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Jing Liu, Rik Van Deun, Luca Pilia, Pieter Geiregat, Flavia Artizzu, "Controlling energy transfer routes in dye-sensitized lanthanide-based nanoparticles for enhanced emission," Proc. SPIE 11277, Organic Photonic Materials and Devices XXII, 112770E (28 February 2020); doi: 10.1117/12.2544218

SPIE.

Event: SPIE OPTO, 2020, San Francisco, California, United States

Controlling energy transfer routes in dye-sensitized lanthanide-based nanoparticles for enhanced emission

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ABSTRACT

Near-infrared luminescent lanthanide (Ln)-doped nanomaterials are currently attracting high interest in view of their sharp f-f emission peaks and long luminescence lifetimes, which establish a unique value for the development of optical amplifiers, lasers and biosensors. To improve the optical pumping of the weakly absorbing lanthanide ions (Ln³⁺), the doped nanoparticles are coupled with an organic dye sensitizer able to efficiently harvest light and subsequently transfer the absorbed energy to the emitter. However, this through-space “remote” sensitization is severely subjected to energy losses due to competitive energy migration or deactivation routes limiting the overall luminescence quantum yields. The implementation of the Förster’s model of resonance energy transfer on the basis of advanced ultra-fast transient absorption and photoluminescence spectroscopy with the support of density functional theory calculations demonstrate that the sensitization efficiency from the dye to the doped nanoparticle is strictly regulated by the geometry and localization of the transition dipole moment of the dye molecule. Within the nanoparticle, the energy transfer pathways can be harnessed through the spatial confinement of ‘energy bridges’, accepting energy from the surface dyes and donating to core emitters. We show that the FITC (fluorescein-isothiocyanate) dye allows reaching exceptional sensitization efficiency close to unity for the NIR-emitting triad Nd³⁺, Er³⁺ and Yb³⁺.

Keywords: Lanthanides, energy transfer, nanoparticles, dye sensitization, near-infrared emission, Förster’s theory, calcium fluoride, excited singlet and triplet states

1. INTRODUCTION

Lanthanide (Ln)-doped fluoride nanoparticles are currently very popular in view of the outstanding luminescence properties related to the intrashell f-f transitions of Ln³⁺, delivering high color purity and high excited state densities.¹⁻² Moreover, the combination of selected pairs of Ln³⁺ in these systems allows for intermetallic energy transfer phenomena giving rise to new functionalities as controlled energy migration, upconversion (the combination of two or more photons into a higher energy photon) and even downconversion (i.e. multi-photon emission following one-photon excitation).¹⁻³ These materials offer enormous potentialities for the development of highly performing optical devices, such as amplifiers, lasers and biosensors/bioprobes.³⁻⁴ However, bare nanoparticles suffer from inefficient optical pumping due to the low absorption cross-section of the Ln³⁺. A significant improvement of the emission intensity can be achieved by coupling the doped nanoparticles with an organic dye, which is able to harvest light with high efficiency and then transfer it to the Ln³⁺ emitter.⁵ In the absence of a direct bonding between the energy donor (dye), anchored to the surface of the nanoparticle, and the acceptor (Ln³⁺), embedded into the fluoride matrix, this dye-to- Ln³⁺ sensitization process occurs through a through space dipolar coupling mechanism according to the Förster’s model of resonance energy transfer.⁶ Nonetheless, the energy transfer process at the organic-inorganic interface remains a crucial point for the quantum efficiency of such hybrid emitters.⁷⁻⁹ In fact, it is subjected to severe energy losses related to competitive routes such as external deactivation or even energy back transfer.¹⁰⁻¹¹ At the same time, energy migration from the sensitized surface Ln³⁺ to core emitters must be controlled to avoid collateral dissipation phenomena such as cross-relaxation.¹¹⁻¹² Despite the intense research in the field, so far, the key factors governing the efficiency of the dye-to- Ln³⁺ sensitization remain largely speculative and no direct evidence of the evolution of the photocycle has been provided.⁸ In this contribution, we apply the Förster’s model of

