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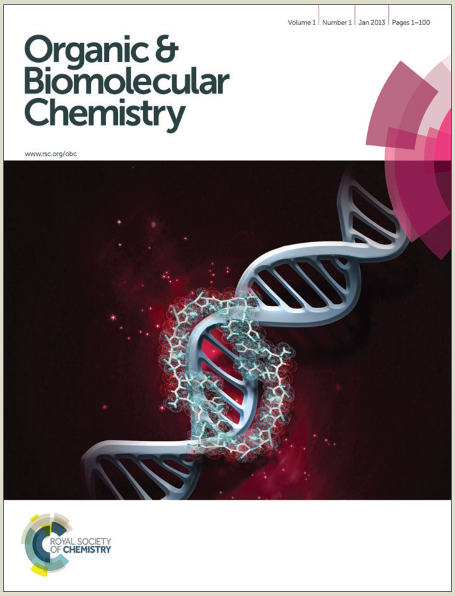

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ARTICLE

Energy Transfer Between Amphiphilic Porphyrin Polymer Shells and Upconverting Nanoparticle Cores in Water-Dispersible Nano-assemblies

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The synthesis of water-dispersible nano-assemblies containing upconverting nanoparticles (UCNPs) and porphyrin molecules using a one-pot method is described. When the nano-assemblies are excited by 980 nm near-infrared light, the intensity of the 'green emission' band of the UCNP is reduced due to a combination of Föster Resonace Energy Transfer (FRET) and emission-reabsorption. This process is also responsible for the emission from the porphyrin chromophores despite the fact they do not absorb near-infrared light.

Introduction

Porphyrins and metalloporphyrins are ubiquitous as acceptors in Föster Resonace Energy Transfer (FRET) acceptor-donor pairs,[1] where the donors can include organic chromophores,[2–9] fluorescent polymers[10,11] and quantum dots.[12] The use of these systems as optical probes for detecting metal ions[3] and studying protein unfolding,[9] and sensitizers to generate singlet oxygen,[4,6,7,11,12] induce apoptosis and act as anti-microbial agents explains the importance to develop simple systems capable of operating in a wide range of environments.

Upconverting nanoparticles (UCNPs) composed of crystalline $NaYF_4$ doped with trivalent lanthanide ions such as Er^{3+}, Tm^{3+} and Ho^{3+} have interesting optical properties of their own.[13,14] The most intriguing one is their ability to absorb multiple photons of 980 nm near-infrared (NIR) light and combine them to emit UV and visible photons of several wavelengths in the electromagnetic spectrum. It is, therefore, not surprising to find UCNPs used as FRET donors.[15,16]

The examples where upconverting nanoparticles and porphyrins have been used as energy-transfer donor-acceptor pairs for nano-theranostics[17–20] demand complicated chemical modification to the macrocycle[18] and/or multi-step surface modifications to the UCNPs.[17,19,20] A simpler, more universal method to unite these two useful energy-transfer components would help expand their use in aqueous environments.

