

Sensitization of Upconverting Nanoparticles with a NIR-emissive Cyanine Dye Using a Micellar Encapsulation Approach

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Abstract

Photon upconversion nanomaterials have a wide range of applications, including biosensing and deep-tissue imaging. Their typically very weak and narrow absorption bands together with their size dependent luminescence efficiency can limit their application potential. This has been addressed by increasingly sophisticated core-shell particle architectures including the sensitization with organic dyes that strongly absorb in the near infrared (NIR). In this work, we present a simple water-dispersible micellar system that features energy transfer from the novel NIR excitable dye, 1859 SL with a high molar absorption coefficient and a moderate fluorescence quantum yield to oleate-capped NaYF₄:20% Yb(III), 2%Er(III) upconversion nanoparticles (UCNP) upon 808 nm excitation. The micelles were formed using the surfactants Pluronic F-127 and Tween 80 to produce a hydrophilic dye-UCNP system. Successful energy transfer from the dye to the UCNP could be confirmed by emission measurements that revealed the occurrence of upconversion emission upon excitation at 808 nm and an enhancement of the green Er(III) emission compared to direct Er(III) excitation at 808 nm.

Introduction

Upconversion nanoparticles (UCNP) have many interesting features that are of high importance in various fields of applications such as bioimaging, bioanalytical assays, photodynamic therapy, and solar cells [1]–[4]. One of the main limitations of UCNP is the very weak (10^{-20} cm²) absorption cross section [5] due to parity-forbidden 4f-4f transitions [6] in conjunction with the very narrow absorption bands (full width at half maximum (FWHM) of the absorption band of about 10 nm – 20 nm in the ultraviolet, visible, and near infrared spectral region). Moreover, their photoluminescence quantum yields are relatively low and depend on excitation power density as well as on the surface-to-volume ratio, due to the multiphotonic nature of the upconversion (UC) process and surface quenching effects, particularly for core-only UCNP [7], [8]. Near infrared (NIR) dyes coupled to UCNP can provide a potential strategy to boost UCNP brightness, the product of the molar absorption coefficient or cross section and the photoluminescence quantum yield as shown before [1]–[3]. The relatively broad absorption bands and the strong absorption cross section of organic dyes render them ideal light harvesters and energy donors for UCNP (Fig. 1), [6], [9]. Moreover, these dyes can also help shifting the excitation of the dye-UCNP systems from typically 980 nm for Yb-doped UCNP closer to 800 nm, which fits better into the biological spectral window and prevents heating effects by water absorption [10]. This can increase the applicability of these materials, especially for biological studies.