resonance energy transfer to unravel the temporal, spectral and spatial parameters governing the efficiency of the sensitization process from the fluorescein isothiocyanate dye (FITC) to the near-infrared (NIR) emitting triad Nd^{3+} , Er^{3+} and Yb^{3+} . Results are obtained and interpreted on the basis of photoluminescence (PL) and advanced transient absorption (TA) spectroscopy data supported by Density Functional Theory (DFT) calculations. We show that the mechanisms of energy transfer within the hybrid dye/nanoparticle assembly are strictly determined by sub-nm donor-acceptor distances beyond the spectral overlap between the donor emission and the acceptor absorption. By the engineered design of the nanoparticle architecture and the selection of small sized dye molecules exceptional sensitization efficiencies close to unity are achieved.

2. RESULTS AND DISCUSSION

2.1 Dye-sensitized nanoparticles and sensitization mechanism

To study the dynamics and efficiency of the dye to Ln^{3+} energy transfer and its dependence on the nature of the Ln^{3+} emitter, we synthesized small-sized (< 4 nm) CaF_2 nanoparticles doped with Nd^{3+} , Er^{3+} and Yb^{3+} at 30% doping molar concentration (Fig.1a).¹³ These ions are particularly relevant either for their NIR emission, of high interest in telecommunication and laser technology, as well as for the construction of upconversion systems for solar cells and biological applications. As dye, we selected the commercially available FITC in view of its high absorption cross section ($\sim 3 \times 10^{-16} \text{ cm}^2$ at $\lambda_{\text{max}} = 500 \text{ nm}$), broad spectral features with emission in the green visible range (vide infra), and a suitable carboxylate group able to bind to the surface of the nanoparticle (Fig. 1b).

Figure 1. a. TEM image of CaF_2 nanoparticles doped with 30 mol% Ln^{3+} (Nd^{3+} , Er^{3+} or Yb^{3+}); insets report the high-resolution image evidencing the typical interplanar distance of 0.31 nm of the (211) plane of the CaF_2 cubic phase and the nanoparticles size distribution. b. Structural formula of FITC (left) and DFT-calculated optimized geometry for the FITC monoanion coordinated to a Ca^{2+} ion on the surface of the nanoparticle (right). The red dot represents the transition dipole moment vector μ for the lowest energy HOMO-LUMO transition, pointing outward the plane. c. General scheme of the photocycle in a dye-sensitized Ln system herein shown for the FITC/ Nd^{3+} couple. The Nd^{3+} emissive level is highlighted in orange.

As shown in Fig. 1c, the photocycle leading to Ln^{3+} emission in dye-sensitized systems consists of a multi-step process: after dye photoexcitation, energy transfer (ET) to the upper energy levels of the Ln^{3+} can in principle occur directly from the singlet S_1 state (SET) or through the triplet state T_1 (TET) after singlet to triplet intersystem crossing (ISC). This latter event is prohibited by the spin selection rule but could be triggered in the presence of the Ln^{3+} due to the strong spin orbit

coupling associated to the heavy ions (heavy atom effect). Energy is transferred with more efficiency to the Ln^{3+} upper levels that are close in energy to the dye donor state (resonance condition), but as a rule of thumb, the feeding state should be higher than the acceptor emissive level to avoid energy back transfer.¹⁰ FITC, whose first excited singlet state S_1 is placed at $\sim 19000 \text{ cm}^{-1}$ is therefore a suitable sensitizer for the triad of the NIR-emitting Nd^{3+} , Er^{3+} and Yb^{3+} , whose emissive levels place at ~ 11200 , ~ 6500 and $\sim 10200 \text{ cm}^{-1}$, respectively. Even so, Yb^{3+} represents a special case among the Ln ions because of its simple two-level manifold configuration, limiting the energy range for establishing resonance with the dye donor states. As such, the sensitization efficiency is expected to be highly dependent on the nature of the Ln^{3+} acceptor, as it will be discussed further.

