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Investigation of ground and excited state photophysical properties of gadolinium phthalocyanine

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ABSTRACT

In this present work, we investigated the singlet excited state absorption (ESA) spectrum and intersystem crossing dynamics of gadolinium phthalocyanine (GdPc) in toluene. For that, we employed the femtosecond wavelength-tunable Z-scan and picosecond Pulse Train Fluorescence (PTF) techniques to determine, respectively, the singlet ESA cross-section on a wide spectral range (from 460 up to 740 nm) and the intersystem crossing time (singlet–triplet transition). We observed that the ESA spectrum presents distinct absorption behaviors, i.e., saturable (SA) and reverse saturable absorption (RSA). We have also been able to identify regions in which the excited state absorption cross-section has the same magnitude as the ground state one (at 600 and 720 nm). The RSA effect was observed for wavelengths shorter than 600 nm and longer than 720 nm, while SA occurs in the Q-band region, located between 600 and 720 nm. To describe the main singlet–singlet transitions, we measured the fluorescence decay time and employed a rate equation model considering a three-energy-level-diagram. Ratios between excited and ground state absorption cross-section from 0.4 to 4 were observed along the ESA spectrum. From these results, we calculated the transition dipole moment between the excited states for the main electronic transitions of GdPc. To obtain the intersystem crossing time, we incorporated an additional level in our model and used the PTF technique to probe the population transfer to the triplet state. Our results pointed out that the intersystem crossing time is higher than 300 ns, which corresponds to a maximum triplet quantum yield of 1.5%.

1. Introduction

The understanding of singlet and triplet excited state absorption (ESA) properties of lanthanide phthalocyanines are of foremost importance for the development of new and efficient optoelectronic and photonic devices based in organic materials [1–5]. Phthalocyanines can be modified and analyzed in solid state as thin films, in solution or in the powder state [6,7]. Due to its structural flexibility, the synthesis and structure-property relationship of phthalocyanines continue attracting attention from the scientific community. For example, phthalocyanines with distinct ligands and central atoms have been used in various applications, such as the photovoltaic material in solar cells [8,9], all-optical switching [10], optical power limiting [11–13], molecular electronics [14,15], 3D optical data storage [16], sensors [17,18], electrochromic and photochromic systems [19,20] and photodynamic therapy [21–23], and so on.

The great number of distinct applications for phthalocyanine is directly related to their interesting optical and electronic features, as high chemical stability, two-dimensionality system rich in π-electrons, modification of the electronic distribution of the macrocycle ring by the central metal and strong metal-to-ligand charge transfer character [24–26]. Among these compounds, complexes containing gadolinium in their macrocycle or attached to phthalocyanine or porphyrins are interesting system to medical applications as photosensitizers for photodynamic therapy [27,28]. Moreover, lanthanide phtalocyanines with pronuncied nonlinear optical effect and fast response time has been used as saturable absorbers for development of passive mode locking and Q-switching of lasers [29,30], i.e., for generation of ultrashort pulses in laser systems. In this context, the aim of this study is to investigate the singlet ESA properties and triplet intersystem crossing time of gadolinium phthalocyanine (GdPc) dissolved in toluene solution. For that, we employed the femtosecond wavelength-tunable Z-scan to determine the singlet ESA cross-section on a wide spectral range (from 460 up to 740 nm) and picosecond Pulse Train Fluorescence (PTF) technique to found the intersystem crossing time. Our results pointed out different effect along the ESA spectrum as, for instance,

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reverse saturable absorption (RSA) between 460 and 600 nm and saturable absorption (SA) in the Q-band region (600–720 nm). These regions were modeled employing the rate equations approach and from them, the ESA cross-sections values were determined. Moreover, using the two-level energy approximation, we estimated the transition dipole moments between the excited states for the main singlet electronic states. Finally, using the picosecond PTF technique, we found that the triplet quantum yield for the GdPc dissolved in toluene is very small due to their long intersystem crossing time (>300 ns).

2. Experimental

All chemicals were of reagent grade and used as supplied (Sigma–Aldrich). The experimental procedure performed for the synthesis of neutral radical state GdPc was adapted from the one described in Ref. [31]. The GdPc molecular structure is illustrated in Fig. 1. We prepared GdPc/toluene solutions with concentrations of 6×10^{-6} and 1.5×10^{-4} mol L^{-1}, for ground and excited state absorption measurements respectively. For the optical measurements, the samples were placed in 2-mm thick fused silica cuvettes. The steady-state absorption and photoluminescence spectra were recorded using a Shimadzu UV-1800 spectrophotometer and a Perkin Elmer LS55 fluorimeter respectively.

Excited state absorption measurements were carried out employing the open-aperture Z-scan [32], using 120-fs laser pulses from an optical parametric amplifier pumped by 150-fs pulses at 775 nm, delivered by a Ti:sapphire chirped pulse amplified system, operating at 1-kHz repetition rate. The Z-scan measurements were carried out with energies ranging from 20 to 150 nJ/pulse, with beam waist size ranging from 14 to 18 μm. More details about the Z-scan setup employed are described in Ref. [33].

