

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

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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 NaYF₄: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 organomolecule. 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 enhance 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.¹⁻⁴ 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.²⁻⁷ Several approaches have addressed the inclusion of photonic functionalities into supramolecular gels.⁸ For example, gels with chromophore units have been used as photocatalysts^{9,10} and excitation energy transfer has been studied in supramolecular gels formed by photoactive fibers which contained entrapped dyes.¹¹⁻¹⁵ Recently, we reported orthogonal fibrillization of two fluorescent supramolecular gelators.¹⁶ Additionally, supramolecular gels have been used as photon upconversion matrixes based on the triplet-triplet-annihilation mechanism via organic molecules.^{17,18} Some studies have been also devoted to hybrid systems of noble (Ag and Au) metallic nanoparticles NPs and supramolecular networks.¹⁹ In this case, supramolecular gels act as scaffold to support the NPs²⁰⁻²² which in some of cases were prepared in situ,²³⁻²⁶ and can find application as antibacterial soft materials²⁶⁻²⁹ or catalysts.³⁰ Some studies have evaluated the influence of the molecular gel network in the photoluminescence of NPs.³¹⁻³⁴ Core/shell semiconductor nanocrystals of CdSe/ZnS, or quantum dots (QDs), have been incorporated into molecular gels affording an improvement in emission quantum yields³⁵ and have been used as sensors of nitric oxide.³⁶

In this work, a soft hybrid system based on IR light upconverting NaYF₄: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 to the preparation of upconverting nanoparticles (UCNPs) about one decade ago.^{37,38} 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.³⁹⁻⁴⁵ Up to our knowledge, only two reports concerning the inclusion of UCNPs in self-assembled organogels are available in the literature. UCNPs could be dispersed in a supramolecular gel matrix formed by a peptide derivative, reinforcing the gel structure.⁴⁶ 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 UCNPs.⁴⁷ Unlike the results reported here, the reversibility of the hybrid gel was not studied and the emission of gelator overlapped with that of the UCNPs. In this work, there is an optical communication between the UCNPs and the organic chromophore, and the light manipulation process is found to be fully reversible and associated to the assembly/disassembly of the gel. Furthermore, the gel provides with much improved stability towards aggregation to the UCNPs.

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 (labelled as compound 1) and the upconverting NaYF₄:Yb/Tm nanoparticles (20%-Yb and 0.5%-Tm molar ratio replacing yttrium ions in the lattice, labelled as UCNPs) were first prepared. The hybrid system (UCNPs-1gel), was prepared as follows: 20 mg of UCNPs were suspended in 2 mL of butanol and sonicated for 5 min in a screw-capped vial. Then, 6×10^{-3} mmol of compound 1 were added and the closed system heated to 80 °C until it was completely solubilized. The system was left cool down until

room temperature for 10 minutes and the hybrid gel was formed. The samples were prepared in cylindrical glass vials with different sizes, and the gel dimensions ranged from 10-15 mm diameter x 5-20 mm height.

The characterization by high-resolution transmission electronic microscopy (HRTEM) was carried out on a JEOL- 2100 LaB₆ 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 ± 5nm, 2 W continuous waveform, stability <5%, laser head 141x46x73 mm) as the pump source. The emission spectra were measured at 1 W output with a focus lens, providing 105 Wcm⁻² 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 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 gelator is a well-known fluorophore,⁴⁸ presenting light absorbance at $\lambda_{\text{max}} = 335$ nm and emission at $\lambda_{\text{max}} = 410$ nm (see Figure 1 and Figure S2). NaYF₄:Yb³⁺/Tm³⁺ upconverting nanocrystals (UCNPs) prepared following a simple solvothermal procedure (See SI)⁴⁹ 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 UCNPs-1gel was designed in such a way that the absorption of the gelator overlaps with the two emission bands of the UCNPs located at ca. 350 nm (Figure 1), and an energy transfer from the UCNPs to the chromophoric residue could take place (see adapted Jablonsky diagram at Figure S8).