2.2 Dye excited state dynamics

Steady-state photoluminescence (PL) spectra in the visible range (Fig. 2a) show that the intense green fluorescence of the free FITC dye (in the presence of trimethylamine as deprotonating agent) is significantly reduced upon binding to the undoped CaF_2 nanoparticles. This effect can be attributed to a redistribution of the electron density of the ligand upon coordination to the CaF_2 cation. Therefore, the $\text{CaF}_2@\text{FITC}$ hybrid system represents the reference material in this case. For the doped nanoparticles, the residual dye fluorescence is further strongly quenched indicating the activation of an efficient decay channel for the FITC S_1 state likely triggered by ET to the Ln^{3+} embedded into the nanoparticle. This effect is significantly more pronounced for Er^{3+} and Nd^{3+} than for Yb^{3+} .

Figure 2. a. Steady state PL spectra of FITC in the free anionic form and combined with undoped and 30% Ln^{3+} (Nd^{3+} , Er^{3+} and Yb^{3+}) doped CaF_2 nanoparticles in chloroform. Excitation wavelength was 450 nm. b. TA spectrum (blue solid line) as differential absorption ΔA at 1 ps time delay of FITC bound to Er^{3+} doped nanoparticles probed in the visible 400-750 nm range. The sample was pumped at 500 nm. No signal was detected by probing in the 800-1200 nm range. Steady state absorption (Abs.) and PL spectra (black dashed lines) are also reported for comparison. c. Decay curves extracted from TA data for the FITC GSB signal at $\sim 505 \text{ nm}$ in the sub-ns time range. Color codes are the same as in panel a.

To study the evolution of the dye excited states in more details and disentangle the dye to Ln sensitization steps, we performed advanced transient absorption (TA) spectroscopy measurements. Differently to conventional PL, this technique provides direct evidence of both the radiative and non-radiative decay channels of the dye excited states by probing the differential absorption $\Delta A = A_t - A_0$ at a delay time t of the probe pulse (A_t) with respect to the excitation pump at $t=0$ (A_0). All the samples showed similar TA features with signal development within 1 ps from initial pulse in the whole probed range.¹⁴ The almost instant signal rising in the entire probed range indicates that the sample TA response is dominated by the excited singlet state S_1 with no evidence of a slow and multistep activation of an excited triplet, contrary to previous claims.⁸ Fig. 2b shows the TA spectrum at 1 ps time delay of the Er^{3+} -doped sample combined with FITC as representative example. A strong negative signal in the region 450-650 nm is observed with three recognizable bands attributable to ground state bleaching (GSB) at 475 and 506 nm and stimulated emission (SE) at 540 nm in agreement with the shape and position of the steady state absorption and fluorescence spectra (Fig 2b). Below 450 nm, an intense positive signal due to excited state absorption (ESA) to superior energy levels is observed. Since this feature is also characterized by an ultrafast ($<1 \text{ ps}$) evolution, it is reliably attributed to a $S_1 \rightarrow S_n$ transition. All the characteristic features, GSB, SE and ESA, display the same temporal dynamics dominating in the 100 ps range. Fig. 2c presents the decay curves for the GSB signal at 505 nm for all the studied samples. Except for the free FITC dye, the decay trend for the other samples is biexponential with a

long-lived component falling beyond the investigated temporal range (50 fs-1 ns). The contribution of the slow component to the overall signal is in agreement with the relative intensity of the dye fluorescence in the hybrid samples with respect to the free FITC. Interestingly, also the signal for the undoped CaF₂ nanoparticles presents a double exponential trend, confirming the hypothesis that the direct coordination of the FITC dye to the nanoparticle affects the electronic distribution and likely changes the oscillator strength. The slow decay signal could be attributed to dye molecules not directly anchored to the nanoparticle or in any case undergoing inefficient energy transfer. Nonetheless, the fast signal components follow the same trend observed with PL spectroscopy (Fig. 1c), with evident dependence of the dynamics on the nature of the Ln³⁺. From all these observations it can be reliably inferred that the sensitization mechanism from the FITC dye to Ln³⁺ proceeds through SET.¹⁴ Retrieved time constants for the fast excited singlet decay channel obtained from curve fitting of experimental data after subtraction of the slow component are reported in Table 1. The sensitization efficiencies estimated from decay times data, through the simplified relation (1):

$$\eta_{\text{sens}} = 1 - \tau_{\text{Ln}}/\tau_{\text{dye}}, \quad (1)$$

where τ_{Ln} and τ_{dye} are the lifetimes of the dye in the presence and in the absence (i.e. the undoped CaF₂ nanoparticles) of the Ln³⁺ acceptor, are also reported.

