Energy Transfer in Ce$_{0.85}$Tb$_{0.15}$F$_3$ Nanoparticles-CTAB Shell-Chlorin e$_6$ System

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Abstract
Formation and electronic excitation energy transfer process in the nanosystem consisting of Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanoparticles, cetrimonium bromide (CTAB) surfactant, and chlorin e$_6$ photosensitizer were studied. It was shown that chlorin e$_6$ molecules bind to Ce$_{0.85}$Tb$_{0.15}$F$_3$ NP in the presence of CTAB forming thus Ce$_{0.85}$Tb$_{0.15}$F$_3$ NP-CTAB-chlorin e$_6$ nanosystem. We consider that binding occurs via chlorin e$_6$ embedding in the shell of CTAB molecules, formed around NP. In the Ce$_{0.85}$Tb$_{0.15}$F$_3$ NP-CTAB-chlorin e$_6$ nanosystem, electronic excitation energy transfer from Ce$^{3+}$ to chlorin e$_6$ takes place both directly (with the 0.33 efficiency for 2 μM chlorin e$_6$) and via Tb$^{3+}$.

Keywords: Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanoparticles, Chlorin e$_6$, Electronic excitation energy transfer, Photodynamic therapy

Background
Photodynamic therapy (PDT) is the method for the treatment of cancer, where the photosensitizer excitation by the light leads to the generation of singlet oxygen that is toxic for the tumor tissue [1]. But despite of several advantages, the drawback of this method is the very small depth of the light penetration into the tissue [2]. Thus, the idea of X-ray-inducible PDT based on X-ray-excited sensitizers composed of scintillating and photosensitizing parts with the electronic excitation energy transfer (EEET) from the first to the last one seems attractive [3]. Recently, a number of nanosystems based on this concept were described with various materials used as scintillators, different photosensitizer molecules, and several ways of binding them into a system [2, 4–9]; X-rays induced singlet oxygen generation [2, 6, 7, 9], cell destruction [4, 5, 7], and tumor destruction in mice [7] were demonstrated.

One of the options to choose scintillator for the above-described nanosystems is using lanthanide fluoride nanoparticles (NPs) [5, 9, 10]. Since f-f transitions of the majority of lanthanides are strongly forbidden, while in the case of Ce$^{3+}$ its f-d transitions are allowed, generally, the lanthanide ions except Ce$^{3+}$ cannot be efficiently excited by light in the UV-visible spectral region [11]. Thus, for the study of photophysics properties, CeF$_3$-based [8, 12, 13] or Ce$^{3+}$-doped [8, 10, 11] nanoparticles are used; excitation of Ce$^{3+}$ results either in its own emission or in that of another lanthanide ion dopant (e.g., Tb$^{3+}$) due to EEET [12, 13]. Excitation energy transfer from lanthanide nanoparticles to electrostatically bound [8, 9] or covalently attached [8, 10] photosensitizers was demonstrated.

Chlorin e$_6$ is a known compound with photosensitizing properties used in PDT of cancer [14, 15]; its combination with scintillating lanthanide fluoride NP could be promising for the X-ray-inducible PDT. Nanosystems containing conjugates of La$_{0.9}$Ce$_{0.1}$F$_3$ to chlorin e$_6$ were studied in [10], though Tb-doped NPs were not investigated with chlorin e$_6$ because of poor spectral overlap [10]. At the same time, EEET from Tb-doped NP to protoporphyrin IX was demonstrated in [16]. Thus, the possible role of Tb$^{3+}$ doping agent in EEET pathways taking place in nanosystems containing lanthanide fluoride NP and chlorin e$_6$ photosensitizer should be studied. X-ray-induced scintillation emission spectra of CeF$_3$ NP (both undoped and Tb$^{3+}$-doped) were similar to their photoluminescence spectra excited in ultraviolet spectral region [9, 16–18]. EEET processes in Tb$^{3+}$-doped cerium fluoride NP are also expected to be similar for the cases of X-rays and ultraviolet light excitation. Therefore, studies of energy transfer between the sensitizer and Tb$^{3+}$-doped CeF$_3$ NP can be carried out using UV excitation as a...
model. Here, we study formation and EEET process in the nanosystem consisting of Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanoparticles, cetrimonium bromide (CTAB) surfactant, and chlorin e$_6$ photosensitizer.