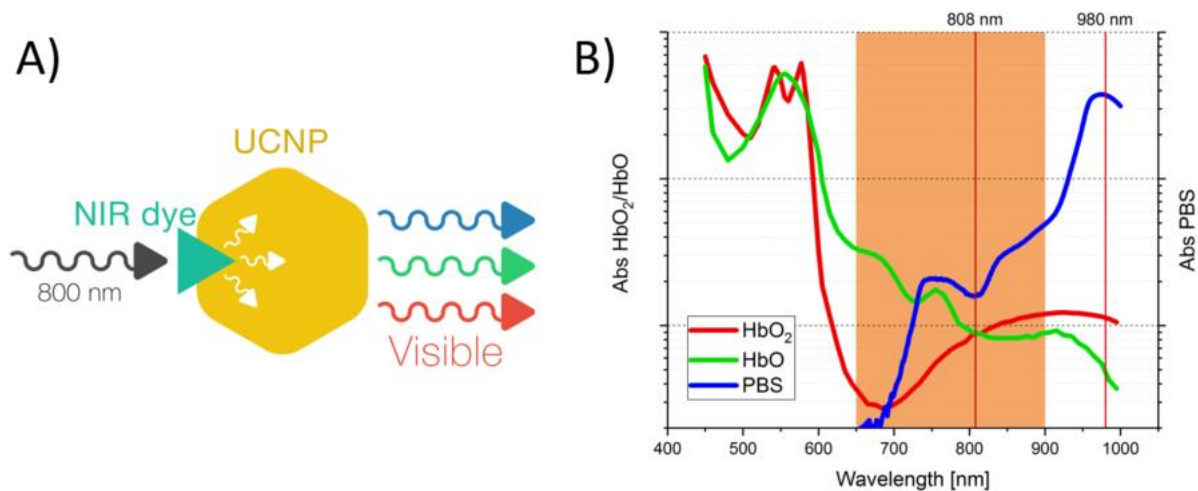


Fig. 1. **A)** General scheme of a light-harvesting system where NIR-dye molecules collect and transfer energy to core-only UCNP to generate upconversion luminescence (UCL). **B)** Absorption spectra of deoxyhemoglobin (Hb), oxyhemoglobin (HbO₂), and phosphate buffered saline (PBS), showing the “biological spectral window” that is typically used for *in vivo* imaging, as well as the spectral position of the laser lines at 808 nm and 980 nm. Data for Hb and HbO₂ are taken from reference [11].

Dye sensitization of UCNP can occur via the Förster mechanism (through electrostatic interactions between a donor and an acceptor presented as point dipoles) and/or the Dexter mechanism (involving the bilateral exchange of electrons between donor and acceptor in a spin-conserved singlet–singlet or triplet–triplet transfer) from light harvesting organic dyes located directly at or in the immediate vicinity of the UCNP surface across the organic/inorganic interface to the optically active lanthanide ions incorporated in the UCNP [5]. The latter is significant only at very short donor-acceptor distances (~ 10 Å or less), while electrostatic interactions can occur over longer distances (10–100 Å).

The first successful attempt of dye sensitized UC was reported by Zou et al. [12]. The authors used the dye IR-806, which is a carboxylic acid derivative of the commercially available dye IR-780, attached to UCNP by replacing the oleylamine ligands on the as-synthesized oleylamine-coated UCNP. Upon excitation at 800 nm, this dye-UCNP system produced the typical upconversion luminescence (UCL) spectrum of Yb, Er co-doped materials with the green and red Er(III) emission bands. This initiated an increasing number of studies of dye-UCNP systems prepared by attaching NIR dyes to UCNP with different ligand functionalities [5], [6], [9], [13], [14]. Other strategies included the modification of UCNP with an inactive protective shell to minimize surface quenching of the lanthanide ions [6], [13] or adding an active shell of NaYF₄ doped with Yb(III) or Nd(III) to further increase the energy transfer efficiency [14]. In the majority of these studies, the exact nature of the dye-UCNP energy transfer mechanism was not explained in detail. Only recently, Garfield et. al. [15] reported that in the case of the dye IR-806 attached to NaGdF₄ nanoparticles (undoped and doped with Yb(III) and Er(III)), the Gd(III) ions seem to mediate intersystem crossing of the antenna dyes and thereby, nonradiative energy transfer from the dye’s triplet state energy.

The NIR dye, IR-806, chosen by Zou et al. [12] in their proof-of-concept study, absorbs strongly between 650 nm – 850 nm with a maximum at 806 nm. Although the overlap between the emission spectrum of this dye and the absorption spectrum of the UCNP is not ideal, sensitized UCL could be observed. In this work, we investigate dye sensitization of UCNP using the custom-made NIR dye 1859 SL [15] that has a photoluminescence quantum yield that is comparable to IR-806, yet its emission spectrum overlaps better with the absorption bands of the UCNP. Moreover, this dye

can form emissive J-aggregates in aqueous solution and its absorption below 600 nm is weak which is essential to minimize the absorption of the emitted upconverted photons. Dye-UCNP systems were obtained by a simple and experimentally easy and inexpensive approach by encapsulating the dye molecules in a micelle surrounding hydrophobic oleate-stabilized core-only NaYF₄: 20%Yb(III), 2%Er(III) UCNP with the aid of different surfactants. This approach was first described by Tao et al. [16] who embedded the dye IR-1061 in a poly(acrylic acid) matrix and then conjugated the dye-PAA with DSPE-mPEG (a polyethylene glycol-conjugated phospholipid) coated nanoparticles.

Materials and Methods

Lanthanide chlorides used for the synthesis of the UCNP were purchased from Sigma Aldrich with high purity (99.99%). Pluronic F-127, sodium oleate, oleic acid, and octadecene (90% technical grade) were obtained from Sigma Aldrich and used without further purification. Tween 80 was purchased from Merck, and the IR dye 1859 SL was synthesized in the research group of Dr. Y. Slominskii according to a published procedure [15]. All solvents employed for the optical measurements were purchased from Sigma Aldrich in spectroscopic grade.