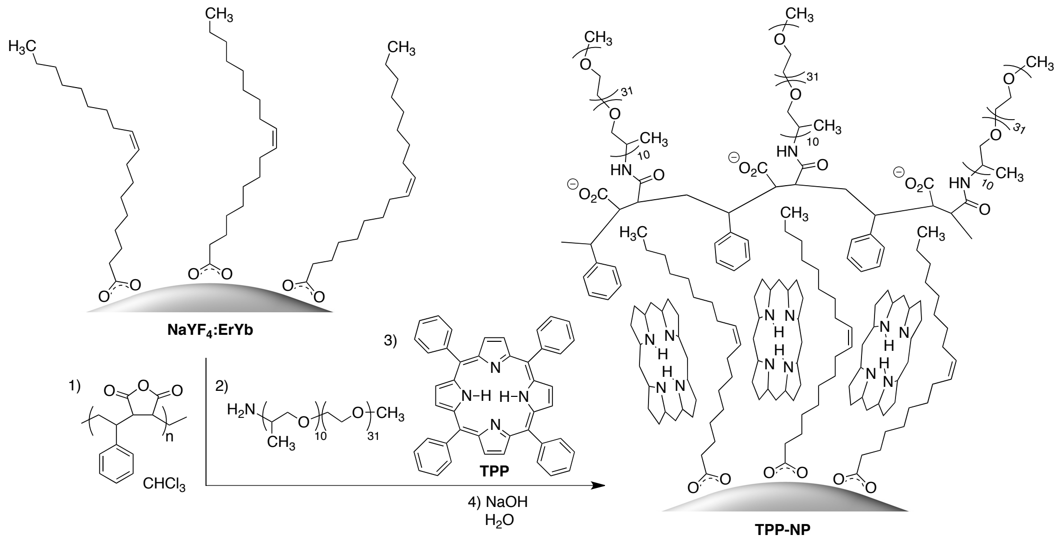
The use of amphiphilic polymers to coat upconverting nanoparticles is a relatively simple and versatile approach to synthesize water-dispersible nano-assemblies, and has been applied multiple times with different polymer structures.[21,22] If water-insoluble organic molecules are also present during the coating process, they end up embedded inside the hydrophobic regions of the polymer matrix in close proximity to the UCNPs.[23,24] We have recently used this one-pot method to produce stable, water-dispersible nano-assemblies containing hydrophobic UCNPs wrapped with organic amphiphilic polymers that also contain highly hydrophobic components.[25] Because the encapsulation method is carried out in one pot and takes advantage of a spontaneous self-assembly process, it represents a more universal way to disperse hydrophobic systems in water with no modifications to the chromophores and no ligand exchange on the nanoparticles. In this report, we describe how this method can be used to produce water-dispersible nano-assemblies containing both UCNPs energy-transfer donor and porphyrin acceptors.