**Methods**

**Materials**

Hydrofluoric acid, isopropyl alcohol, cerium(III) chloride heptahydrate, and terbium(III) chloride heptahydrate were acquired at Sigma-Aldrich Co. and used without further purification. Chlorin e$_6$ (Frontier Scientific Inc.) was kindly provided by T.Y. Ohulchansky (Institute for Lasers, Photonics and Biophotonics at the State University of New York at Buffalo). Fifty millimolar TRIS-HCl buffer (pH 7.2) was used as solvent.

**Synthesis and Characterization of Nanoparticles**

Ce$_{0.85}$Tb$_{0.15}$F$_3$ NPs (0.07 M water solution) were synthesized as described in [19]. Briefly, a mixture of 1.58 g of cerium(III) chloride heptahydrate (4.25 mmol, i.e., 85%) and 0.293 g of terbium(III) chloride heptahydrate (0.75 mmol, i.e., 15%) was dissolved in 15 mL of water and added to 150 mL of isopropyl alcohol. Hydrofluoric acid (20 mmol), dissolved in 50 mL of isopropyl alcohol, was added drop-wise to a cerium and terbium salt solution under vigorous stirring. The resulting white sediment was filtered and washed carefully by pure isopropyl alcohol several times. Then, the suspension was slightly dried to form a paste-like substance and dispersed in 110 ml of distilled water using an ultrasonic bath. The resulting white sediment was filtered and washed carefully by pure isopropyl alcohol several times. Then, the suspension was slightly dried to form a paste-like substance and dispersed in 110 mL of distilled water using an ultrasonic bath. The resulting white sediment was filtered and washed carefully by pure isopropyl alcohol several times. Then, the suspension was slightly dried to form a paste-like substance and dispersed in 110 mL of distilled water using an ultrasonic bath.

Particle size distribution was studied by the dynamic light scattering (DLS) technique using ZetasizerNano ZS (Malvern Instruments) apparatus (Fig. 1). For the obtained Ce$_{0.85}$Tb$_{0.15}$F$_3$ NP, intensity distribution of the hydrodynamic diameter gave main maximum at 62 ± 36 nm (about 97% of intensity) with negligibly small addition of larger fractions. The Z potential of the synthesized NPs was determined as +41 ± 14 mV.

A representative transmission electron microscopy (TEM) image of Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanoparticles obtained in the above-described reaction is provided in Fig. 2. TEM was performed using a Leo 912 AB Omega electron microscope operating at 100 kV. Before the analysis, sols were brought onto the copper grids using micropipette without any specific pretreatment and dried in ambient air. Comparison of Figs. 1 and 2 shows that the size of the nanoparticles obtained by TEM is smaller than the hydrodynamic diameter at the maximum of DLS intensity distribution. We believe this is connected with the peculiar property of the DLS method that the DLS intensity by a particle is proportional to the sixth power of its radius; thus, larger particle makes higher contribution to the DLS intensity as compared to smaller one. Recalculation of the obtained intensity distribution to nanoparticle number distribution according to the mentioned sixth power relation resulted in a maximum at 24 ± 7 nm that is in agreement with the TEM results.

**Preparation of Samples**

Concentrated solution of chlorin e$_6$ (10 mM) was prepared in DMF. To prepare the solution of the studied nanosystems, an aliquot (20 μL per 1 mL) of 0.07 M water solution of Ce$_{0.85}$Tb$_{0.15}$F$_3$ nanoparticles was added to the CTAB solution (0.05 mg/mL CTAB concentration was found to be optimal) in 50 mM TRIS-HCl buffer (pH 7.2). An aliquot of chlorin e$_6$ concentrated solution was then added; in order to minimize reabsorption, 2 μM concentration of chlorin e$_6$ was used; at this concentration, chlorin e$_6$ has negligible absorption at the maximum wavelength of Ce$^{3+}$ emission, while at the wavelength of the Soret band maximum (near 400 nm; optical density about 0.3 for the used concentration of chlorin e$_6$), Ce$^{3+}$ emission is already weak. Besides, 5 and 10 μM concentrations of chlorin e$_6$ were additionally used in Tb$^{3+}$ luminescence decay measurements. Solution of chlorin e$_6$ (2 μM) in the presence of concentrated micelles-forming CTAB (1 mg/mL) was used for the comparison.