Table 1. FITC excited singlet ultrafast decay time constants and FITC to Ln sensitization efficiencies.

Sample	τ (ps)	η_{sens} (%)
CaF ₂	200 (10)	-
Yb ³⁺	30 (10)	85
Er ³⁺	15 (2)	92
Nd ³⁺	12 (2)	94

From data in Table 1 it is evidenced that ET from FITC to Nd³⁺ reaches almost unitary efficiency while only slightly lower values are observed for Er³⁺. Instead, sensitization of Yb³⁺ is significantly less effective although the estimated efficiency maintains a relatively high value of 85%.

2.3 Dye to Ln³⁺ Förster's energy transfer

To disentangle the factors allowing for such remarkable sensitization efficiencies, we implemented the Förster's model of resonance energy transfer for the different Ln³⁺ doped particles. According to the model, the donor-acceptor energy transfer rate κ_{Ln} ($=1/\tau_{\text{Ln}}$) depends on temporal, spectral and spatial parameters as related by the following equation (2):

$$\kappa_{\text{Ln}} = \frac{1}{\tau_{\text{dye}}} \frac{9\kappa_j^2}{128\pi^5 n^4 R} J_{\text{Ln}} = \frac{1}{\tau_{\text{dye}}} \left(\frac{R_0}{R} \right)^6 \quad (2)$$

where n is the refractive index of the medium (taken as 1.4459 for CHCl₃). J_{Ln} is the spectral overlap integral between the donor emission and the acceptor absorption (resonance condition) and is expressed through the following equation (2):

$$J_{\text{Ln}} = \int F_{\text{dye}}(\lambda) \sigma_{\text{Ln}}(\lambda) \lambda^4 d\lambda \quad (3)$$

where $F_{\text{dye}}(\lambda)$ represents the donor emission spectral density normalized to unity, and $\sigma_{\text{Ln}}(\lambda)$ is the acceptor absorption cross-section. This parameter is calculated from spectral data (Fig. 3a) and retrieved values are reported in Table 2.

Equation (2) also contains spatial and geometrical parameters referred to the transition dipole moments (μ) of the energy donor, undergoing excited state relaxation, and the energy acceptor, which undergoes excitation from its ground state. R_0 is the Förster's radius which identifies the donor acceptor μ distance (R) at which 50% energy transfer efficiency is realized. In turn, it depends on J_{Ln} and on the dipole orientation factor κ_j^2 . This parameter is determined by the relative orientation between the transition dipole moments of the donor and the j th acceptor and can assume values in the range 0-4. However, while μ can be retrieved from DFT calculations for the dye molecules (Fig. 1b), it cannot be accurately established for Ln³⁺ since they are more rigorously behaving as quadrupoles rather than dipoles. Therefore, we take the average value $\kappa^2 = 2/3$, referred to a random spatial distribution of dipoles, as reliable value for a statistical distribution of Ln ions into the nanoparticle.

Figure 3. a. Spectral overlap of Ln³⁺ absorption (dashed lines) and the FITC fluorescence (solid line). b. FITC to Ln sensitization efficiency (η_{sens}) calculated according to the Förster's model (Equation 1) as a function of the donor-acceptor separation. Inset shows an enlarged portion of the graph at short distances. Color codes are the same as in panel a.

As for the temporal factor τ_{dye} , the time constant (200 ps) of the fast TA signal component for FITC combined with the undoped CaF₂ particles was considered. It is worth underlining that since the rate of the dye-to- Ln³⁺ sensitization is inversely proportional to the donor lifetime, the shortening of the decay dynamics of FITC upon coordination to the nanoparticles is beneficial to the sensitization.

The main parameters of Equation (2) as retrieved from experimental data are reported in Table 2.

Table 2. Förster's parameters at the ultra-fast timescale.

