nanoparticles also occurs through dynamic mechanism, although it is insignificant due to the shielding effect of the silica surface. The inclusion of the Tb(III)-doped silica nanoparticles into phospholipid bilayers influences the quenching of the Tb(III)-centered luminescence by adrenochrome due to its binding with the bilayers deposited onto silica nanoparticles.

1. Introduction

Silica nanoparticles (SNs) doped with lanthanide complexes gain great attention during recent decades due to their applicability in fluorescent and MRI sensing and imaging [1–3]. In this connection correlation between a binding of substrates at a silica/water interface and a fluorescent response of lanthanide complexes within silica nanoparticles is of great importance due to its impact in both sensing and imaging. Non-covalent silica surface decoration is a convenient tool to vary a sensing function of silica coated luminophores due to an impact of an exterior layer in an interfacial binding of substrates. Phospholipid bilayer deposition onto silica nanoparticles (silica beads) or so-called supported lipid bilayers (SLBs) [4–6] is of great importance in growing the blood compatibility of nanomaterial for imaging and drug delivery [7,8]. The binding ability of phospholipid bilayers toward small biorelevant molecules is well known [9,10]. The application of this binding in the development of sensing function for SLB with silica nanoparticles doped with Tb(III) complexes as silica beads is a challenging task. Thus the present work is focused on the sensing function of the Tb(III) doped SLB in comparison with the Tb(III)-doped SNs and the Tb(III) complexes in aqueous solutions.

The sensing of small biorelevant molecules, such as catecholamines is the top of current interest due to their impact in biology and medicine. Catecholamines are bioenergetic amines that play an important role as neurotransmitters in the central nervous system. Epinephrine (EP), often called adrenaline, is an important catecholamine, which acts as a hormone and neurotransmitter in the mammalian central nervous system [11,12]. Many life phenomena, such as contraction of smooth muscles, heart rate, blood pressure, glycogenolysis in the liver and muscle, and lipolysis in adipose tissue are related to the concentration of EP in the blood [13]. Medically, EP has been used as a common emergency healthcare medicine [13]. The measurement of EP concentration in biological fluids such as urine, plasma, and serum is very important in clinical diagnosis of several diseases [14–18]. Catecholamines are very often detected by means of electrochemical or fluorescence techniques [19,20]. Compared with electrochemical procedure, fluorescence detection is more robust and therefore presently more widely applied. The own luminescence of catecholamines is rather weak to be applied in their determination, thus the fluorescent detection commonly requires the performance of sophisticated and expensive synthetic treatment before analysis. The fluorescent response resulting from a complex formation of catecholamines with inorganic or organic chromophores represents another route of fluorescent recognition of catecholamines [19,21–23]. Lanthanide ions exemplify inorganic chromophores, which being bound with catecholamines produce a luminescent response. The sensitization of Tb(III) luminescence

* Corresponding author.
E-mail address: alsu_mukhamet@mail.ru (A. Mukhametshina).

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