Results and discussion

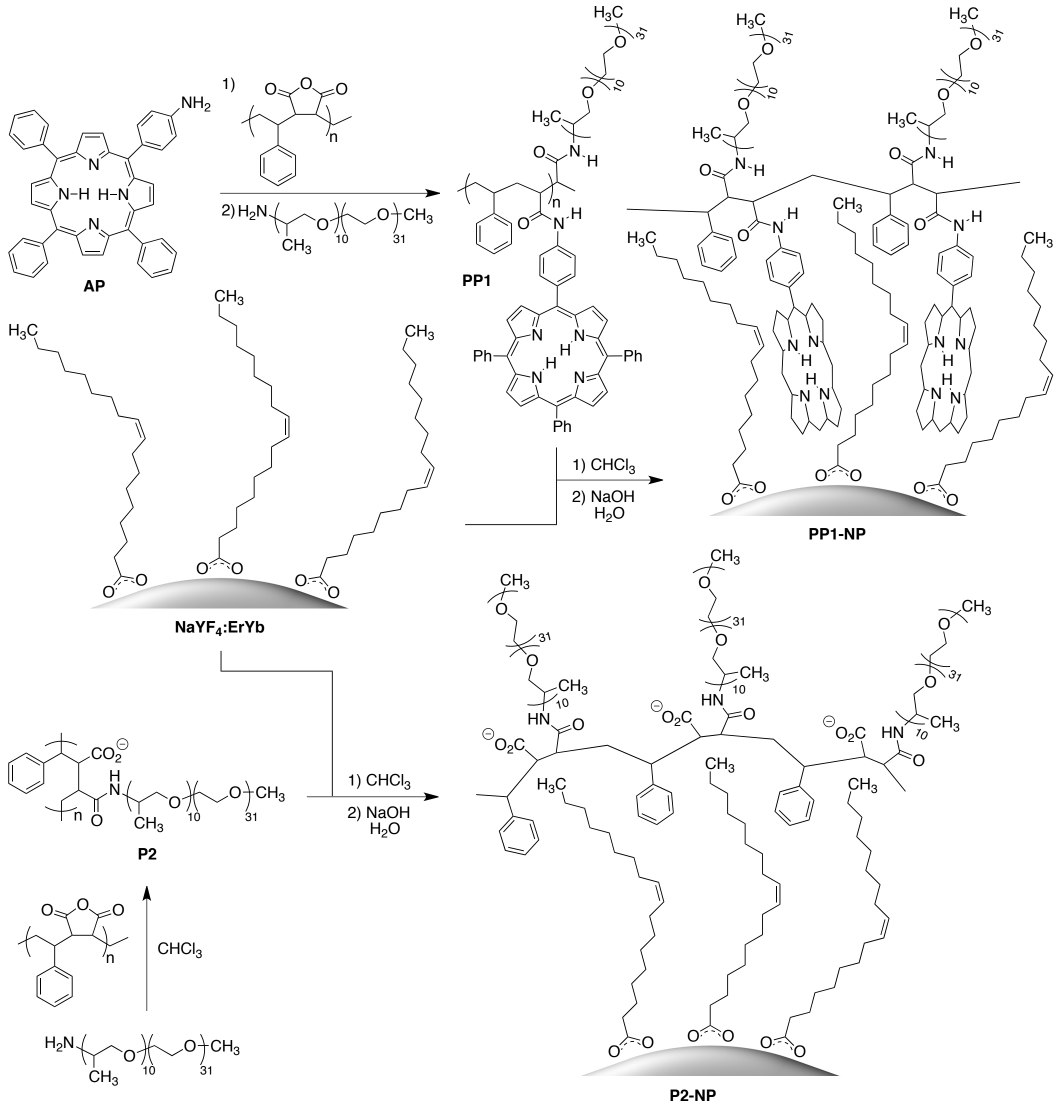
Synthetic procedures

The one-pot procedure is shown in Scheme 1 and involves treating a $CHCl_3$ dispersion of oleate-coated lanthanide-doped (2 mol% Er^{3+} and 20% Yb^{3+}) upconverting nanoparticles (**$NaYF_4$:ErYb**) with poly(styrene-co-maleic anhydride), ring-opening the anhydride groups with poly(propylene glycol)bis(2-aminopropyl ether), introducing the hydrophobic tetra-phenyl porphyrin (**TPP**) and replacing the organic solvent with basic water to drive the self-assembly process. The result is a water-soluble nano-assembly (**TPP-NP**) containing the UCNPs at the core, coated by a hydrophobic layer containing the trapped porphyrins, finally all wrapped in a polar shell. While this procedure was the most convenient, it produced nano-assemblies with a low loading of porphyrin chromophores (51 per nanoparticle).† The system was eventually modified to one where the porphyrin is covalently attached to the polymer as we have recently shown this method produces nano-assemblies with a higher loading of chromophore.[26] The only requirement for this modification is the chromophore possesses an amine functional group to link to the polymer.

The preparation of the nano-assembly containing the upconverting nanoparticles and the porphyrinic polymer is shown in Scheme 2 and starts by stirring 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**AP**) and the copolymer of styrene



Scheme 1 Preparation of nano-assembly **TPP-NP** by wrapping UCNPs with an amphiphilic polymer that traps tetra-phenyl porphyrin (**TPP**) within the hydrophobic shell.



Scheme 2 Preparation of nano-assemblies **PP1-NP** and **P2-NP** by wrapping UCNPs with appropriate amphiphilic polymers **PP1** and **P2**.

and maleic anhydride in $CHCl_3$ to partially ring-open some of the maleic anhydride groups and install the macrocycles. The resulting co-polymer was reacted with poly(propylene glycol)bis(2-aminopropyl ether) overnight at room temperature to ring-open the remaining maleic anhydride groups and generate the porphyrinic polymer (**PP1**), which was used without further purification. This in situ generated polymer was treated with a $CHCl_3$ dispersion of oleate-coated upconverting nanoparticles (**$NaYF_4$:ErYb**). Replacing the $CHCl_3$ solvent by water induces the encapsulation of the UCNPs by polymer **PP1** and generates the water-dispersed nanostructures (**PP1-NP**). A control nano-assembly without the porphyrin (**P2-NP**) was prepared using the same encapsulation protocol by wrapping **$NaYF_4$:ErYb** with polymer **P2**. This is also shown in Scheme 2.

Characterization of nano-assemblies

Size determination. The average diameter for the **PP1-NP** nanostructures is 22.6 ± 0.9 nm according to transmission electron microscopy (Fig. 1a), which only shows the inorganic nanoparticles located at the core of the assemblies. Dynamic light scattering (DLS) analysis suggests an average hydrodynamic size of 28.6 nm for the same structures (Fig. 2a). The difference in the size can be attributed to the fact that DLS estimates the size of the entire nano-assembly including the polymer shell. As expected, the size of the control nano-assembly (**P2-NP**) is the same when measured using TEM (23.7 ± 0.8 nm) since the same inorganic UCNPs were used to prepare both systems. Again, the size of **P2-NP** according to DLS is slightly larger than that measured using TEM. An estimation based on an idealized model where all polyether chains are fully extended suggests the thickness of the polymer shell is 10 nm. Because this is larger than the calculated polymer thickness based on the DLS measurements (~ 6 nm), it is reasonable to assume the polymer coating exists in a compressed form around the UCNPs.