**Spectral Measurements**

Absorption spectra were measured using Specord M40 spectrophotometer (Carl Zeiss, Germany). Luminescence excitation, emission, and anisotropy spectra as well as the
comparison of the integral intensities of Ce\(^{3+}\) emission in the
to chlorin e\(_6\) EEET (E\(_{\text{Ce\,-\text{Ce6}}}\)) was performed by com-
absorption and

curves of luminescence decay in millisecond timescale were
with the help of the Cary Eclipse fluorescent
spectrophotometer (Varian, Australia). Absorption and
fluorescence measurements were performed in 1 cm ×
registered with the help of the Cary Eclipse fluorescent

current of luminescence decay in millisecond timescale were
fluence intensities upon excitation of Ce\(^{3+}\) (I\(_{\text{excCe6}}\)), contribution to this intensity of the own
excitation of chlorin e\(_6\) at this wavelength was sub-
and chlorin e\(_6\) itself (I\(_{\text{excCe6}}\), optical densities of
Ce\(^{3+}\) and chlorin e\(_6\) at the used excitation wavelengths
were equal) according to:

\[
E_{\text{Ce-Ce6}} = \frac{I_{\text{excCe6}}}{I_{\text{emCe6}}} \quad (1)
\]

The value of E\(_{\text{Ce-Ce6}}\) could be also estimated by com-
parison of the integral intensities of Ce\(^{3+}\) emission in the
presence (Int\(_{\text{NP-Ce6}}\)) and in the absence (Int\(_{\text{NP}}\)) of chlorin e\(_6\), given that the reabsorption could be neglected, as:

\[
E_{\text{Ce-Ce6}} = 1 - \frac{\text{IntNP-Ce6}}{\text{IntNP}} \quad (2)
\]

When performing estimation of the efficiency of Ce\(^{3+}\)-to-chlorin e\(_6\) EEET by (1) and (2), spectral sensitivity of the fluorescent spectrophotometer on the excitation
and emission wavelength was taken into account.

Decay curves of Tb\(^{3+}\) luminescence were fitted by three
exponents; the relative intensities B\(_1\), B\(_2\), and B\(_3\) are
calculated as B\(_i\) = A\(_i\) × τ\(_i\) / Σ A\(_i\) × τ\(_i\) (i = 1, 2, 3; τ\(_1\), τ\(_2\), and τ\(_3\) are
the decay times; A\(_1\), A\(_2\), and A\(_3\) are amplitudes of
corresponding exponents). Quantitative estimation of the
efficiency of Tb\(^{3+}\)-to-chlorin e\(_6\) EEET for each of the three
decay components (E\(_{\text{Tb-Ce6}}(t_i)\)) was performed by com-
parison of the decay times of corresponding components
of Tb\(^{3+}\) luminescence at 543 nm in the absence of chlorin
e\(_6\) (τ\(_i\)\(^{\text{Tb}}\)) and in its presence (τ\(_i\)\(^{\text{TbCe6}}\)) as:

\[
E_{\text{Tb-Ce6}}(t_i) = 1 - \frac{\tau_i^{\text{TbCe6}}}{\tau_i^{\text{Tb}}} \quad (3)
\]

Amplitudes A\(_1\), A\(_2\), and A\(_3\) are affected (to different extent for different components) by addition of chlorin e\(_6\) due
to decreased EEET from Ce\(^{3+}\) to Tb\(^{3+}\). Thus, the expression
(3) cannot be applied for calculation of total Tb\(^{3+}\)-to-
chlorin e\(_6\) EEET efficiency using average decay time values.

