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Two-photon excited luminescence of lanthanide complex in monolithic sol–gel hybrid material

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ABSTRACT

A π-conjugated donor functionalized tris-dipicolinate complex, featuring promising two-photon excited luminescence properties in water was successfully embedded in a monolithic sol–gel material. A complete spectroscopic study unambiguously indicates that the europium complex conserves its integrity in this sol–gel matrix and the improvement of the luminescence lifetime clearly indicates a stabilisation of the complex in the matrix. Biphotonic confocal microscopy measurement shows that the Eu(III) luminescence can be sensitized in the sol–gel material using a two-photon antenna process, which is a first step towards the design of doped sol–gel nanoparticles for two-photon imaging applications.

1. Introduction

The unique spectroscopic properties of lanthanide complex (line-shape emission, long excited state lifetime, large apparent Stokes-shift and sensitivity to the local environment) [1] made them very attractive candidates for the design of bio-probes towards bio-imaging, -labeling and -sensing applications [2]. In addition their long excited state lifetime in the ms range for europium or terbium gave the opportunity to carry out time-gated imaging [3] and homogeneous time-resolved fluorescence bioassay [4]. In all these applications the lanthanide excitation process by a classical one-photon antenna effect with excitation wavelength generally below 420–450 nm in the case of europium (the most studied rare-earth). However, these wavelengths are strongly absorbed or scattered by biological media, which strongly limits the penetration depth and therefore restricted the application to surface (2D) imaging. To tackle this drawback, the lanthanide sensitization by a two-photon antenna effect has been developed for about one decade [5]. This third-order nonlinear process consists in the simultaneous absorption of two-photon of half energy under a focalized fs-laser irradiation. As a consequence, the excitation wavelengths are shifted towards the near-infrared spectral range corresponding to the biological transparency window (700–1100 nm) and the intrinsic confocal character gives rise to a 3D-resolution. In a first time, the proof-of-concept of the two-photon antenna effect has been established using lanthanide complexes only stable in organic media [6]. The two-photon cross-section (σ^2 in Göppert-Mayer; 1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1}), which quantifies the efficiency of the two-photon absorption (TPA) process, was optimized up to 775 GM at 740 nm [7], a value in the range of the best organic chromophores. In a second time the proof-of-concept of the two-photon microscopy was established using a tris-dipicolinate terbium crystal [8] opening new avenues for the design of original probes for confocal biphotonic microscopy imaging [9].

In this context, we described the design of donor-π-conjugated functionalized tris-dipicolinate lanthanide complexes **[Na]$_3$[EuL$_3^{1G}$]** (**1**), featuring nine polyetylene glycol (PEG) end-groups to ensure water solubility (Fig. 1) that was successfully used to image fixed cancer cells using two-photon microscopy [9a]. However, this complex exhibit a rather modest water stability due to the partial ligand dissociation upon dilution (Eq. (1) where DPA represents the functionalized or not dipicolinic acid ligand): in the present case 30% of dissociation was measured in the 10^{-4}–10^{-5} M concentration range [10].

$$[Ln(DPA)_3]^{2-} \underset{H_2O}{\rightleftharpoons} [Ln(DPA)_2(H_2O)_x]^- + DPA^{2-} \quad (1)$$

This dissociation, even partial, results the coordination of water molecules, known to act as efficient emission quencher and is experimentally transduced by a strong decrease of the luminescence quantum yield and lifetime. Here, luminescence lifetime of **1** drops down from 1.06 ms to about 0.3 ms upon dilution.

Two stabilisation strategies can be envisaged to hinder this dissociation, which limits the use of this complex in biological relevant applications: (i) a synthetic one aiming to incorporate the two-photon antenna into a more stable macrocyclic ligand [11] or (ii) a formulation by dispersing the complex **1** in silica nanoparticles. This later approach presents the additional advantage to confine