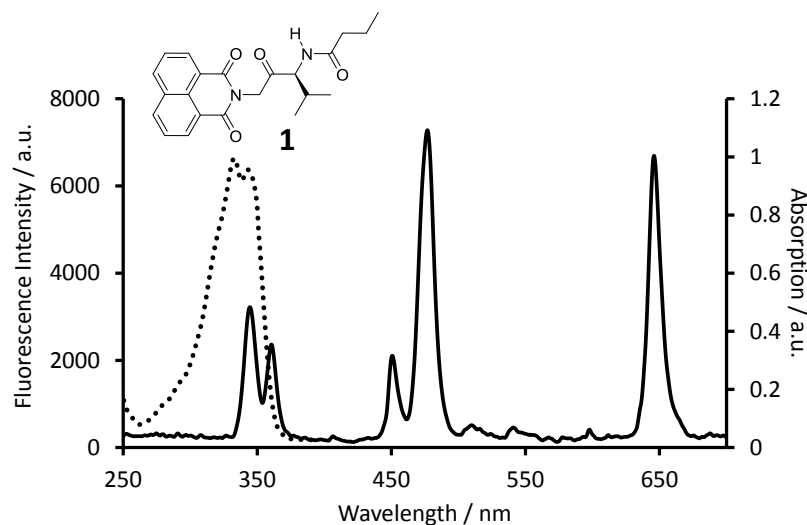


Figure 1. Overlaid absorption spectrum of compound 1 in butanol (dotted line) and emission spectrum of UCNPs ($\lambda_{\text{exc}} = 980$ nm, 105 Wcm^{-2} optical power density).

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.⁵⁰ It means that when the gel is heated from 20 °C to 80 °C a dramatic decrease of the 410 nm emission is

observed, associated to a progressive gel disassembly (Figure 2). This behavior is opposite to that observed by a 4-amino-1,8-naphthalimide analogue which was studied by us recently.¹⁶ Under 980 nm excitation, the pure gel did not exhibit any emission.

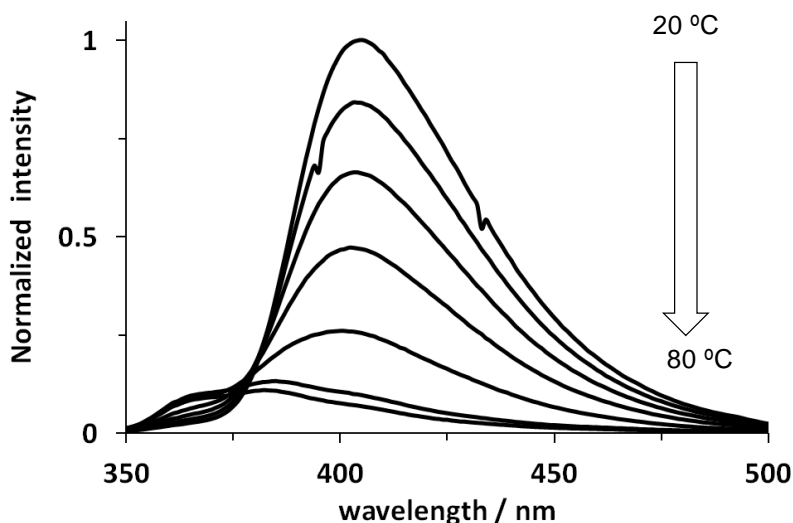


Figure 2. Variable temperature study of the emission spectra of the gel of compound 1 ($\lambda_{\text{exc}}=335\text{nm}$). Intensity at λ_{max} is normalized to 1 for the spectrum at 20 °C.