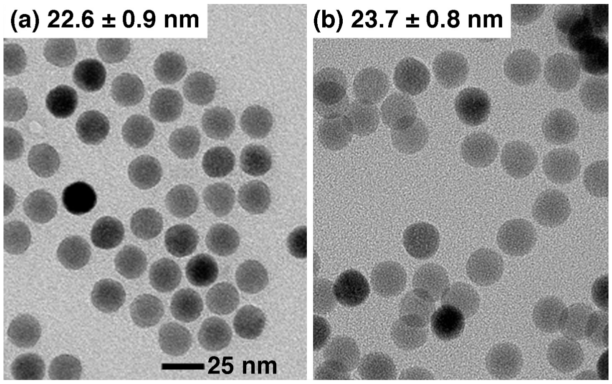


Fig. 1 TEM images of (a) the nano-assemblies containing the UCNPs wrapped with the porphyrinic polymer **PP1-NP** and (b) the control nano-assemblies that have no porphyrins **P2-NP**. The average size of the nanoparticle are shown.

Optical properties. UV-vis absorption spectroscopy of an aqueous solution (7.24 × 10–5 M)[§] of nano-assembly **PP1-NP** shows the characteristic Q bands between 450 nm and 700 nm for a porphyrin (Fig. 3a). These bands are very similar to those for a THF solution (1×10^{-5} M) of the amino porphyrin (**AP**) showing there is no difference between the ground states of the porphyrin within the nano-assembly or freely dissolved in an organic solvent. The difference in the baseline between the two spectra is due to scattering. Using these Q bands and assuming that the molar absorptivities of the porphyrins in **PP1-NP** are the same as those of the amino porphyrin **AP**, we estimate the loading of chromophores within the nano-assembly to be 435 macrocycles per nanostructure.[†]

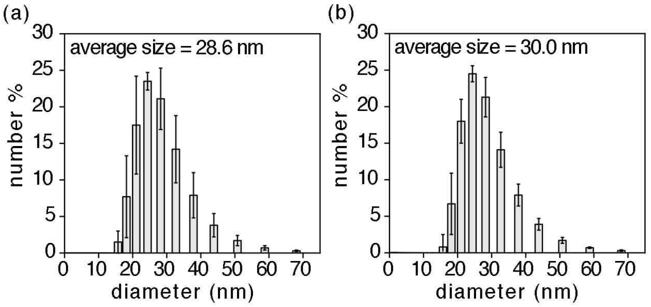


Fig. 2 DLS histograms for (a) the nano-assemblies containing the UCNPs wrapped with the porphyrinic polymer **PP1-NP** and (b) the control nano-assemblies that have no porphyrins **P2-NP**. The average size of the nanoparticles are shown.

Fig. 3a also shows the emission spectrum of the nano-assemblies (**PP1-NP**) when an aqueous solution of them is irradiated with NIR light (980 nm). As is typical for **$NaYF_4$:ErYb** nanoparticles,[14] two sets of relatively sharp bands are observed in the emission spectrum between 500 and 700 nm. The higher energy ‘green’ emissions (504–568 nm) correspond to the $[^2H_{11/2}, ^4S_{3/2}] \rightarrow ^4I_{15/2}$ transitions, while the lower energy ‘red’ emissions (627–684 nm) are a result of the $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions. Both emissions overlap with the absorption of the porphyrins, although the green emission has more significant overlap, which partially explains the differences in the emission spectra between the two nano-assemblies.

Both the green and red emission bands are observed for the nano-assembly lacking the porphyrins (**P2-NP**), albeit the green ones are substantially more intense than those for **PP1-NP** (Fig. 3b). The reduced green emission from the porphyrin-containing nano-assemblies can be attributed to quenching of the UCNPs by the porphyrins as the macrocycles absorb strongly in this region. The quenching is due to a combination of Föster Resonance Energy Transfer (FRET) as already suggested for a similar system[18] and emission-reabsorption.[25–27] In the former case, the UCNPs act as the donors and transfer their excited state energy to the porphyrin acceptors. In the latter case, the light emitted from UCNPs is absorbed by the macrocyclic chromophores encapsulated either in the same nano-assembly or in adjacent nano-assemblies.

