

# Multimodal Light-Harvesting Soft Hybrid Materials: Assisted Energy Transfer upon Thermally Reversible Gelation

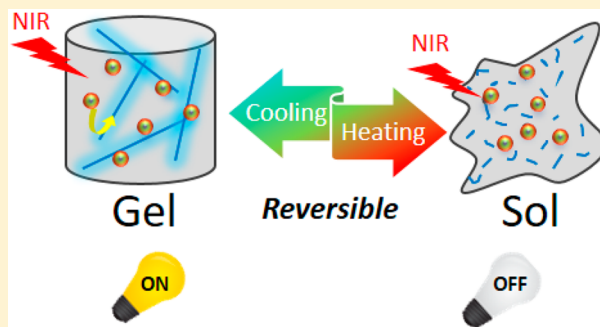
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## S Supporting Information

**ABSTRACT:** Multimodal light-harvesting soft systems able to absorb UV-to-NIR radiations and convert into visible emissions have drawn much attention in the last years in order to explore new areas of application in energy, photonics, photocatalysis, sensors, and so forth. Here, we present a new hybrid system combining a supramolecular photonic gel of naphthalimide-derived molecules self-assembled into fibers and upconverting NaYF<sub>4</sub>:Yb/Tm nanoparticles (UCNPs). The hybrid system presented here manipulates light reversibly as a result of an optical communication between the UCNPs and the photoactive gel network. Upon UV irradiation, the system shows the characteristic emission at 410 nm from the photoactive organo-molecule. This emission is also activated upon 980 nm excitation thanks to an efficient energy transfer from the UCNPs to the fibrillary network. Interestingly, the intensity of this emission is thermally regulated during the reversible assembly or disassembly of the organogelator molecules, in such a way that gelator emission is only observed in the aggregated state. Additionally, the adsorption of the UCNPs with the supramolecular gel fibers enhances their emissive properties, a behavior ascribed to the isolation from solvent quenchers and surface defects, as well as an increased IR light scattering promoted by the fibrillary network. The reported system constitutes a unique case of a thermally regulated, reversible, dual UV and IR light-harvesting hybrid soft material.



## INTRODUCTION

Supramolecular gels based on self-assembled fibrillary networks are soft materials with significant advantages when compared to polymeric analogues such as intrinsic reversibility, stimuli responsiveness, and superior biocompatibility.<sup>1–4</sup> The increasing attention paid to supramolecular gels is related to their applicability as new soft materials in areas such as molecular electronics, controlled release, tissue engineering, or catalysis, among others.<sup>2–7</sup> Several approaches have addressed the inclusion of photonic functionalities into supramolecular gels.<sup>8</sup> For example, gels with chromophore units have been used as photocatalysts<sup>9,10</sup> and excitation energy transfer has been studied in supramolecular gels formed by photoactive fibers which contained entrapped dyes.<sup>11–15</sup> Recently, we reported orthogonal fibrillization of two fluorescent supramolecular gelators.<sup>16</sup> Additionally, supramolecular gels have been used as photon upconversion matrixes based on the triplet–triplet-annihilation mechanism via organic molecules.<sup>17,18</sup> Some studies have also been devoted to hybrid systems of noble (Ag and Au) metallic nanoparticles (NPs) and supramolecular networks.<sup>19</sup> In this case, supramolecular gels act as scaffold to support the NPs,<sup>20–22</sup> which in some of cases were prepared in situ,<sup>23–26</sup> and can find application as antibacterial soft materials<sup>26–29</sup> or catalysts.<sup>30</sup> Some studies

have evaluated the influence of the molecular gel network in the photoluminescence of NPs.<sup>31–34</sup> Core/shell semiconductor nanocrystals of CdSe/ZnS, or quantum dots (QDs), have been incorporated into molecular gels, affording an improvement in emission quantum yields<sup>35</sup> and have been used as sensors of nitric oxide.<sup>36</sup>