The hybrid system containing the UCNPs within the fibrillary network has a good translucent/transparent (depending on the concentration of UCNPs and the cooling rate of the gel) appearance. Figure 3 left shows the picture of the hybrid UCNPs-1gel under natural, UV and NIR light. Electron microscopy revealed that the hybrid material is formed by thin self-assembled fibers isolated and well-dispersed UCNPs mostly stacked at the surface of the fibers (Figure 3 right). It could be argued that the solvophobic oleic acid units covering the UCNPs provide anchorage points to the surface of the fibers as described, for example, for the interaction with polymers.^{51,52}

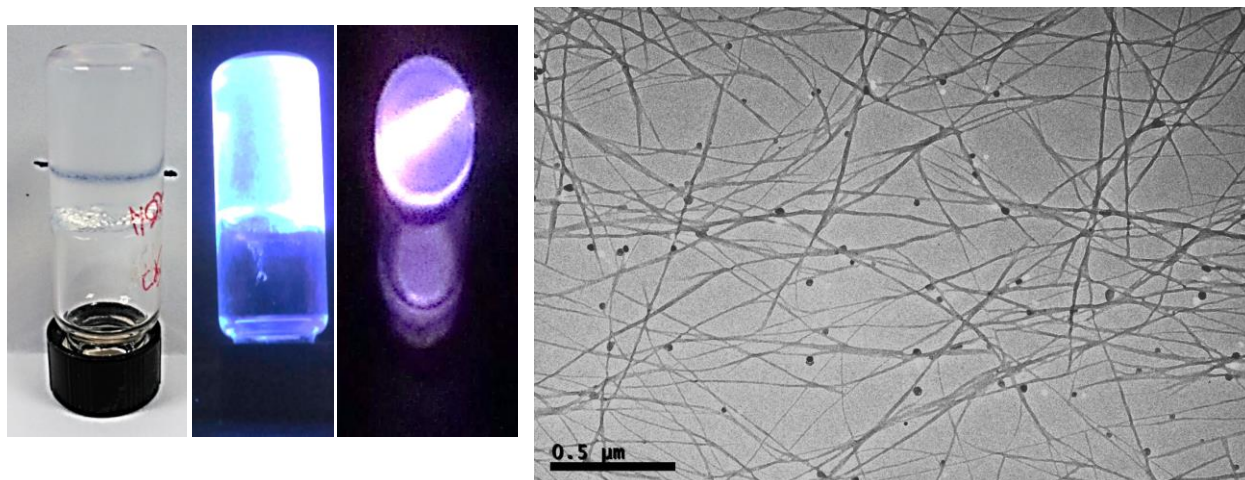


Figure 3. Left) Pictures of the hybrid UCNP-1 gel under natural light, UV lamp excitation and 980nm laser irradiation. Right) Transmission electron microscopy image of the hybrid UCNP-1 gel.

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.

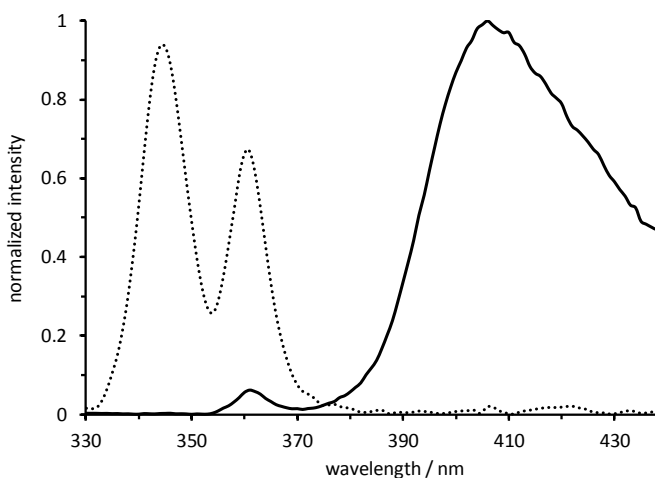


Figure 4. Overlaid of the emission spectra of UCNP (dotted line) and hybrid UCNP-1 gel (upon 980 nm excitation). Intensity at λ_{\max} for both systems is normalized to 1.

Interestingly, the hybrid system only originates IR-promoted emission at 410 nm in the gel state (Figure 5), being this process cancelled 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 UCNPs-1gel constitutes a thermally regulated light upconverting soft material.