Three-exponential fit of the Tb\(^{3+}\) decay curves was also
used to estimate real decrease of Tb\(^{3+}\) luminescence
intensity upon addition of chlorin e\(_6\). Cary Eclipse fluores-
cent spectrophotometer uses pulsed xenon lamp (80 Hz;
2 μs pulse width at half peak height) for luminescence ex-
citation, setting the intensity measured before each pulse
(thus, in about 12.5 ms after previous pulse) as zero for
the background correction. Hence, the intensity of Tb\(^{3+}\)
luminescence that has decay times in ms range is artifi-
cially reduced; but addition of chlorin e\(_6\) leads to the decay
time decrease and thus less significant artificial reduction
of the intensity. So, the Tb\(^{3+}\) luminescence quenching ap-
parent from the spectra is less strong than the real one.
Thus, we estimated the real intensities of Tb\(^{3+}\) lumines-
ce and thus its real decrease upon chlorin e\(_6\) addition
using the results of the three-exponential fit of the lumini-
scence decay curve as A\(_1\) × τ\(_1\) + A\(_2\) × τ\(_2\) + A\(_3\) × τ\(_3\).

Results and Discussion

EEET in NP-CTAB-Chlorin e\(_6\) Nanosystem

First of all, it should be mentioned that it is not possible to
prepare the nanosystem with EEET consisting of the syn-
thesized Ce\(_{0.85}\)Tb\(_{0.15}\)F\(_3\) NP and the monomer form of
chlorin e\(_6\) based only on electrostatic interactions without
any linking group or some binding substance. While in the
distilled water, chlorin e\(_6\) molecules form aggregates on
any linking group or some binding substance. While in the

In order to form model nanosystem containing
Ce\(_{0.85}\)Tb\(_{0.15}\)F\(_3\) NP and chlorin e\(_6\) surfactant CTAB was used
that was reported as a stabilizer for lanthanide fluoride NPs
in [11]. Thus, to the solution of NPs in the presence of
0.05 mg/mL CTAB, 2 μM of chlorin e\(_6\) was added. Absorp-
tion spectrum of the obtained solution in comparison with

![Fig. 2 TEM image of Ce\(_{0.85}\)Tb\(_{0.15}\)F\(_3\) nanoparticles](image-url)
these of chlorin e₆ free and in the presence of CTAB micelles (i.e., CTAB of the concentration 1 mg/mL) is presented in Fig. 3. Absorption spectra of chlorin e₆ in the presence of CTAB micelles and CTAB-NP nanosystems are similar but significantly different from chlorin e₆ spectrum in buffer. Thus, we could suppose that in both cases, chlorin e₆ molecules are built in a shell formed by CTAB molecules; supposed arrangement of the components in the NP-CTAB-chlorin e₆ nanosystem is schematically presented in Fig. 4.

Fluorescence emission spectra of Ce₀.₈₅Tb₀.₁₅F₃ NP in the presence of CTAB (Fig. 5) demonstrate broad band corresponding to Ce³⁺ emission (320 nm) and narrow bands of Tb³⁺ ions (490, 543, 584, and 621 nm) as described in the literature [13]. Addition of chlorin e₆ (Fig. 5) results in decrease of the intensity of Ce₀.₈₅Tb₀.₁₅F₃ NP emission bands as well as in appearance of the band corresponding to chlorin e₆ fluorescence (670 nm). This could be explained as EEET of Ce₀.₈₅Tb₀.₁₅F₃ NP excitations to the chlorin e₆ molecules bound to the CTAB shell of Ce₀.₈₅Tb₀.₁₅F₃ NP. This conclusion could be also supported by fluorescence excitation measurements (Fig. 6). In the normalized fluorescence excitation spectra of chlorin e₆ (emission at 680 nm) besides its own Soret and Q-bands, we observe the band at 250 nm, which coincides with the one in the excitation spectrum of Ce₀.₈₅Tb₀.₁₅F₃ NP (emission at 320 nm); this is consistent with EEET from Ce³⁺ ions to chlorin e₆. The increase in the fluorescence anisotropy of chlorin e₆ in the presence of NP-CTAB (data not presented) is one more proof of the formation of NP-CTAB-chlorin e₆ nanosystem.