In this work, a soft hybrid system based on IR light upconverting NaYF<sub>4</sub>:Yb/Tm nanoparticles (UCNPs) and a fluorescent supramolecular network containing naphthalimide-derived molecules is described. Bulk upconverting lanthanide-based crystals have been known for decades, but there has been a resurgence of their study associated with the preparation of upconverting nanoparticles (UCNPs) about one decade ago.<sup>37,38</sup> Manipulation of IR radiation using UCNPs has been found to be of much interest because the UV–vis output can be used to promote several chemical processes or to develop a number of applications in the fields of lighting and displays, energy, photocatalysis, sensing, bioanalytics, and theranostics.<sup>39–45</sup> To our knowledge, only two reports concerning the inclusion of UCNPs in self-assembled organogels are available

Received: June 30, 2017

Revised: September 11, 2017

Published: September 13, 2017



in the literature. UCNP could be dispersed in a supramolecular gel matrix formed by a peptide derivative, reinforcing the gel structure.<sup>46</sup> However, the gel matrix was acting as a passive scaffold. In another report, a photoactive supramolecular gel formed by a derivative of *trans*-stilbene experienced energy transfer from UCNP.<sup>47</sup> Unlike the results reported here, the reversibility of the hybrid gel was not studied and the emission of gelator overlapped with that of the UCNP. In this work, there is an optical communication between the UCNP and the organic chromophore, and the light manipulation process is found to be fully reversible and associated with the assembly/disassembly of the gel. Furthermore, the gel provides much improved stability toward aggregation to the UCNP.

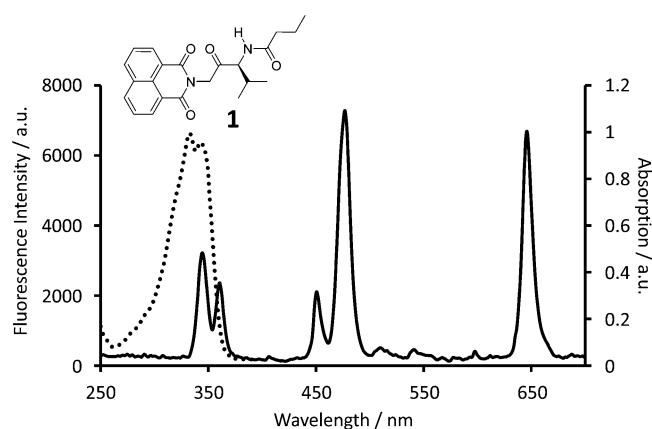
## EXPERIMENTAL SECTION

The synthesis of the hybrid supramolecular gel is fully described in the [Supporting Information](#) file (SI). In a typical procedure, the organogelator molecule (labeled as compound 1) and the upconverting NaYF<sub>4</sub>:Yb/Tm nanoparticles (20%-Yb and 0.5%-Tm molar ratio replacing yttrium ions in the lattice, labeled as UCNP) were first prepared. The hybrid system (UCNP-1gel) was prepared as follows: 20 mg of UCNP was suspended in 2 mL of butanol and sonicated for 5 min in a screw-capped vial. Then,  $6 \times 10^{-3}$  mmol of compound 1 were added and the closed system heated to 80 °C until it was completely solubilized. The system was left to cool down until room temperature for 10 min, and the hybrid gel was formed. The samples were prepared in cylindrical glass vials with different sizes, and the gel dimensions ranged from 10 to 15 mm diameter  $\times$  5–20 mm height.