Absorption and fluorescence spectra and the photoluminescence quantum yields (QY) were measured with a CARY 5000 absorption spectrometer (Varian) and the FSP920 fluorescence spectrometer (Edinburgh Instruments) equipped with a xenon lamp and a 980 nm laser diode. The emission lifetimes were obtained with FLS980 and FLS920 fluorescence lifetime spectrometers (Edinburgh Instruments). A more detailed experimental procedure describing the relative QY measurements using the dye IR 140 as quantum yield standard [17] as described by Würth et al. [18] can be found in the Supporting Information (SI). Energy transfer and photostability studies of micellar UCNP–cyanine dye systems were done with a Lambda 900 (UV/Vis/NIR) absorption spectrometer (Perkin Elmer) and a FLS980 fluorescence lifetime spectrometer (Edinburgh Instruments), respectively. All measurements were carried out at room temperature in 1 cm quartz cells (Hellma).

Dynamic light scattering (DLS) measurements of the UCNP–cyanine dye systems were performed with a DLS Zeta Potential Analyzer, Zetasizer Nano ZS90 (Malvern).

Upconversion nanoparticle preparation:

NaYF₄: 20%Yb(III), 2%Er(III) were synthesized according to a previously reported procedure with some modifications [19]. The synthesis and analytical characterization of the nanoparticles are provided in the SI.

Sample preparation:

Stock solutions of 1859 SL dye in chloroform (0.47 mg/mL, 0.45 mM), Pluronic F-127 in water (200 mg/mL, 0.016 M) and oleic acid capped UCNP in chloroform (50 mg/mL) were mixed in various proportions as shown in Table 1.

Sample	1	2	3	4	5	6	7
1859 SL, μg	0	4.2	12.8	25.6	38.4	51.6	25.6
F-127, g	0.01	0.01	0.01	0.01	0.01	0.01	0.01
UCNP, mg	20	20	20	20	20	20	0
Dye-to-UCNP ratio ($\mu\text{g}/\text{mg}$)	0	0.21	0.64	1.28	1.92	2.58	0

Table 1. Composition of the Pluronic F-127 encapsulated samples

The samples were prepared in the compositions indicated in Table 1. After mixing, each sample was dried under argon in a 50 mL round bottom flask. Dried samples were redispersed in 2 mL of Milli-Q water under sonication in an ultrasonic bath.

In the Tween 80 experiments, the same procedure was applied. Stock solutions of 1859 SL dye in chloroform (0.62 mg/mL, 0.59 mM), Tween 80 in water (500 mg/mL, 0.382 M), and oleic acid capped UCNP in chloroform (7 mg/mL) were mixed in various proportions, as specified in Table 2.

Sample	1	2	3	4	5
Dye stock, μg	0	1.05	2.80	9.80	16.80
Tween 80 stock, g	0.03	0.03	0.03	0.03	0.03
UCNP stock, mg	0.35	0.35	0.35	0.35	0.35
Dye-to-UCNP ratio ($\mu\text{g}/\text{mg}$)	0	3	8	28	48

Table 2. Composition of the Tween 80 encapsulated samples

Results and discussion

The absorption and emission spectra of dye 1859 SL are shown in Figure 2. This includes the spectra of the monomeric dye in DMSO as well as the absorption and emission spectra of its J-aggregates formed in water at a higher dye concentration. The fact that this dye forms J-aggregates with a very strong absorption band at 946 nm could enable studying whether dye sensitization of UCNP can occur with J-aggregates known for their very high molar absorption coefficients. QY measurements of the monomeric dye in DMSO and its J-aggregates in water revealed, however, QY of 11.9% and only 0.04%, respectively. The low QY of the J-aggregates prevented us from further investigations of their use as light-harvesting antennas.