Sample	J_{Ln} (nm ⁶)	R_0 (nm)
Yb ³⁺	3.00×10^2	0.47
Er ³⁺	4.8×10^3	0.74
Nd ³⁺	5.3×10^3	0.76

Fig. 3b depicts the trend of the sensitization efficiency, calculated from Equation (1) by using the rate constants retrieved from Equation (2), for the different FITC/Ln³⁺ pairs on varying R . As can be seen, the curves exhibit a plateau of values close to unity only for very short distances below ~ 0.3 nm for Yb³⁺ and ~ 0.4 nm for Er³⁺ and Nd³⁺, beyond which they present an abrupt drop corresponding to a dramatic lowering of η_{sens} for marginal increases of R . The experimental sensitization efficiency values retrieved from time-resolved measurements (Table 1) are consistent with a donor-acceptor μ separation in the range 0.40-0.45 nm. This distance is compatible with the spatial separation of the DFT-calculated transition dipole moment vector of the FITC dye to the surface of the nanoparticle as depicted in Fig. 1b. Therefore, the small size and the particular geometrical arrangement of the FITC dye upon binding to the nanoparticle surface explain the exceptional dye-to-Ln³⁺ sensitization efficiency in these systems.

2.4 Controlling energy transfer routes within the nanoparticle

As evidenced by the above results, the single absorption band of Yb³⁺ (Fig. 3a) limits its sensitization efficiency due to the poor J_{Yb} (Table 1) resulting in a very short R_0 (Table 2 and Fig. 3b). On the other hand, Nd³⁺, which has several absorption bands in the visible to the near-infrared region (Fig. 3a), is known to be an effective sensitizer toward Yb³⁺ and its role as energy bridge between an organic chromophore and Yb³⁺ has been demonstrated in molecular complexes¹⁵ and in dye-sensitized nanoparticles¹³ (Fig. 4a,b). However, such lanthanide-bridged cascade energy transfer mechanism suffers from energy losses through radiative or dissipative routes due to uncontrolled energy migration and cross relaxation processes. The most effective strategy to harness and channel the absorbed energy relies on the control of the relative positions and the distance between Nd³⁺ and Yb³⁺ through a designed core/shell structure based on the confinement and separation of the donor and acceptor units (Fig. 4a). For a shell thickness well below the Förster's critical radius of 50% energy transfer efficiency (which falls below 1 nm), the energy transfer process will be so fast (in the sub-ns time range) to rule out any competitive dissipation process.

Figure 4. a. Scheme of a dye-sensitized $\text{Nd}^{3+}/\text{Yb}^{3+}$ core/shell nanoparticle where the shell thickness (expressed as R_{DA} , donor-acceptor distance) is much smaller than the Förster's radius R_0 . b. Scheme of the energy flow from a photoexcited dye to Nd^{3+} to Yb^{3+} . c. Yb^{3+} emission intensity in FITC-sensitized co-doped $\text{Nd}^{3+}/\text{Yb}^{3+}$ nanoparticles (blue); FITC-sensitized Yb^{3+} -doped nanoparticles (orange) and bare Yb^{3+} -doped nanoparticles (black). Reprinted with permission from ref. 13. Copyright 2019 American Chemical Society.

It has been demonstrated that in core/shell CaF_2 nanoparticles with a 0.4 nm-thick Nd^{3+} -doped shell, an emission intensity enhancement from core- Yb^{3+} by $\sim 40\%$ with respect to pure Yb^{3+} -doped samples is achieved upon sensitization through FITC (Fig. 4c). This effect is originated from the improved Yb^{3+} sensitization efficiency leading to an increase in the overall quantum yield due to the suppression of competitive dissipative channels.¹³