The characterization by high-resolution transmission electronic microscopy (HRTEM) was carried out on a JEOL-2100 LaB<sub>6</sub> microscope, at an accelerating voltage of 200 kV, with an Inca Energy TEM 200 (Oxford) energy dispersive X-ray spectroscopy (XEDS). The gel samples were deposited over Ni grids coated with a carbon film before TEM observation. The absorption spectra were measured on a Cary 500 Scan UV-vis-NIR spectrophotometer (Varian) equipped with an integrating sphere. The upconversion spectra were measured using an infrared laser diode (model RLMDL-980-2W, Roithner LaserTechnik, 980 nm  $\pm$  5 nm, 2 W continuous waveform, stability <5%, laser head 141  $\times$  46  $\times$  73 nm) as the pump source. The emission spectra were measured at 1 W output with a focus lens, providing 105 W cm<sup>-2</sup> optical power density on the sample. A StellarNet EPP2000-UV-vis spectrometer was employed for the fluorescence detection in the visible region. Additional experiments on the hybrid system were carried out in a transparent cuvette using the setup shown in the [SI](#) using a spectrofluorimeter JASCO FP-8300.

## RESULTS AND DISCUSSION

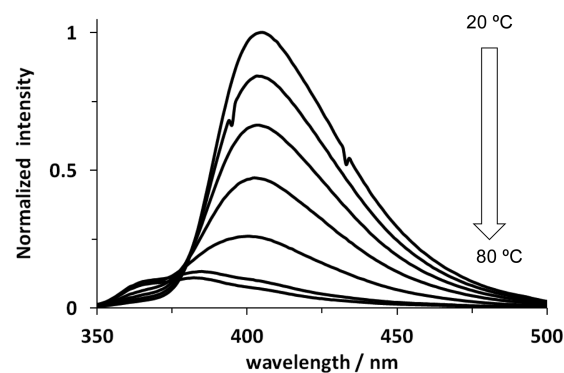
Compound 1 (see [Figure 1](#)) is a low molecular weight gelator derived from 1,8-naphthalimide chromophore. When compound 1 is dissolved in a hot solution of butanol and the clear solution is left to cool down to room temperature, supramolecular gels are formed. The minimum concentration required for gelation (mgc) was 5 mM with a transition from gel to solution ( $T_{gel}$ ) taking place at 65 °C using a vial inversion test. Transmission electron microscopy of the xerogel revealed the usual entanglement of fibers observed commonly in supramolecular gels ([Figure S1](#), [Figure S1](#) from [Supporting Information](#) file). The 1,8-naphthalimide unit introduced in the



**Figure 1.** Overlaid absorption spectrum of compound 1 in butanol (dotted line) and emission spectrum of UCNP ( $\lambda_{exc}$  = 980 nm, 105 W cm<sup>-2</sup> optical power density).

gelator is a well-known fluorophore,<sup>48</sup> presenting light absorbance at  $\lambda_{max}$  = 335 nm and emission at  $\lambda_{max}$  = 410 nm (see [Figure 1](#) and [Figure S2](#)). NaYF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> upconverting nanocrystals (UCNP) prepared following a simple solvothermal procedure (see [SI](#))<sup>49</sup> produce different emissions with maximum intensity at wavelengths of 345, 355, 450, 475, and 650 nm ([Figure 1](#)) upon excitation at 980 nm. The hybrid system UCNP-1gel was designed in such a way that the absorption of the gelator overlaps with the two emission bands of the UCNP located at ca. 350 nm ([Figure 1](#)), and an energy transfer from the UCNP to the chromophoric residue could take place (see adapted Jablonsky diagram in [Figure S8](#)).

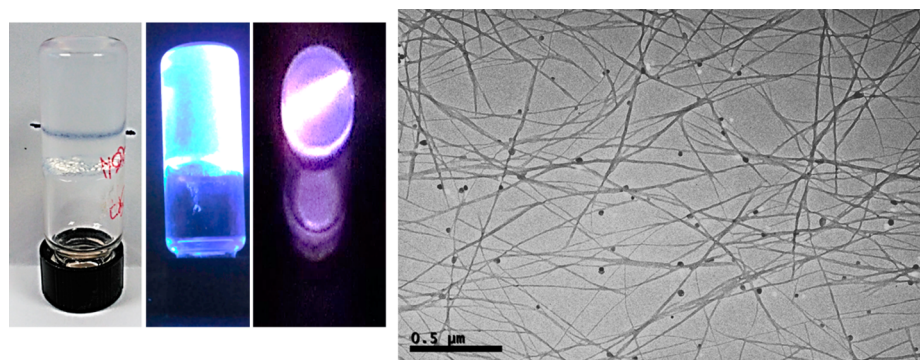
Examination of the fluorescent properties of the pure gel formed by compound 1 revealed a strong aggregation induced emission effect upon excitation with 335 nm light.<sup>50</sup> This means that when the gel is heated from 20 to 80 °C a dramatic decrease of the 410 nm emission is observed, associated with a progressive gel disassembly ([Figure 2](#)). This behavior is