It is seen from Fig. 5 that the addition of chlorin e₆ leads to the narrowing and short-wavelength shift of the Ce³⁺ emission band. Difference of the unquenched and quenched Ce³⁺ bands gives the broad band with the maximum near 355 nm (Fig. 5) that most possibly corresponds to the emission of the perturbed Ce³⁺ states; these states were supposed to be the traps for the non-perturbed Ce³⁺ excitations transferring these excitations to either Tb³⁺ dopant or to the attached photosensitizer [8]. It should be added that the mentioned difference spectrum does not contain any significant component similar to that of Soret band of chlorin e₆; thus, at these concentrations, the impact of reabsorption on the Ce³⁺ emission quenching by chlorin e₆ could be considered as negligible. Based on Ce³⁺ emission spectra in the presence and in the absence of chlorin e₆, efficiency of EEET could be estimated by comparing integral intensities of Ce³⁺ emission according to (2); the value of EEET efficiency equal to 0.33 was obtained for the 2 μM concentration of chlorin e₆. Increasing the chlorin e₆ concentration results in more significant EEET efficiency.
values, but these values also contain higher reabsorption contribution.

Efficiency of EEET from Ce³⁺ to chlorin e₆ could be also estimated from the fluorescence excitation spectra by comparison of chlorin e₆ fluorescence intensities upon excitation of Ce³⁺ (at 271 nm; contribution to this intensity of the own excitation of chlorin e₆ at this wavelength was subtracted using the normalized excitation spectrum of chlorin e₆ in CTAB micelles (Fig. 6)) and chlorin e₆ in the presence of CTAB micelles (1 mg/mL CTAB; emission at 680 nm; red dashed line)

Efficiency of EEET from Ce³⁺ to chlorin e₆ could be also estimated from the fluorescence excitation spectra by comparing chlorin e₆ fluorescence intensities upon excitation of Ce³⁺ (at 271 nm; contribution to this intensity of the own excitation of chlorin e₆ at this wavelength was subtracted using the normalized excitation spectrum of chlorin e₆ in CTAB micelles (Fig. 6)) and chlorin e₆ in the presence of CTAB micelles (1 mg/mL CTAB; emission at 680 nm; red dashed line) and chlorin e₆ itself (at 406 nm; optical densities of Ce³⁺ at 271 nm and chlorin e₆ at 406 nm are equal) according to (1). Surprisingly, the value of EEET efficiency of about 0.06 was obtained that is much less than the value of 0.33 obtained according to (2). We could suppose that the EEET efficiency calculation based on (1) cannot be applied in our case. Perhaps Ce³⁺-to-chlorin e₆ EEET brings chlorin e₆ molecule to the vibronic levels with higher ability to further intersystem conversion as compared to the photoexcitation at 406 nm; this would cause decreased fluorescence quantum yield of chlorin e₆ leading to lower values of apparent EEET efficiency than calculated by (1).

It should be mentioned that the close proximity of Ce₀.₈₅Tb₀.₁₅F₃ NP causes the strong decrease in the fluorescence intensity of chlorin e₆; the same effect was noticed in [10]. The possible reason for this could be the heavy atom effect, i.e., more intensive transition of the excitations to the triplet state due to the close proximity of Ce and Tb atoms causing spin-orbit interactions in chlorin e₆ molecule. One more possible explanation could be EEET between chlorin e₆ molecules in the case where they are bound to NP-CTAB nanosystem at the mutual distances that are close enough for chlorin e₆-chlorin e₆ energy transfer.

EEET Pathways in NP-CTAB-Chlorin e₆ Nanosystem
It is interesting to study in more details the pathway of EEET from NP to chlorin e₆. It is known that EEET from Ce³⁺ to Tb³⁺ ions takes place inside Ce₀.₈₅Tb₀.₁₅F₃ nanoparticles [12, 13]. When adding chlorin e₆ to the nanosystem, the following additional processes could occur besides the mentioned Ce³⁺-to-Tb³⁺ EEET: (i) EEET from Ce³⁺ perturbed states directly to chlorin e₆ and (ii) EEET from excited Tb³⁺ ions to chlorin e₆ molecules.