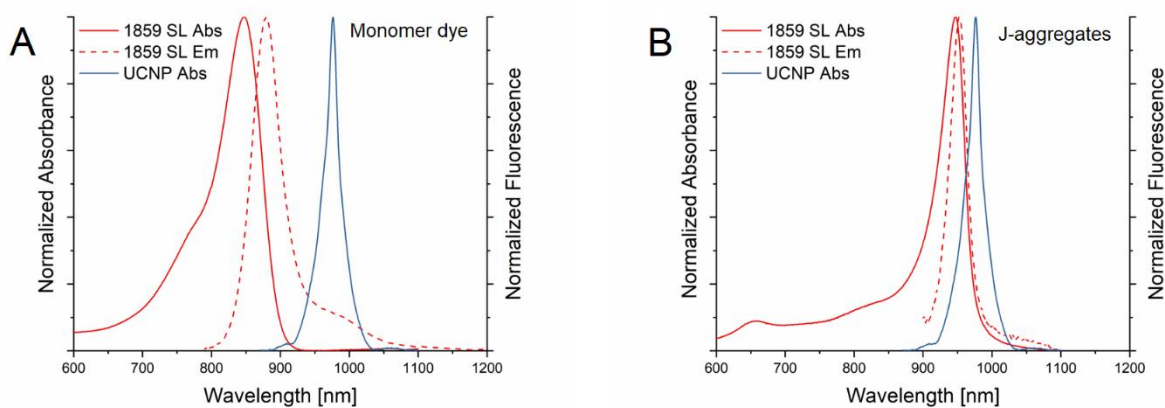


Fig. 2. Normalized absorption (solid red line) and emission (dashed line) spectrum of monomeric dye 1859 SL in DMSO (left panel, **A**) and J-aggregate of the dye in water (right panel, **B**) showing the overlap of the emission spectrum of 1859 SL and the absorption spectrum of the UCNPs which is shown in the figure (solid blue line).

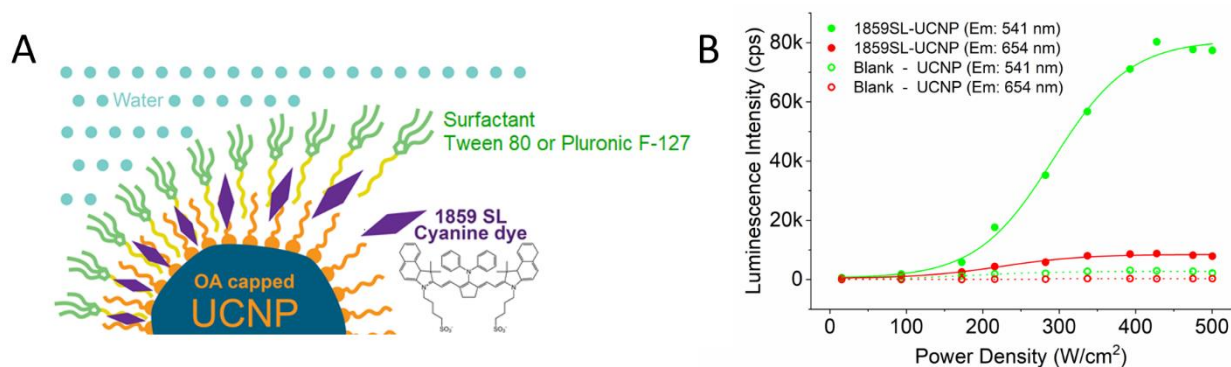


Fig. 3. A) Schematic representation of the concept of embedding UCNPs and cyanine dyes into micelles using the surfactants Pluronic F-127 or Tween 80, wrapped around the oleic acid-capped UCNPs. **B)** Power dependent upconversion emission of the green (541 nm; green symbols) and red band (654 nm; red symbols) of Pluronic F-127 micelles loaded with UCNPs only (empty circles) and with UCNPs and 1859 SL dye (filled circles). The luminescence measurements were done at 808 nm excitation. The relative luminescence intensities measured under comparable measurement conditions for the dye-sensitized UCNPs and the control system, are provided in numbers of counted photons.

In order to assess the occurrence of dye sensitization, we compared the luminescence behavior of the micellar-encapsulated 1859 SL – UCNPs systems with that of a control system, here micellar-encapsulated UCNPs lacking the dye, studied under identical measurement conditions. The 1859 SL – UCNPs@Pluronic F-127 system shows strong upconversion emission at 541 nm and 654 nm upon excitation at 808 nm (Fig. 3, right panel and Fig. 4), while only very weak emission was observed for the control system lacking the dye, under identical conditions. The weak emission arising from the UCNPs in the control system originates from the direct excitation of the ⁴I_{9/2} energy level of Er(III). The strong enhancement of the upconversion luminescence in the order of 21 provides clear evidence of dye sensitization.