**Figure 2.** Variable temperature study of the emission spectra of the gel of compound 1 ( $\lambda_{exc}$  = 335 nm). Intensity at  $\lambda_{max}$  is normalized to 1 for the spectrum at 20 °C.

opposite to that observed by a 4-amino-1,8-naphthalimide analogue which was studied by us recently.<sup>16</sup> Under 980 nm excitation, the pure gel did not exhibit any emission.

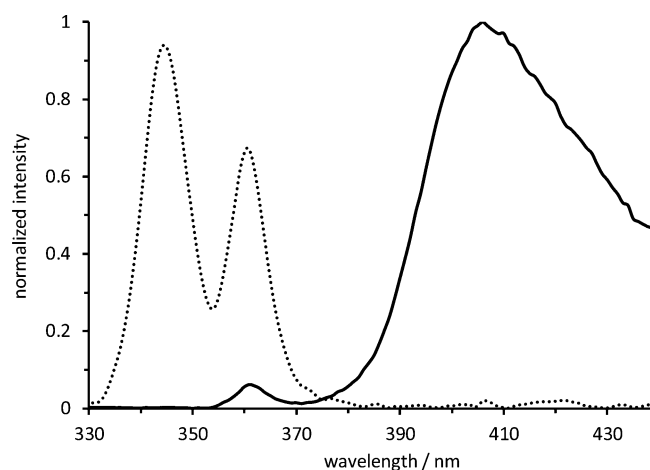
The hybrid system containing the UCNP within the fibrillary network has a good translucent/transparent (depending on the concentration of UCNP and the cooling rate of the gel) appearance. [Figure 3](#) left shows the picture of the hybrid UCNP-1gel under natural, UV, and NIR light. Electron



**Figure 3.** (Left) Pictures of the hybrid UCNP-1 gel under natural light, UV lamp excitation, and 980 nm laser irradiation. (Right) Transmission electron microscopy image of the hybrid UCNP-1 gel.

microscopy revealed that the hybrid material is formed by thin self-assembled fibers isolated and well-dispersed UCNP mostly stacked at the surface of the fibers (Figure 3 right). It could be argued that the solvophobic oleic acid units covering the UCNP provide anchorage points to the surface of the fibers as described, for example, for the interaction with polymers.<sup>51,52</sup>

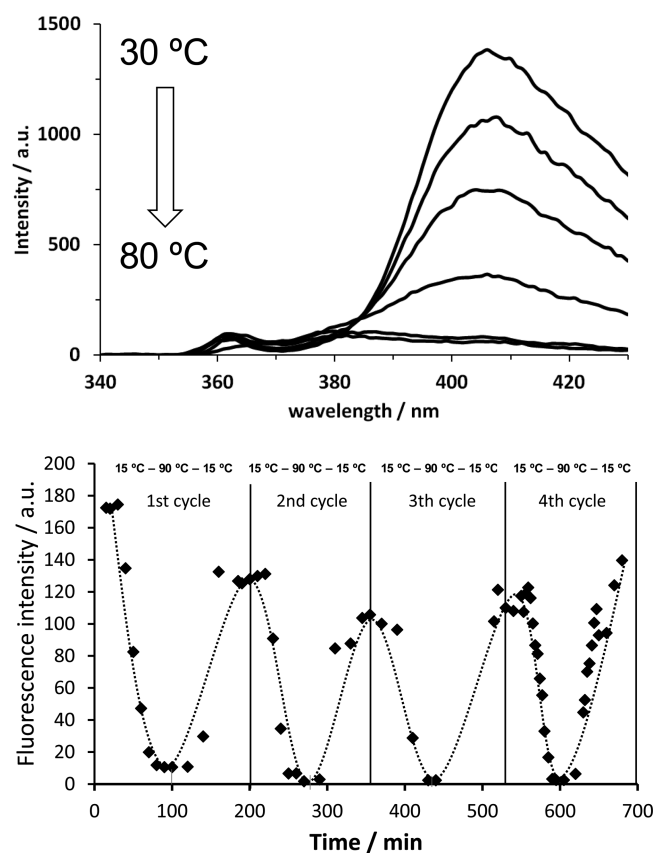
Next, the emission of UV-vis light upon irradiation of the UCNP-loaded gels with 980 nm IR light was studied. It was found that the emission of the UCNP at ca. 350 nm disappears and the emission band at 410 nm emerges (Figure 4). This is a consequence of the overlapped emission of the UCNP and the absorption of compound 1, as expected.