The differences in the red emissions between the two nano-assemblies are more complex (Fig. 3c). On first glance, the emissions appear to be the same. But further inspection shows there are significant differences. While the emissions at wavelengths of maximum intensity are only slightly reduced in **PP1-NP** compared to **P2-NP**, the emissions on either side of these bands are increased (compare grey and white shaded areas in Fig. 3c). The fact that the red emissions from **PP1-NP** are not quenched as much as the green emissions is due to two facts: (1) The absorption band of porphyrin that overlaps with the red emission from the UCNPs (around 650 nm) is much less intense than the band that overlaps with the green emission. Therefore, the extent of both FRET and emission-reabsorption

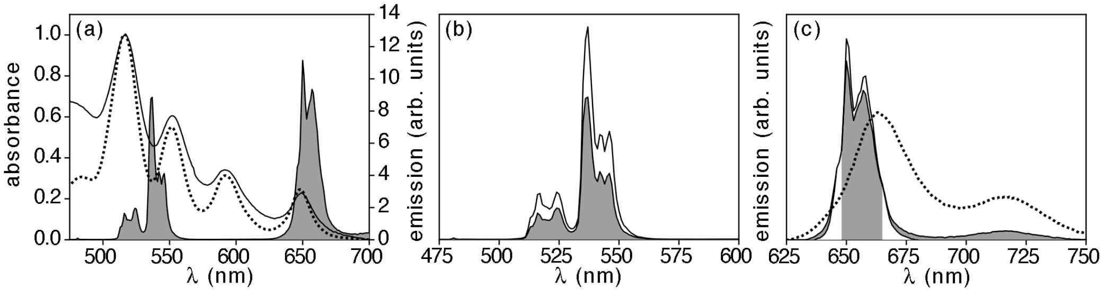


Fig. 3 (a) Selective UV-vis absorption spectra of an aqueous solution (7.24×10^{-5} M) of the nano-assemblies containing the UCNPs wrapped with the porphrinic polymer **b** (solid line), and a THF solution (1×10^{-5} M) of the amino porphyrin **AP** (dotted line), and the emission spectra of the same solution of **PP1-NP** (grey shaded area) when excited by 980 nm light. (b) Comparison of the green emissions for the aqueous solution of **PP1-NP** (grey shaded area) when excited by 980 nm light with an equivalent solution of control system **P2-NP** (white shaded area) when excited by 980 nm light. (c) Comparison of the red emissions for the aqueous solution of **PP1-NP** (grey shaded area) when excited by 980 nm light with an equivalent solution of control system **P2-NP** (white shaded area) when excited by 980 nm light and the amino porphyrin **AP** (dotted line) when excited by 550 nm light.

will be reduced for the red emission. (2) There are two additional emission bands appearing in region between 625 nm to 750 nm, which originate from the porphyrin. This second fact is demonstrated by comparing the emission spectrum of a THF solution of the amino porphyrin **AP** when it is irradiated with 550 nm as the excitation source (Fig. 3c). This excitation produces two emission bands from 625 nm to 690 nm and from 690 nm to 750 nm. The first explains why the red emissions from **PP1-NP** are not as reduced as much as expected and the increase in emission on either side of the major bands when the sample is excited with 980 nm light. The second emission can be observed as a new band in Fig. 3c. A similar, albeit very weak, band can be observed for the original tetra-phenyl porphyrin nano-assemblies (**TPP-NP**).[†]

The new emission band appearing between 700 nm and 750 nm in the emission spectrum of **PP1-NP** is not due to direct excitation of the porphyrin as this chromophore is transparent to 980 nm NIR light. The porphyrin is emitting from an excited state that is produced through energy transfer from the green emission of the UCNP donor to the macrocyclic acceptor.

Experimental

Materials and methods

General. All solvents and reagents used for synthesis, chromatography, UV-vis and fluorescence spectrophotometric measurements were purchased from Aldrich and used as received, unless otherwise noted. Solvents for NMR analysis were purchased from Cambridge Isotope Laboratories and used as received. Column chromatography was performed using silica gel 60 (230–400 mesh) from Silicycle Inc. The $NaYF_4$ nanoparticles co-doped with 2% Er^{3+} and 20% Yb^{3+} (**$NaYF_4$:ErYb**) were synthesized using a modification of a recently reported procedure.[28] 5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (**AP**) was synthesized as described in the literature.[29,30] Poly(propylene glycol)bis(2-aminopropyl ether) was received as a gift from Huntsman Inc. Cumene terminated poly(styrene-co-maleic anhydride) was purchased from Aldrich. PEG 2000 was purchased from Rapp Polymere GmbH Inc. All volumes for absorption, emission and concentration measurements/studies were measured out using an autopipette.