Next, the 1859 SL–UCNPs@Pluronic F-127 system was optimized regarding the dye content to achieve an efficient sensitization. A dye content between 0.64–1.28 µg per milligram of UCNPs was found to be optimal for this system (Fig. 4.A and B). Higher dye loading concentrations led to reabsorption and possibly also self quenching of the dye molecules, lowering the luminescence intensity of the antenna dyes and the dye-UCNPs system. As can be seen by comparing the emission intensities of the micellar system lacking the NIR dye (red line in Figure 4.B) with the emission

intensity of the same system containing 0.64 $\mu\text{g/mL}$ 1859 SL acquired under identical conditions, a strong enhancement of the upconversion luminescence can be achieved. The very weak luminescence of the micellar system upon excitation at 808 nm in the absence of the dye is attributed to direct excitation of erbium ions.

While the 1859 SL-UCNP@Pluronic F-127 system demonstrated promising luminescence features and underlined the feasibility of using such a micellar system for dye sensitization, DLS measurements of this system showed a hydrodynamic diameter of the micelles of about 1 μm (SI, Fig. S3). This reveals that the system was not colloiddally stable in water for a longer period of time and may tend to form agglomerates in water.

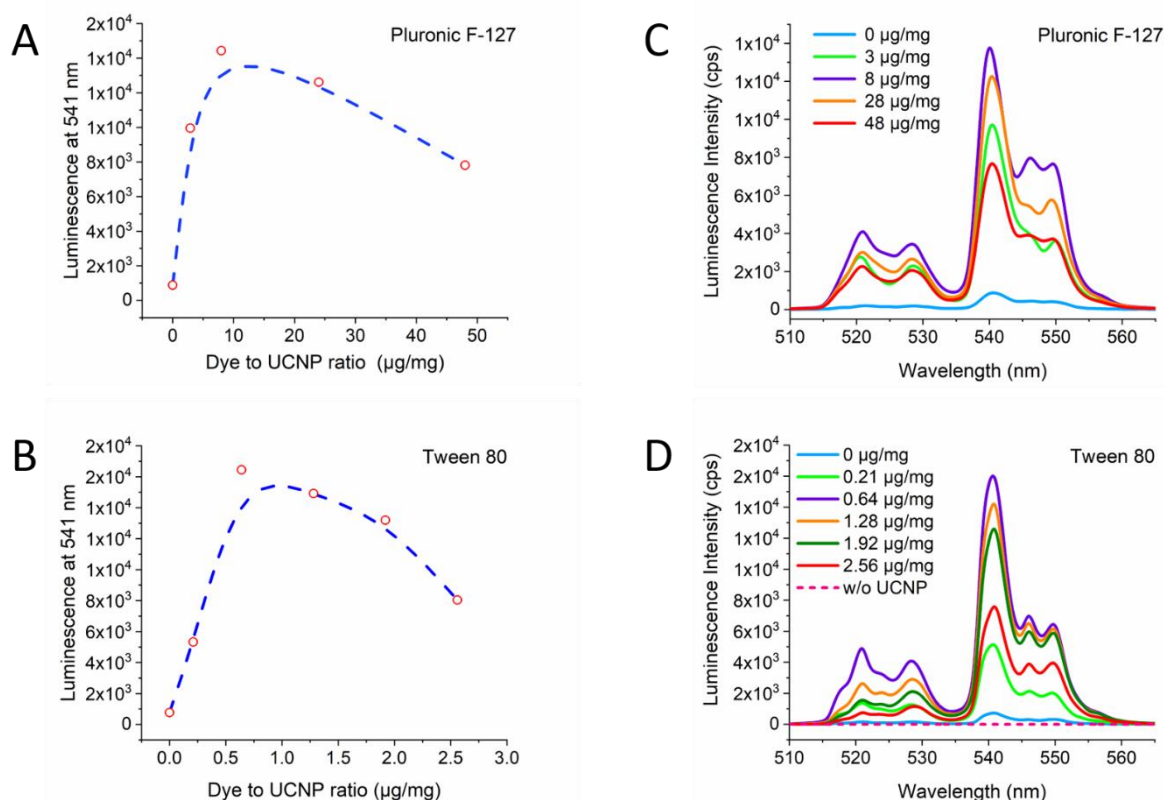


Fig. 4. Green upconversion emission of **A)** Pluronic F-127 and **B)** Tween 80 micelles loaded with UCNP and 1859 SL dye as a function of sensitizer-to-UCNP ratio. The luminescence was monitored at 541 nm. Emission spectra of **C)** Pluronic F-127 and **D)** Tween 80 micelles loaded with various UCNP-to-1859 SL dye ratios excited at 808 nm with an excitation power density of 390 W/cm^2 . The emission spectrum shown in blue in panels **(B)** and **(D)** refers to a control sample, here Tween-encapsulated UCNP lacking the NIR dye, and originates from the emission of Er(III) directly excited at 808 nm. All measurements were performed in water.