3. MATERIALS AND METHODS

Synthetic procedures: CaF_2 nanoparticles and Ln^{3+} -doped CaF_2 nanoparticles at 30% doping concentration were synthesized through a thermal decomposition method described elsewhere. Briefly, 0.7 mmol of $\text{Ca}(\text{CF}_3\text{COO})_2$ and 0.3 mmol of $\text{Ln}(\text{CF}_3\text{COO})_3$ oleate-amine solution were mixed in a 50 mL three-neck round-bottom flask. The resulting mixture was degassed under vacuum to remove water and oxygen at 120°C for 40 min and then heated to 310°C for 20 min under nitrogen flow with constant stirring. The obtained nanoparticles were centrifuged and washed by addition of acetone several times, finally redispersed in chloroform. The obtained suspension (12 mg/mL) was then mixed with a solution of FITC in chloroform (0.3 mg/mL). The mixture was stirred with heating at 45°C for 16 h. The final solution was washed with acetonitrile and redispersed in chloroform. **Microscopy:** TEM images were collected using JEOL JEM-2200FS transmission electron microscope operated at 200 kV. **Spectroscopy:** UV-vis absorption spectra were recorded with a double beam Perkin Elmer Lambda 900 UV/Visible/NIR spectrometer in transmission mode. Time resolved and steady-state photoluminescence spectroscopy was performed on clear suspensions of the samples in CHCl_3 . The photoluminescence spectra were recorded on an Edinburgh FLSP 920 UV-vis-NIR spectrofluorimeter with a 450 W xenon lamp as the steady state excitation source and an incident average power of $2 \text{ mW}/\text{cm}^2$ in the whole excitation range. Transient Absorption Measurements were performed by photo-exciting the samples using 100 femtosecond pulses (1 kHz) at 500 nm, created from an 800 nm Ti:S laser (Spitfire Ace, Spectraphysics) through frequency mixing in a TOPAS optical parametric amplifier (Light Conversion). Broadband probe pulses were generated in a CaF_2 (350-700 nm) and YAG crystals (850 - 1300 nm) using the 800 nm as a seed. The probe was delayed using a delay stage with maximum delay of up to 3.3 ns (Newport TAS). Noise levels of 0.1 mOD (RMS) are obtained by averaging over 5000 shots per time delay. Using 2 mm path length cuvettes, the samples were stirred during pump-probe measurements to avoid effects of photo-charging and sample degradation. Beam area and shape were evaluated using a Thorlabs CCD Beam profiler. **DFT calculations:** Ground-state electronic structure calculations of FITC coordinated to a Ca^{2+} ion were performed at Density Functional Theory (DFT)¹⁶ level employing the GAUSSIAN 16¹⁷ software package. The functionals used were B3LYP¹⁸⁻¹⁹. The ground state geometries were obtained both in the gas phase and CHCl_3 by full geometry optimization without any symmetry constrain. The basis set employed for all atoms was the valence triple-zeta 6-311+G(d,p)²⁰⁻²¹. All structures were input using ArgusLab 4.0.²²

4. CONCLUSIONS

In summary, we have shown that the energy transfer processes in dye-sensitized lanthanide doped nanoparticles are strictly governed by the spatial separation between the energy donor and acceptor units both at the organic-inorganic interface and between optically communicating lanthanide ions within the nanoparticle. These conclusions are corroborated by the implementation of the Förster's model of resonance energy transfer on the basis of experimental spectroscopic data and DFT calculations which pointed out that donor-acceptor distances well below the Förster's radius (sub-nm) are necessary to achieve high sensitization efficiencies beyond the spectral resonance between the donor emission and the acceptor absorption. For the dye to Ln^{3+} energy transfer process, advanced spectroscopic studies have evidenced that this mechanism occurs directly from the singlet excited state of the organic chromophore, therefore the resonance of the dye fluorescence with the Ln^{3+} absorption establishes the correct spectral parameter to be considered for the assessment of the dye to Ln^{3+} sensitization. The FITC dye can realize exceptional sensitization efficiencies close to unity towards the highly resonant Nd^{3+} and Er^{3+} thanks to the short distance (~ 0.4 nm) of its transition dipole moment (related to its first singlet excited state) from the surface of the nanoparticle. Instead, the poor spectral overlap between the dye emission and Yb^{3+} absorption can be overcome by resorting to the co-incorporation of Nd^{3+} as "energy bridge". Almost unitary sensitization efficiencies of Yb^{3+} can be achieved by FITC to Nd^{3+} to Yb^{3+} cascade energy transfer in core-shell nanoparticles where Nd^{3+} is confined into an ultra-thin (~ 0.4 nm) external layer.

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