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Efficient “antenna effect” in the complex of (+) catechin and Tb(III) lodged inside the nano-cavity of β-cyclodextrin

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ABSTRACT

A complex of Tb(III) with (+) catechin (C) has been profitably encapsulated within the β-CD cavity at physiological pH = 6.9 in aqueous medium. The ternary system exhibits a remarkable ‘antenna effect’ compared to the complex of Tb(III) with C. Time resolved measurement of Tb(III) emission in H_2O and in D_2O directly proves the protection of Tb(III) from O—H oscillator within the cavity. The rotational correlation time of bound C obtained from time resolved anisotropy further confirms the motional restriction of C in the ternary system providing enhanced energy transfer efficiency. The simple system may help improve designing imaging technique in aqueous medium.

1. Introduction

The efficient sensitization of Ln(III) emission in various medium is an active area of research for developing biological imaging technique, biomedical assay [1–9] in the visible and in the NIR regions [10]. The Ln(III) emission is characterized by the narrow band width, the longer lifetime and the large Stoke’s shift from the excitation source. These features help possible to develop such applications. Several Ln(III) complexes have been also studied for developing two photon microscopy [11–15].

The main hurdle to derive enhanced ‘antenna effect’ for Ln(III) in aqueous medium is the protection of the first coordination sphere of Ln(III) from the O—H oscillator which due to its vibronic coupling quenches the Ln(III) emission through the non-radiative decay [16,17]. One also needs the complex to be kinetically stable in aqueous medium. Furthermore, the co-ordinating ligands of Ln(III) must have a high absorbing $\pi\pi^*$ singlet state (S_1). Assuming Dexter’s exchange mechanism being operative in the sensitization process the corresponding lowest $\pi\pi^*$ triplet state of the ligand acting as donor state must be suitably located compared to the emissive state of Ln(III) in order to minimize the back energy transfer (ET). It is also desirable to enhance the population of the lowest triplet (T_1) state of the ligand by increasing the Inter System Crossing ($S_1 \rightarrow T_1$) rate. The presence of a charge transfer (CT) state arising from metal to ligand or metal to counter anion located either between the S_1 and the T_1 state of the ligand or between the T_1 state and the emissive state of Ln(III) could facilitate deactivation through the CT state acting as a non-radiative channel and thus diminishing the sensitization efficiency.

The synthesis and characterization of various d–f hybrid complexes using Ru(III), Os(III), Ir(III), Re(III) and Pt(III) [18–31] have been carried out to enhance the ET efficiency using the MLCT state as the donor state. The majority of the d–f hybrid complexes, however, exhibit sensitization effect in non aqueous medium.

Lanthanide-based luminescent hybrid materials have also been developed [32]. Various hosts used include sol–gel hybrid, porous hybrid like zeolites and meso porous silicates, intercalation compound, various polymer materials, hydrogels and organogels, nanocomposite materials [32]. However, there is no report of direct encapsulation of a lanthanide complex within the nano cavity of cyclodextrins.

Cyclodextrins (CD) (α, β and γ) are known to form host guest complexes with various guests having proper molecular dimension comparable to the size of the nano cavity of CD [33–36]. Cyclodextrins, cyclic oligosaccharides, composed of glucopyranose units usually are reported as truncated cone structure with a hydrophobic cavity possessing a unique feature of the difference of polarity between the internal and the external surfaces. The displacement of water molecules by apolar substrates represents a

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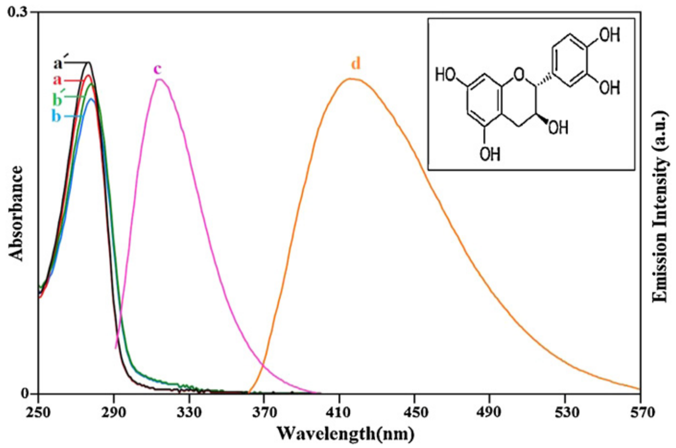

Fig. 1. Absorption spectra of (a) C, (a′) C + Tb(III), (b) C + β-CD, (b′) C + Tb(III) + β-CD in aqueous Tris–HCl buffer at pH 6.9 at 300 K; (c) fluorescence spectra of C in aqueous Tris–HCl buffer at pH 6.9 at 300 K; (d) phosphorescence spectra of C in 40% ethylene glycol at 77 K; ([β-CD] = 10,000 μM, [C] = 25 μM, [Tb(III)] = 25 μM). Inset: Molecular structure of (+) catechin (C).

thermodynamically favourable process for host guest complex formation [35]. The hydrophobicity of the nano cavity of cyclodextrins has been explored by characterization of the host–guest complex by various spectroscopic methods and by theoretical calculations [36].

