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Remote-Control Photoswitching Using NIR Light

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The use of dithienylethene (DTE) photoswitches to achieve spatial and temporal control of molecular processes and optoelectronic properties has received significant attention in recent years.¹ This attention is well deserved and due to the fact that the photoswitches can be toggled back and forth between two structurally and electronically different isomers (Scheme 1) having properties that can be fine-tuned by decorating the molecular backbone with functional groups so they can be applied to a wide range of technologies, from optical data storage and processing² to photo-release³ and photodynamic therapy.⁴

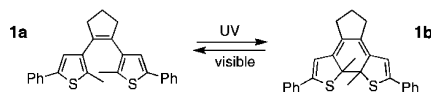
One of the major drawbacks of these versatile photoresponsive systems is the need for ultraviolet and visible light to induce the ring-closing and ring-opening reactions, respectively. Both types of light are associated with detrimental effects such as inducing unwanted side reactions and low penetration into biological tissue.⁵ More practical systems are those that undergo multiphoton processes in the near-infrared (NIR) region of the spectrum where the probability of inducing chemical reactions is reduced and 3D control can be achieved (a key to photodynamic therapy and volumetric data storage applications).⁶ Because photochromic compounds often have low two-photon-absorbing cross sections,⁶ a better alternative is to induce the DTE reactions in a “remote control” process by using antennae species that absorb NIR light and transfer the harnessed energy to the photoswitch.

Photon upconverting nanoparticles (UCNPs), in particular hexagonal NaYF₄ nanocrystals doped with lanthanide ions, are ideal for “remote control” photoswitching.⁷ (1) They efficiently absorb NIR light and convert it to wavelengths that can be used to trigger appropriate DTE photoswitches. (2) The key electronic excitations occur in real energy levels, requiring significantly lower intensities of light than conventional two-photon absorbing dyes. (3) They do not suffer from photobleaching. (4) They can be coated with biocompatible polymers and antibodies to decrease toxicity, prolong circulation time, and increase tissue selectivity, rendering them particularly useful in biomedical applications.⁸

In this paper, we demonstrate how DTE photoswitches undergo their ring-closing and ring-opening reactions using NIR light in the presence of two types of UCNPs that emit UV and visible light. In a preliminary study, we also illustrate the concept of “remote control” photorelease using the DTE architecture. A recent publication⁹ describes the use of UCNPs and a DTE for optical memory applications. Although effective quenching of the UCNP emission by one of the DTE isomers was achieved, “remote control” switching was not demonstrated, likely due to the use of the less-efficient upconverting LaF₃ nanoparticles, a lower laser power, and/or the occurrence of an energy-transfer process, which produces a state with different properties from our case.

We chose to use NaYF₄ nanoparticles because they are some of the best UCNPs known to date, and depending on their composition

Scheme 1



they can emit ultraviolet, violet, blue, green, and red light upon absorbing NIR (980 nm) light. The “remote control” switching of DTE **1** by UCNPs NaYF₄ doped with 0.5 mol % Tm³⁺ and 30 mol % Yb³⁺ (NaYF₄:TmYb) and NaYF₄ doped with 2 mol % Er³⁺ and 20 mol % Yb³⁺ (NaYF₄:ErYb) is the focus of our studies. The ring-open isomer (**1a**) absorbs UV light,¹⁰ which induces ring closing to form **1b**. This light can be generated when a dispersion of the UV-emitting NaYF₄:TmYb nanoparticles absorb NIR light. The ring-opening reaction (**1b** → **1a**) is triggered by visible light, which can be produced by a dispersion of the green-emitting NaYF₄:ErYb.

DTE **1a** and both UCNPs are prepared according to literature procedures.¹⁰ TEM images of the UCNPs demonstrate their nearly monodisperse particle size (Figure 1a and 1b) of 25.3 ± 1.4 and 25.6 ± 1.3 nm for NaYF₄:TmYb and NaYF₄:ErYb, respectively. Powder X-ray diffraction¹⁰ confirms that the synthesized particles are hexagonal in phase with no significant impurity phases present. The well-defined peaks of the X-ray pattern demonstrate the high crystallinity of the doped NPs, and a crystallite size of ~23 nm can be determined for

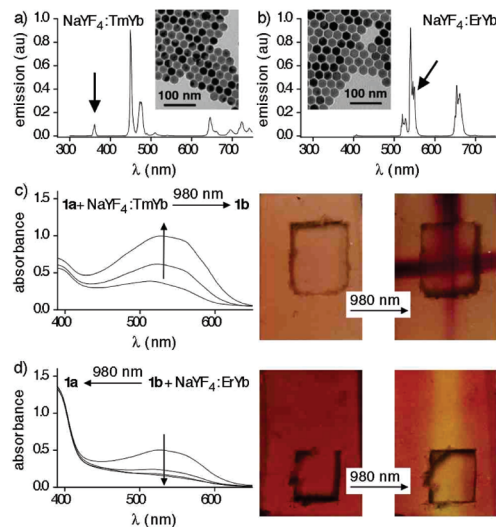


Figure 1. Emission spectra of colloidal CHCl₃ solutions of (a) NaYF₄:TmYb and (b) NaYF₄:ErYb UCNPs when excited with a 980 nm laser diode.¹¹ The light used to trigger photoswitch **1** is highlighted. TEM images are shown as insets. Changes in the UV–vis absorption spectra (left) and cropped photographs (right) of acrylic films (12 × 8 × 1 mm) containing (c) **1a** + NaYF₄:TmYb, and (d) **1b** + NaYF₄:ErYb as they are irradiated with 980 nm light. The stripes observed in the right panel of (c) and (d) correspond to the direction of the beam of the 980 nm laser.¹⁰ The irradiation in (c) was carried out two times with perpendicular orientations. The small squares in all images are the cut-out holes in the sample holder through which the absorbance was measured.