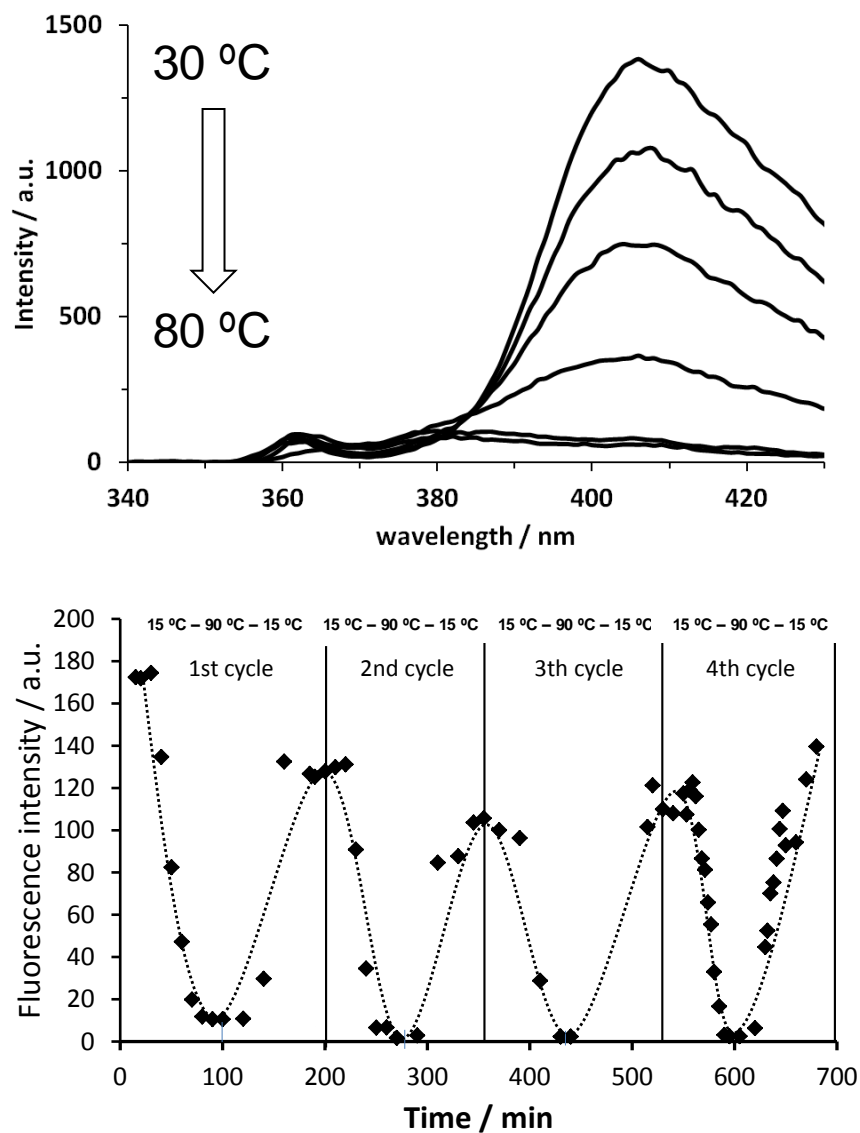


Figure 5. Top: Variable temperature study of the emission spectra of the hybrid UCPNs-1gel ($\lambda_{\text{exc}} = 980 \text{ nm}$). Bottom: Variation of the emission intensity at 410 nm for the hybrid system UCPNs-1 upon heating-cooling cycles. Dotted line is used as guide to the eye ($\lambda_{\text{exc}}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

It is important to remark that the light emitted by UCNPs at ca. 350 nm is absorbed by compound 1 either when the hybrid system is in the gel state (at 30°C-assembled) or in the sol state (80°C-disassembled) (see Figure 5). This fact has implications for the mechanism of energy transfer taking place in the system. At 80°C the fibers are disassembled and spatial proximity between UCNPs and naphthalimide units is precluded, discarding a dipole-dipole energy transfer mechanism like resonance energy transfer (RET).⁵³ Therefore, a photon reabsorption process, also known as inner filter effect, emerges as the most plausible mechanism for energy transfer between UCNPs both in gel and solution states although RET can't be discarded to take place in the former case. The inner filter effect has been used in sensing applications based on UCNPs.⁵⁴