In this report our aim is to lodge a Tb(III) complex of proper molecular dimension in the nano cavity of β-CD having the cavity diameter 6.0–6.5 Å with the height of torus being 7.9 Å. For this purpose one needs a suitable ligand which forms a kinetically stable complex with Tb(III) in aqueous medium and which can also be encapsulated within β-CD cavity having approximate volume per molecule = 252 Å^3. To this effect, we envisage a ternary system consisting of catechin (+) (C) (Inset in Fig. 1) with Tb(III) and β-CD. C is known to form preferably 1:1 complex with β-CD [37] and is also found to bind Tb(III). The encapsulation of the complex within β-CD will serve two purposes (i) protection of Tb(III) from the O—H oscillator (ii) tight binding by the hydrophobic environment of β-CD hindering the free rotation of the ligand which could in turn enhance the ET efficiency from the ligand to Tb(III). A sol–gel film incorporating a cyclodextrin supramolecule modified with Tb(III) macrocycle when exposed to biphenyl in aqueous solution was found to exhibit sensitized Tb(III) emission [38]. In this system biphenyl in the cyclodextrin receptor acts as donor [38]. β-CD modified with a Ln(III) diethylenetriaminepentaacetic acid macrocycle was also used as a host to trigger Ln(III) emission in the presence of biphenyl as a sensitizer [39].

In this work, we report the remarkably efficient ‘antenna effect’ observed in a ternary system where the complex of Tb(III) with C is encapsulated into the nano cavity of β-CD compared to the complex of Tb(III) with C in aqueous medium at physiological pH (=6.9). The steady state and the time resolved emission study of C and Tb(III) in the binary systems [C with β-CD; Tb(III) with C and Tb(III) with β-CD] and in the ternary system consisting of C, Tb(III) and β-CD in aqueous medium have been presented. The binding constant of C with β-CD has been evaluated and compared with the values obtained by other methods [37,40,41]. The time resolved emission of Tb(III) in all the binary and in the ternary systems in both H_2O and D_2O buffer have been carried out to study the mechanism of the enhanced sensitization effect and the efficient shielding of Tb(III) inside the cavity of β-CD. Time resolved anisotropy of the emission of C in the β-CD complex and in the ternary system has been used to explore the change of motional restriction of C in the complex induced by the nano cavity of β-CD. The result of the theoretical calculation of the geometry of C within the β-CD cavity [36] has been used to explain the shielding effect provided by the β-CD cavity.

2. Experimental

2.1. Materials and methods

All the chemicals were of the purest grade available and were used as received. (+) Catechin (C), terbium nitrate ($Tb(NO_3)_3$), β-cyclodextrin (β-CD), α,α,α-Tris-(hydroxymethyl)-methylamine and Deuterium oxide (99.9 at.%) were purchased from Sigma–Aldrich, USA. The 0.1(M) Tris–HCl buffer of pH 6.9 was prepared in triply distilled water and in D_2O medium and used for making all experimental solutions. The stock solutions of C were prepared using the extinction coefficient in water (ε = 10,233 M^{-1} cm^{-1} at 276 nm). The binary complexes were prepared by mixing of 25 μM C with 10,000 μM β-CD and 10,000 μM β-CD with 25 μM Tb(III). The ternary system was prepared by using 25 μM C, 25 μM Tb(III) and 10,000 μM β-CD in Tris buffer of pH 6.9. The pH 6.9 was chosen to prevent the oxidation of catechin to quinone [42] at higher pH and taking into consideration of the physiological pH. All the systems were kept for 3 h and then used for spectroscopic study. Any inner filter effect has been eliminated by using the prescribed concentration of the species used.

2.2. Instrumentation

UV–vis absorption spectra were recorded on a Hitachi U-4010 spectrophotometer at 300 K. The steady state emission measurements were carried out using a Hitachi Model F-7000 spectrofluorimeter equipped with a 150-W xenon lamp, at 300 K using a stoppered cell of 1 cm path length. Emission studies at 77 K were made using a Dewar system having a 5 mm outer diameter quartz tube. Phosphorescence spectra were measured in a Hitachi F-7000 spectrofluorimeter equipped with phosphorescence accessories using 40% ethylene glycol matrix. The samples were excited at 280 nm using a 10 nm band pass, and the emission band pass was 5 nm.

The nanosecond lifetime of the singlet state Time resolved anisotropy were measured using TCSPC setup from PTI, USA using the sub-nanosecond pulsed LED source (290 nm having pulse width 600 ps [full width at half-maximum] (from PicoQuant, Germany) operating at high repetition rate of 10 MHz driven by PDL 800-B driver, PicoQuant, Germany. LED profiles were measured at 290 nm with a band-pass of 3 nm using Ludox as the scatterer. Decay measurement using ‘magic angle’ detection with an emission polarizer set at 54.7° were carried out and no detectable difference in the fitted τ values with those obtained from normal decay measurements were observed.

The decay parameters were recovered using a non-linear iterative fitting procedure based on the Marquardt algorithm [43]. Deconvolution technique used can determine the lifetime up to 150–200 ps. The quality of fit has been assessed over the entire decay, including the rising edge, and tested with a plot of weighted residuals and other statistical parameters e.g. the reduced χ^2 ratio [44].

The decay times of the Tb(III) complexes in the microsecond region were also acquired by phosphorescence decay mode in QM-30 fluorimeter from PTI, USA using a gated detection system having start and end window time 150 μs and 10,000 μs respectively. The phosphorescence decay of C was measured by phosphorescence timebased mode in QM-30 fluorimeter from PTI, USA. The decay parameters were recovered using a non-linear iterative fitting procedure based on the Marquardt algorithm [43].