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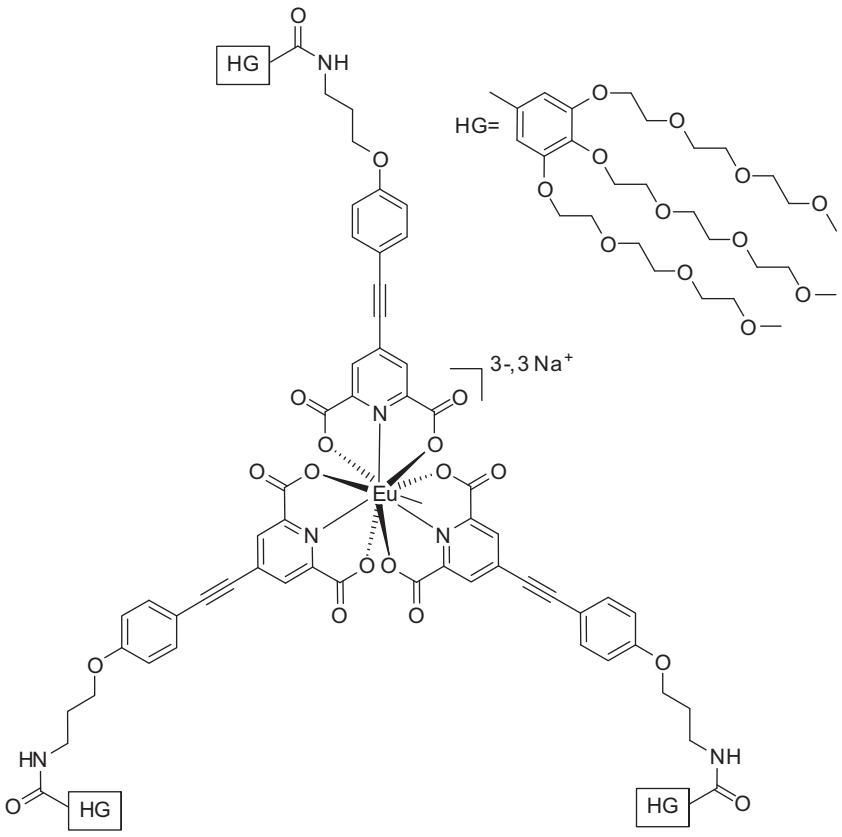

Fig. 1. Structure of the ligands and related complexes $\mathbf{[Na]_3[EuL_3^{1G}]}$ (HG = hydrosolubilizing group).

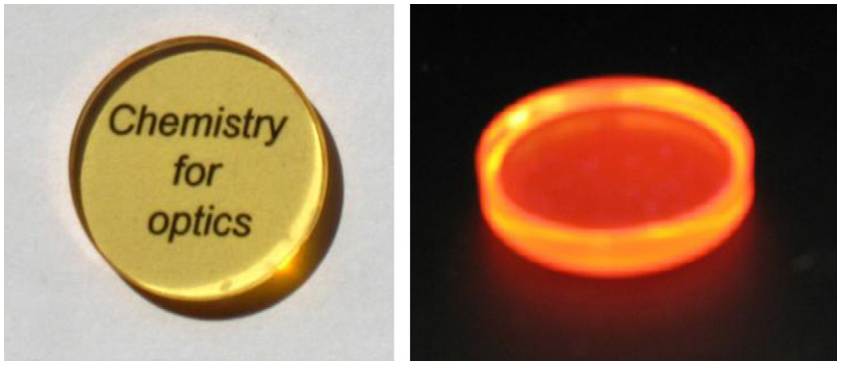

Fig. 2. Picture of the polished monolithic sol–gel material without (left) and with (right) UV irradiation.

large number of chromophores in nanoscale volume resulting in an enhancement of the TPA efficiency [12]. Recently, Wang and co-workers described biphotonic imaging of cancer cells using lanthanide complex containing nanoparticle [13]. With the long term objective to prepare such nanoparticle, we report in this article a study aiming to evaluate the stability and compatibility of **1** in a monolithic sol–gel matrix. Moreover such monolithic material can be used for further applications in optical filters or sensors. The synthesis of the material is described and its spectroscopic properties (absorption, emission, TPA) are compared with the solution ones measured in dichloromethane (DCM) and water.

2. Results and discussion

The synthesis of $\mathbf{[Na]_3[EuL_3^{1G}]}$ (Fig. 1) was achieved as described elsewhere [9a]. In this molecule, the conjugated moiety was used to increase the intrinsic molar absorption coefficient and to efficiently reach sensitization of the Eu(III) from the charge transfer (CT) excited state. The hydrosolubilizing group (HG, Fig. 1) as the counter ion of the complex (sodium in the case of the described complex) was appended to gain solubility in protic solvent despite the moderate stability in such solvent (*vide infra*). This latter fact allows the preparation of the sol–gel matrix with concentration high enough to prevent any dissociation of the lanthanide complex.

2.1. Synthesis of the material

The complex preliminary dissolved in THF (1 mL) was mixed with the sol–gel precursor solution $MeSi(OEt)_3$ (3 mL). The mixture is microfiltrated (teflon filter 0.45) in a Teflon vessel. Three drops of aminopropyltriethoxysilane solution (0.1 mM in ethanol) were added to neutralize the acidic traces [14]. The sample was heated for 48 h at 70 °C, and for 24 h at 100 °C. After