To measure the fluorescence lifetime of the sample, pulses at 532 nm from the second harmonic of a Q-switched and mode-locked Nd:YAG (70 ps) were employed. The 532 nm beam was focused into the sample, placed in a 2 mm-thick fused silica cuvette, with a lens of focal length $f = 12$ cm. Experimental details about of the time-resolved fluorescence setup can be found in Ref. [34]. The same experimental setup was used to measure the intersystem crossing time by employing the PTF technique, whose details can be found in Ref. [35].

3. Results and discussions

In Fig. 2, the solid lines represent the linear absorption spectrum of GdPc in toluene solution. This spectrum exhibits two characteristic absorptions bands of phthalocyanine compounds, denominated B- and Q-band, centered at 335 and 640 nm, respectively, which are attributed to $\pi \rightarrow \pi^*$ transitions from the phthalocyanine macrocycle [7].

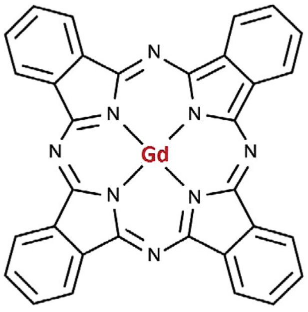

Fig. 1. The molecular structure of GdPc.

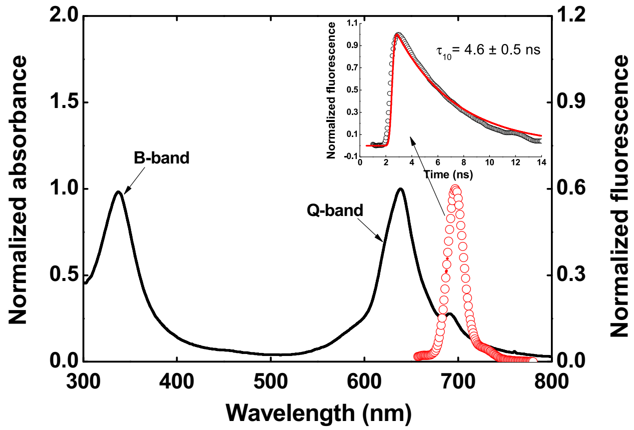

Fig. 2. Normalized linear absorption (solid line) and fluorescence (circles) spectra for the GdPc. The inset depicts the fluorescence decay obtained using 70-ps pulses.

The circles in Fig. 2 illustrate the normalized fluorescence spectrum at room temperature, obtained with excitation at 640 nm (peak of Q-band). The fluorescence spectrum presents a maximum at 698 nm, which is associated with the radiative emission from the Q-band to the ground state of macrocycle. We measured the fluorescence lifetime decay by using as excitation source a 70-ps laser at 532 nm and obtained a value of 4.6 ± 0.5 ns (see inset of Fig. 2). In general, lanthanide phthalocyanines present fluorescence decay of order of nanosecond as can be seen in Refs. [36,37]. We also measured the fluorescence quantum yield of this emission using the rhodamine B ($\phi = 0.69$ in ethanol) as a standard and the methodology described in Ref. [38]. With such procedure we found $\phi_f^{GdPc} = 1.62 \times 10^{-4}$. Such value is on order of magnitude of the one reported for gadolinium porphyrin [39], for example.

Fig. 3 shows the ground (solid lines) and excited (circles) states absorption spectra for GdPc in toluene. The singlet ESA spectrum was determined by performing open-aperture Z-scan measurements with femtosecond pulses (160 fs) and low repetition rate (1 KHz). In this case, the short pulse duration allows obtaining pure singlet state absorption, since the intersystem crossing time (singlet to triplet) for GdPc is of the order of nanosecond, as it will be shown later. Furthermore, the low repetition rate (1 KHz) helps to avoid cumulative effects between consecutive pulses, coming from possible triplet–triplet absorption [40,41].

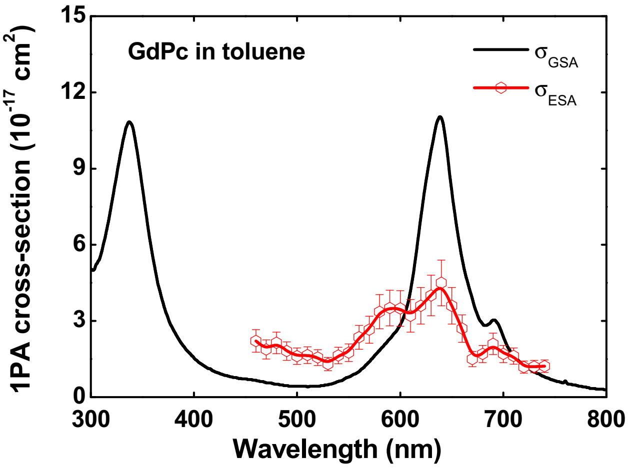

Fig. 3. Molecular ground (solid lines) and excited (circle squares) state absorption cross-section spectra for GdPc/toluene solution obtained using the rate equation model to describe the Z-scan data.