Optical Spectroscopy. UV-vis absorption spectroscopy was performed using a Varian Cary 300 Bio spectrophotometer. Fluorescence measurements were performed using a PTI Quantamaster spectrofluorometer. A JDSU 980 nm laser diode (device type L4-9897510-100M) coupled to a 105 um (core) fibre was employed as the excitation source. The output of the diode laser was collimated and directed on the samples using a Newport F-91-C1-T Multimode Fiber Coupler. The visible emissions were collected from the samples at π/2 from the incident beam in the plane of the spectrometer. All of the colloidal samples were held in a square quartz cuvette with an interior width 4 mm and length 10 mm (Starna Cells, Part # 9F/Q/10). All spectra were corrected for instrument sensitivity.

Transmission Electron Microscopy. (TEM). TEM images were obtained using a Tecnai Osiris Scanning Transmission Electron Microscope operating at 200 keV. For the nanoparticles dispersed in $CHCl_3$, a small amount of this dispersion was drop-cast on a carbon formvar-coated copper grid (400 mesh, Ted Pella, Part # 01754-F) and air-dried before imaging. The shape and size of the **$NaYF_4$:ErYb** nanoparticles were evaluated from the collected TEM images. The size of the nanoparticles was calculated from over 50 particles located at different areas of the TEM grid. For samples dispersed in water, dilute colloids of the nanoparticles dispersed in water (5 µL) were placed on thin, carbon formvar-coated copper grids held by anti-capillary tweezers (Ted Pella, Part # 501-4). Water was then slowly removed under reduced pressure in a vacuum desiccator.

Dynamic Light Scattering (DLS). DLS measurements were carried out using a Malvern Zetasizer Nano-ZS. The colloidal samples were held in a 10 mm path length plastic cuvette (BrandTech, Catalog # 759220). A nanoparticle concentration of ~0.4 mg/mL[£] was employed for the measurements. All DLS measurements were conducted at 25 °C.

Synthesis of the hybrid nano-system TTP-NP. A solution of cumene terminated poly(styrene-co-maleic anhydride) (25 mg, 0.016 mmol, M_n = 1700) was treated with a solution of poly(propylene glycol)bis(2-aminopropyl ether) (160 mg, 0.016 mmol, M_n = 2070) in $CHCl_3$ (1.0 mL) drop wise. After stirring for 8 h at room temperature, the reaction mixture was treated with a solution of the oleate-coated UCNPs (**$NaYF_4$:ErYb**) in $CHCl_3$ (250 µL, 43 mg/mL) and a stock solution of tetra-phenyl porphyrin TTP (4×10^{-7} mol). After stirring overnight at room temperature, the reaction mixture was evaporated to dryness using a rotary evaporator. The oily residue was treated with aqueous NaOH (3 mL, 0.001 M, pH 11), sonicated for 5 min and any trace amounts of $CHCl_3$ were carefully removed using a rotary evaporator to afford a clear aqueous solution. This solution was transferred using a pipette into two 1.5 mL conical centrifugation tubes and centrifuged at 20600 RCF for 25 min. The supernatant was removed from the pellets of nanoparticles using a pipette, and the pellets were re-dispersed in deionized water (1.5 mL for each sample) with the help of sonication. The tubes were centrifuged for 25 min at 20600 RCF and the supernatant was removed from the pellets of nanoparticles using a pipette. The nanoparticles were re-dispersed in deionized water (1.5 mL for each sample) with the help of sonication, the two samples were combined and passed through a 0.2 μm filter (Acrodisc® Syringe Filter) to obtain the final stock solution of encapsulated nanoparticles for further use.