**Figure 4.** Overlay of the emission spectra of UCNP (dotted line) and hybrid UCNP-1 gel (upon 980 nm excitation). Intensity at  $\lambda_{\text{max}}$  for both systems is normalized to 1.

Interestingly, the hybrid system only originates IR-promoted emission at 410 nm in the gel state (Figure 5), with this process being canceled when the gel is disassembled at 80 °C, a behavior directly related to the aggregation induced emission properties of compound 1. The system showed good reversibility and several heating-cooling cycles could be performed, restoring the upconversion to 410 nm at low temperatures. Consequently, the system formed by UCNP-1gel constitutes a thermally regulated light upconverting soft material.

It is important to remark that the light emitted by UCNP at ca. 350 nm is absorbed by compound 1 when the hybrid system is either in the gel state (at 30 °C-assembled) or in the sol state (80 °C-disassembled) (see Figure 5). This fact has implications

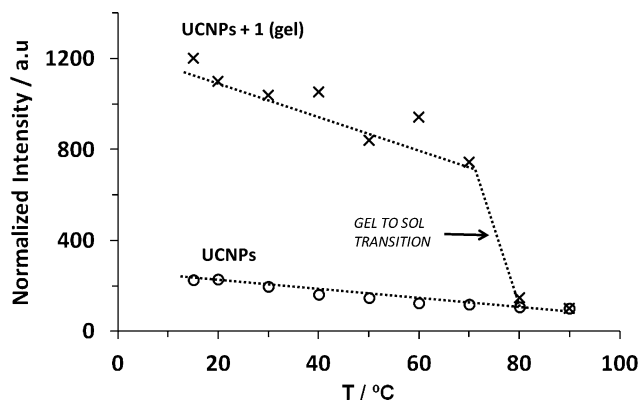


**Figure 5.** Top: Variable temperature study of the emission spectra of the hybrid UCNP-1gel ( $\lambda_{\text{exc}} = 980$  nm). Bottom: Variation of the emission intensity at 410 nm for the hybrid system UCNP-1 upon heating-cooling cycles. The dotted line is used as a guide to the eye ( $\lambda_{\text{exc}} = 980$  nm).

for the mechanism of energy transfer taking place in the system. At 80 °C the fibers are disassembled and spatial proximity between UCNP and naphthalimide units is precluded, discarding a dipole-dipole energy transfer mechanism such as resonance energy transfer (RET).<sup>53</sup> Therefore, a photon reabsorption process, also known as the inner filter effect, emerges as the most plausible mechanism for energy transfer between UCNP in both gel and solution states although RET cannot be discarded to take place in the former case. The inner filter effect has been used in sensing applications based on UCNP.<sup>54</sup>



Aside from the previous results, it is noteworthy that the emission intensity of the UCNP's in the presence of the supramolecular gel is clearly improved. Variable temperature studies were carried out for suspensions of the UCNP's in butanol in the presence and absence of compound 1. As can be seen in Figure 6, the emission of the UCNP's at 475 nm