First of all, since the excited state lifetime of Tb³⁺ ions is extremely long as compared to that of Ce³⁺ [8, 13], decrease in the Ce³⁺ emission intensity upon addition of chlorin e₆ means the direct EEET from Ce³⁺ to chlorin e₆ (with the 0.33 efficiency for 2 μM chlorin e₆). Further, it is seen from Fig. 5 that together with the decrease in Ce³⁺ emission, this of Tb³⁺ diminishes as well. The apparent decrease in the Tb³⁺ emission band intensity upon addition of chlorin e₆ is about 20–23%, but the total intensity values of the millisecond Tb³⁺ emission are biased by the spectrofluorometer (see "Spectral measurements" subsection in the "Methods" section); real intensity decrease was estimated using Tb³⁺ luminescence decay curves as 56% (543-nm band for 2 μM chlorin e₆) exceeding that for Ce³⁺ (33% for 2 μM chlorin e₆). Thus, the Tb³⁺ emission quenching could be due both to (i) Tb³⁺-to-chlorin e₆ EEET and to (ii) decreased Ce³⁺-to-Tb³⁺ EEET (and thus reduced population of excited levels of Tb³⁺) caused by competition with the direct Ce³⁺-to-chlorin e₆ EEET. The observed decrease in the Tb³⁺ emission decay time upon the addition of chlorin e₆ (Fig. 7) points to the existing of EEET from excited Tb³⁺ ions to chlorin e₆ molecules; such transfer was also reported for protoporphyrin IX in [16]. It should be mentioned that while the spectral overlap of Tb³⁺ emission with chlorin e₆ absorption could be poor, extremely high values of the donor (i.e., Tb³⁺) excited state lifetime could still lead to efficient EEET at significant distances.

To analyze in more details the quenching of Tb³⁺ emission, let us look at the components of the three-exponential fit of the decay curve for the most intensive Tb³⁺ luminescence band at 543 nm (Table 1). It is seen that the decay times of all three components decrease upon the addition of chlorin e₆ pointing to EEET from Tb³⁺ to chlorin e₆ for all of them. EEET efficiency calculated according to (3) for all three components turns out to be the highest (0.42 for 2 μM of chlorin e₆) for the shortest component $\tau_1$ and the lowest (but still as high as 0.15 for 2 μM of chlorin e₆) for the longest component $\tau_3$. At the same time, while the amplitude $A_1$ of the shortest component stays about the same at different concentrations of chlorin e₆ that of the medium one $A_2$ does not change at 2 μM of chlorin e₆ and decreases almost twice at its highest concentration of 10 μM. At the same time, the amplitude $A_3$ of the longest component decreases the most strongly (more than twice at 2 μM and more than 10 times at
10 μM of chlorin \(e_6\). We could thus suppose that the luminescence intensity corresponding to the shortest component \(\tau_1\) (and the medium one \(\tau_2\) at the low concentrations of chlorin \(e_6\)) decreases mainly due to EEET from Tb\(^{3+}\) to chlorin \(e_6\). At the same time, the intensity of the longest component \(\tau_3\) diminishes due to both (i) EEET from Tb\(^{3+}\) to chlorin \(e_6\) (that reduces \(A_3\)) and (ii) decreased population of Tb\(^{3+}\) excited states due to competition of EEET from Ce\(^{3+}\) to Tb\(^{3+}\) with that from Ce\(^{3+}\) to chlorin \(e_6\) (that reduces \(A_3\)). We could further speculate that the short-time emitting Tb\(^{3+}\) ions receive excitations without competition with Ce\(^{3+}\)-to-chlorin \(e_6\) EEET. At the same time, these short-time emitting Tb\(^{3+}\) ions surprisingly demonstrate the highest Tb\(^{3+}\)-to-chlorin \(e_6\) EEET efficiency. The possible explanation could be as follows (Fig. 8). We could suppose that Ce\(^{3+}\) perturbed states (that demonstrate luminescence near 355 nm (Fig. 5)) are mostly connected with Ce\(^{3+}\) ions situated close to the surface of the NP. In this case, Tb\(^{3+}\) ions with shorter decay times are supposed to be situated near the NP surface as well and close to perturbed Ce\(^{3+}\) ions (Fig. 8, A). This results in (i) high Ce\(^{3+}\)-to-Tb\(^{3+}\) EEET rate (due to short distance) leaving no place for competition by Ce\(^{3+}\)-to-chlorin \(e_6\) EEET, and (ii) high rate of subsequent Tb\(^{3+}\)-to-chlorin \(e_6\) EEET. At the same time, Tb\(^{3+}\) ions with longer luminescence decay times are supposed to be situated further from the NP surface (generally, higher distance from surface means lower impact of various quenchers that is consistent with higher luminescence decay times); they receive excitations from the perturbed Ce\(^{3+}\) ions which do not neighbor short-time emitting surface Tb\(^{3+}\) ions in close proximity (Fig. 8, B). This results in (i) lower Ce\(^{3+}\)-to-Tb\(^{3+}\) EEET rate that permits partial redirection of Ce\(^{3+}\) excitation flow to the Ce\(^{3+}\)-to-chlorin \(e_6\) EEET pathway and (ii) lower rate of subsequent Tb\(^{3+}\)-to-chlorin \(e_6\) EEET.