Synthesis of hybrid nano-system PP1-NP. A solution of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin **AP** (1 mg, 0.002 mmol) in $CHCl_3$ (3 mL) was treated with cumene terminated poly(styrene-co-maleic anhydride) (25 mg, 0.016 mmol, M_n = 1700) at room temperature. After stirring overnight, the reaction mixture was treated with a solution of poly(propylene glycol)bis(2-aminopropyl ether) (160 mg, 0.016 mmol, M_n = 2070) in $CHCl_3$ (1.0 mL). After stirring for 8 h at room temperature, the reaction mixture was treated with a solution of the oleate-coated UCNPs (**$NaYF_4$:ErYb**) in $CHCl_3$ (250 μL, 43 mg/mL).[¶] After stirring overnight at room temperature, the reaction mixture was evaporated to dryness using a rotary evaporator. The oily residue was treated with aqueous NaOH (3 mL, 0.001 M, pH 11), sonicated for 5 min and any trace amounts of $CHCl_3$ were carefully removed using a rotary evaporator to afford a clear aqueous solution. This solution was transferred using a pipette into two 1.5 mL conical centrifugation tubes and centrifuged at 20600 RCF for 25 min. The supernatant was removed from the pellets of nanoparticles using a pipette, and the pellets were re-dispersed in deionized water (1.5 mL for each sample) with the help of sonication. The tubes were centrifuged for 25 min at 20600 RCF and the supernatant was removed from the pellets of nanoparticles using a pipette. The nanoparticles were re-dispersed in deionized water (1.5 mL for each sample) with the help of sonication, the two samples were combined and passed through a 0.2 μm filter (Acrodisc® Syringe Filter) to obtain the final stock solution of encapsulated nanoparticles for further use.

Synthesis of the control nano-system P2-NP. A solution of cumene terminated poly(styrene-co-maleic anhydride) (25 mg, 0.016 mmol, M_n = 1700) was treated with a solution of poly(propylene glycol)bis(2-aminopropyl ether) (160 mg, 0.016 mmol, M_n = 2070) in $CHCl_3$ (1.0 mL) drop wise. After stirring for 8 h at room temperature, the reaction mixture was treated with a solution of the oleate-coated UCNPs (**$NaYF_4$:ErYb**) in CHCl3 (250 μL, 43 mg/mL). After stirring overnight at room temperature, the reaction mixture was evaporated to dryness using a rotary evaporator. The oily residue was treated with aqueous NaOH (3 mL, 0.001 M, pH 11), sonicated for 5 min and any trace amounts of $CHCl_3$ were carefully removed using a rotary evaporator to afford a clear aqueous solution. This solution was transferred using a pipette into two 1.5 mL conical centrifugation tubes and centrifuged at 20600 RCF for 25 min. The supernatant was removed from the pellets of nanoparticles using a pipette, and the pellets were re-dispersed in deionized water (1.5 mL for each sample) with the help of sonication. The tubes were centrifuged for 25 min at 20600 RCF and the supernatant was removed from the pellets of nanoparticles using a pipette. The nanoparticles were re-dispersed in deionized water (1.5 mL for each sample) with the help of sonication, the two samples were combined and passed through a 0.2 μm filter (Acrodisc® Syringe Filter) to obtain the final stock solution of encapsulated nanoparticles for further use.

Conclusions

We have successfully demonstrated how to fabricate water-dispersible nano-assemblies by encapsulating upconverting nanoparticles (UCNPs) and porphyrin molecules into one nanostructure using amphiphilic polymer shell. We conclude that there are optical interactions between UCNPs and porphyrin molecules based on the observations that (1) the intensity of the ‘green emission’ band of the nano-assembly is reduced due to FRET and emission-reabsorption effects, and (2) the porphyrin chromophores in the nano-assembly also exhibit fluoresce as a result of absorbing the ‘green emission band’ of UCNPs generated upon irradiation with 980 nm light. We anticipate these conveniently prepared water-dispersible nano-assemblies containing UCNPs and porphyrin molecules will have potential applications in photodynamic therapy and as optical probes.

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Notes and references

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† See Supporting Information for details.

§ This concentration is determined from UV-vis spectrum of **PP1-NP** based on the assumption that the molar absorption coefficient of the amino porphyrin **AP** is the same as those of the porphyrins in the **PP1-NP**.

£ This is an estimated value based on assumption that all the nanoparticles were transferred from the organic solution to the aqueous solution after the encapsulation process.

¶ This value was calculated based on the volume and mass of air-dried aliquots sample of the original UCNPs in $CHCl_3$ solution.

Electronic Supplementary Information (ESI) available: Calculations for the loading of porphyrin chromophores in nano-assemblies **TPP-NP** and **P1-NP** and optical characteristics of **TPP-NP**. See DOI: 10.1039/b000000x/

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