**Figure 6.** Variable temperature study of the emission intensity at 475 nm of UCNP's (suspended in butanol) and hybrid UCNP's-1 gel. Values are normalized taking as reference the intensities measured at 90 °C for both systems ( $\lambda_{\text{exc}} = 980$  nm).

measured in the range 20–90 °C varies weakly, being moderately higher at low temperatures. However, in the presence of gelator 1 a very notable dependence with temperature was detected. It is important to recall that in the range 20–90 °C a progressive thermal disassembly of the gel network takes place and the system is converted from a gel to a solution. For the sake of comparison, it was decided to analyze the behavior of both samples, with and without gelator, normalizing the results to the emission intensity measured at 90 °C for pure UCNP's. This seems reasonable because in both cases free and disperse UCNP's and no aggregates are present. In this way, the fluorescence intensity at 20 °C in the presence of the gelator is much higher than that observed in the presence of UCNP's alone, with a 6-fold increase (Figure 6).

The process was found to be reversible and after a heating–cooling cycle, the emission was restored to initial values. These results indicate an improvement of the lanthanide nanocrystals emission ascribable to their interaction with the fibrillar network. A plausible rationale for this behavior is based on the partial isolation from the solvent experienced by the UCNP's upon adsorption on the gel fibers, avoiding in this way strong quenching effects from the high vibrational states of the hydroxyl groups of butanol. Such quenching effects have been demonstrated unequivocally in the case of water molecules and other alcohols.<sup>55,56</sup> It is also important to mention that the fibrillar network avoids the clustering of the UCNP's, leading to a more homogeneous and uniform luminescent material. Additionally, the scattering of IR light in the supramolecular gel could also enlarge the interaction of the laser with the UCNP's, contributing to the observed emission.<sup>47</sup>

## CONCLUSIONS

We present a new hybrid system combining a supramolecular photonic gel of naphthalimide-derived molecules self-assembled into fibers and upconverting  $\text{NaYF}_4\text{:Yb/Tm}$  nanoparticles (UCNP's). The hybrid system presented here manipulates light reversibly as a result of an optical communication between

the UCNP's and the photoactive gel network. Radiative excitation energy transfer occurs very efficiently affording a transformation of the light emitted from the nanoparticles. Upon NIR radiation, the UCNP's emission overlapping the absorption of the gel chromophore is removed and a new emission from the 1,8-naphthalimide acceptor appears at 410 nm. This fact corresponds to a light-harvesting process. This process is only active in the form of gel as a result of the aggregation induced emissive properties of the supramolecular gelator. Reversible gel disassembly is promoted by temperature changes, giving place to a temperature regulated tunable photonic soft material. Additionally, the interaction of the UCNP's with the self-assembled fibers fosters the emissive relaxation pathways more than nonradiative decays. This fact is accompanied by a greater exposure of the NIR radiation from the gel scattering, originating an outstanding improvement of the emission intensity. This effect can also be ascribed to isolation from the solvent of the nanoparticles upon interaction with the gel fibers together with IR light scattering produced by the self-assembled gel network. Hybrid UCNP's-gel systems such as those described here are envisaged to be used in applications related to IR-based sensing or light manipulation in general, especially taking into account the possibility of their miniaturization in the form of micro-/nanogels for biomedical applications.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b06441.

Experimental details regarding UCNP's and gelator preparation as well as hybrid gel formation and its fluorescence studies (PDF)

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

Ministerio de Economía y Competitividad of Spain (grants CTQ2015-71004-R and MAT2015-64139-C4-1-R) and Universitat Jaume I (grants P1.1B2015-76 and P1.1B2014-21) are thanked for financial support. C.F.-L. thanks Ministerio de Economía y Competitividad of Spain for a FPI fellowship. F.G. thanks Generalitat Valenciana for a Santiago Grisolia fellowship. Technical support from SCIC of University Jaume I is acknowledged.

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