To overcome the agglomeration issues with Pluronic F-127 [20], Tween 80 was used for encapsulating OA-capped UCNP (Fig. 3 B). As with Pluronic F127, the 1859 SL dye molecules can be trapped inside the hydrophobic organic surfactant shell of the UCNP within a distance that is close enough for energy transfer from dye molecules to the UCNP.

The optimized micellar system, 1859 SL-UCNP@Tween 80, showed better results in terms of a narrower size distribution and colloidal stability in DLS. Moreover, it also revealed efficient dye sensitization of the UCNP emission, with the intensity of the upconversion emission depending on the dye-to-UCNP ratio as observed previously for the Pluronic F-127 system (Figure 4). The optimal dye content for the Tween 80 systems is about 8 μg per milligram of UCNP (Figure 4, panels B) and D)). The strongly enhanced upconversion of the micellar system that contains UCNP

and the optimum dye concentration (purple spectra in Figure 4, panels B) and D)) compared to that of the control system provides solid proof of successful energy transfer from the dye molecules to the UCNP under these conditions.

In both types of micellar systems, however, dye photodegradation occurred at the very high excitation power densities used for these studies (SI, Fig. S4). Similar photostability issues have been also reported for other NIR dye sensitized systems [9].

Conclusion

We demonstrated a successful strategy for simple and easy to prepare upconversion nanoparticle (UCNP) systems with dye sensitization of the upconversion emission, using a near infrared (NIR) absorbing and emitting cyanine dye, core-only UCNP, and micelle-forming surfactants. Excitation of the dye with an 808 nm CW laser showed strong fluorescence emission of the UCNP with an enhancement factor of about 21 compared to the excitation of the dye-lacking UCNP control sample under identical conditions which produced only very weak emission, arising from the direct excitation of Er(III) ions. This confirms energy transfer from the excited dye molecules to the Yb(III) ions, followed by energy transfer to the subsequently emitting Er(III) ions (energy transfer upconversion). This shifts the excitation of the Yb(III), Er(III)-doped NaYF₄ UCNP core from 980 nm to 808 nm located in the biologically relevant first diagnostic window where water absorption and hence heating effects are minimized.

This strategy could be realized with the two well-known and biocompatible surfactants Pluronic F-127 [21]–[24] and Tween 80 [20], underlining its versatility. This micellar encapsulation ensures that the dye molecules are in close neighborhood to the UCNP surface and hence the optically active lanthanide ions within these UCNP, as required for energy transfer. Moreover, this approach is fast, inexpensive, and experimentally simple without the need of chemical surface modification of the UCNP [13], [25], modification of the dye [12], [13], [26] or covalent binding [27]. With their hydrophobic moieties, Pluronic F-127 and Tween 80 can confine 1859 SL in the hydrophobic pocket around oleic acid capped UCNP. Additionally, this approach renders the systems well dispersible in water, particularly in the case of Tween, which is an important requirement in biological applications. Our micellar encapsulation approach could be also interesting for theranostic applications in the future as the hydrophobic interior of such micellar systems can be used as an efficient nanocarrier for water-insoluble drugs [20].

The exact mechanisms involved in the demonstrated energy transfer still require further investigations which were beyond the scope of the current study. Presently, we cannot say whether dye sensitization by the NIR dye 1859 SL can be attributed merely to direct energy transfer from the dye's singlet state or whether its triplet state is also involved as observed by Schuck and colleagues [28] for NaGdF₄ UCNP. Here, particularly the close proximity of the heavy and paramagnetic Gd(III) lanthanide ions induces intersystem crossing in the antennae cyanine dyes, with the dye triplet states then acting as energy donors.

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The authors have declared that no conflicting interests exist.

Authors contribution:

Maysoon I. Saleh, Ihor D. Panas and Florian Frenzel contributed equally to this work.

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