Aside of the previous results, it is noteworthy that the emission intensity of the UCNPs in the presence of the supramolecular gel is clearly improved. Variable temperature studies were carried out for suspensions of the UCNPs in butanol in the presence and absence of compound 1. As can be seen in Figure 6, the emission of the UCNPs at 475 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 UCNPs. This seems reasonable because in both cases free

and disperse UCNPs and no aggregates are present. In this way, fluorescence intensity at 20 °C in the presence of the gelator is much higher than that observed in the presence of UCNPS 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 UCNPs upon adsorption on the gel fibers, avoiding in this way strong quenching effects from the high vibrational states of hydroxyl groups of butanol. Such quenching effects have been demonstrated unequivocally in the case of water molecules and other alcohols.^{55,56} It is also important to mention that the fibrillary network avoids the clustering of the UCNPs, 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 UCNPs, contributing to the observed emission.⁴⁷

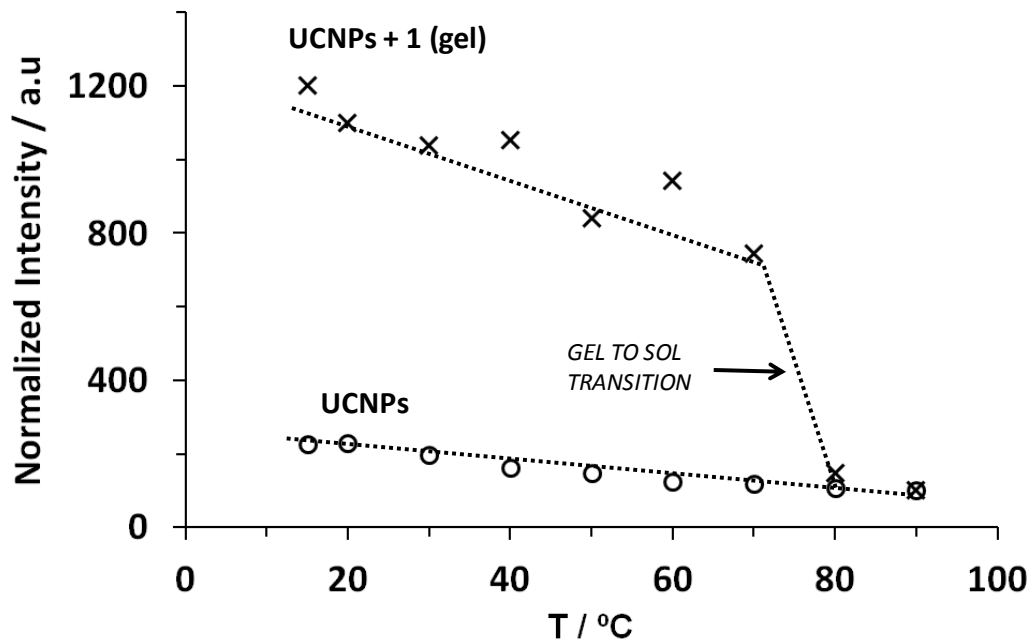


Figure 6. Variable temperature study of emission intensity at 475 nm of UCNPs (suspended in butanol) and hybrid UCNPs-1 gel. Values are normalized taken as reference the intensities measured at 90 °C for both systems ($\lambda_{\text{exc}} = 980 \text{ nm}$).

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 (UCNPs). The hybrid system presented here manipulates light reversibly as a result of an optical communication between the UCNPs 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 UCNPs'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 tuneable photonic soft material. Additionally, the interaction of the UCNPs with the self-assembled fibers fosters the emissive relaxation pathways more than non-radiative 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 UCNPs-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

The following files are available free of charge.

Experimental details regarding UCNPs and gelator preparation as well as hybrid gel formation and its fluorescence studies. (PDF)

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TOC Graphic