Basing on the above observations, photophysics processes in the Ce\(_{0.85}\)Tb\(_{0.15}\)F\(_3\) NP-CTAB-chlorin \(e_6\) nanosystem could be as follows. Suggesting that perturbed Ce\(^{3+}\) ions are mainly localized near to the NP surface, for the part of these ions situated close to Tb\(^{3+}\) ones EEET only to Tb\(^{3+}\) takes place. For the other Ce\(^{3+}\) ions, competition between EEET to Tb\(^{3+}\) (localized at higher distance from the NP surface) and to chlorin \(e_6\) exists. For both cases, excitations of Tb\(^{3+}\) are further transferred to chlorin \(e_6\).

| Chlorin \(e_6\) concentration | \(\tau_1\), ms | \(B_1\), a.u. | \(E_{\text{ETb-Ce}}(\tau_1)\) | \(\tau_2\), ms | \(B_2\), a.u. | \(E_{\text{ETb-Ce}}(\tau_2)\) | \(\tau_3\), ms | \(B_3\), a.u. | \(E_{\text{ETb-Ce}}(\tau_3)\) |
|-----------------------------|----------------|-------------|----------------|----------------|-------------|----------------|----------------|-------------|----------------|
| 0 μM                        | 0.69           | 34          | 0.02           | 2.35           | 81          | 0.17           | 6.13           | 147         | 0.81           |
| 2 μM                        | 0.40           | 48          | 0.04           | 1.71           | 84          | 0.29           | 5.18           | 64          | 0.67           | 0.15         |
| 5 μM                        | 0.31           | 47          | 0.06           | 1.32           | 63          | 0.36           | 4.51           | 29          | 0.58           | 0.27         |
| 10 μM                       | 0.27           | 44          | 0.10           | 1.06           | 61          | 0.42           | 3.98           | 14          | 0.48           | 0.35         |

\(\tau_1, \tau_2\), and \(\tau_3\) are the decay times; \(A_1, A_2\), and \(A_3\) are the amplitudes; \(B_1, B_2\), and \(B_3\) are the relative intensities (calculated as \(B_i = A_i \times \tau_i / \sum A_i \times \tau_i \), \(i = 1, 2, 3\)) of the three-exponential fit \(E_{\text{ETb-Ce}}(\tau_i)\) is the EEET efficiency calculated for the corresponding decay component according to the expression (3).
Conclusions

1. Chlorin e₆ molecules bind to Ce₀.₈₅Tb₀.₁₅F₃ NP in the presence of CTAB forming thus the Ce₀.₈₅Tb₀.₁₅F₃ NP-CTAB-chlorin e₆ nanosystem. We consider that binding occurs via chlorin e₆ embedding in the shell formed around NP by CTAB molecules.

2. In the Ce₀.₈₅Tb₀.₁₅F₃ NP-CTAB-chlorin e₆ nanosystem, electronic excitation energy transfer from Ce³⁺ to chlorin e₆ takes place both directly (with the 0.33 efficiency for 2 μM chlorin e₆) and via Tb³⁺.

Abbreviations

CTAB: Cetrimonium bromide; DLS: Dynamic light scattering; EEET: Electronic excitation energy transfer; NP: Nanoparticles; PDT: Photodynamic therapy; TEM: Transmission electron microscopy.

Authors’ Contributions

ML and LX carried out the spectral measurements and calculations and wrote the article. OS performed the synthesis of nanoparticles and participated in the discussion of the nanosystem model. AM performed the DLS characterization of the nanoparticles. NG and VY participated in the design of the study, discussion of the results, and coordination. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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