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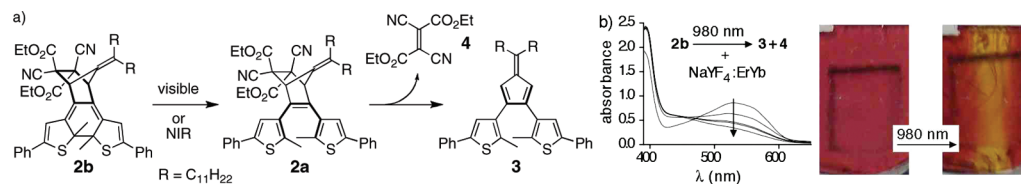


Figure 2. (a) Scheme illustrating the ring-opening and release reactions of bicyclic compound **2b** as it is irradiated with visible or NIR light. (b) Changes in the UV-vis absorption spectra (left) and cropped photographs (right) of an acrylate film ($8 \times 7 \times 1$ mm) containing **2b** + NaYF₄:ErYb as it is irradiated with 980 nm light. The stripe observed in the right panel corresponds to the direction of the beam of the 980 nm laser.

both types of UCNPs from the line broadening of the diffraction peaks, which correlate well to the TEM data.

DTE **1a** absorbs UV light (365 nm) and undergoes efficient conversion to its ring-closed counterpart (**1b**) as illustrated by the changes in the UV-vis absorption spectrum¹⁰ and the visual color change of a CH₃CN solution from colorless to red. Visible light (>450 nm) triggers the reverse reaction and regenerates the original spectrum. These wavelengths correspond to those emitted by the UCNPs, which have upconversion emission spectra that match those reported previously.⁷ Of the five emissions observed for NaYF₄:TmYb ranging from ultraviolet to near-infrared (Figure 1a), the highest energy emission is appropriate for photocyclization (**1a** → **1b**). In the case of NaYF₄:ErYb, violet, green, and red emissions are observed (Figures 1b), with the second one appropriate to induce ring opening (**1b** → **1a**).¹²

To ensure that the UCNPs and DTE remain in close enough proximity to promote reabsorption of the light emitted from the nanocrystals by the organic chromophore, we chose to demonstrate “remote control” switching by casting both components in a polymer composite material comprised of cross-linked poly(ethylene glycol)dimethacrylate and toluene, which provides a flexible environment for the photoreactions of **1**.¹³

When a pale yellow film containing **1a** and an excess of NaYF₄:TmYb is irradiated with 980 nm diode laser light, the film only changes to a red color along the path of the beam of light (Figure 1c), which can be attributed to the photocyclization reaction (**1a** → **1b**). This reaction is supported by the changes in the absorption spectrum, which match those for a sample of **1a** irradiated with UV light.¹⁰ Similarly, a film containing **1b** and NaYF₄:ErYb undergoes decolorization only along the path of the light (Figure 1d). The ring-opening reaction (**1b** → **1a**) is also supported by spectral changes that match those for a sample of **1b** irradiated with visible light. The fact that the reactions of the DTE chromophore are triggered by absorbing the light generated by the UCNPs is demonstrated by irradiating a film containing **1b** but no NaYF₄:ErYb, which undergoes almost no change in its color or its UV-vis spectrum (see Figure S5 in the Supporting Information).

We recently demonstrated how visible light could be used to trigger the release of a small molecule from a DTE derivative by inducing the ring-opening reaction of a “locked” species.³ The process is based on the creation of an unstable ring-open compound that spontaneously undergoes a reverse Diels–Alder reaction to generate a fulvene and a dienophile as illustrated by analogous compounds shown in Figure 2a. We now demonstrate that we can trigger the release using NIR light and UCNPs.

Dithienylfulvene **3** is synthesized using our original methods with some minor modifications.¹⁰ The ring-closed Diels–Alder product (**2b**) is produced as a mixture of four stereoisomers after treating **3** with an excess of diethyl dicyanofumarate and exposing the unstable intermediate (**2a**) to UV light. When an acrylate film containing **2b** and NaYF₄:ErYb is exposed to 980 nm light in an analogous manner as for **1b**, similar color changes can be observed

(Figure 2b) showing that “remote control” switching also operates in this system. When probed using UV-vis absorption spectroscopy, in addition to the decrease in the absorption band at 550 nm, which signifies ring opening (**2b** → **2a**), an increase in an absorption band at 400 nm is observed. This increase can be attributed to the appearance of dithienylfulvene **3** through the spontaneous release from **2a**. Irradiation of this film with 365 nm light results in no observable spectral changes supporting the success of the release even in the relatively solid matrix since any remaining ring-open isomer would be converted back to its ring-closed counterpart (**2b**).

Our demonstration of “remote control” switching using the versatile DTE architecture and upconverting doped nanocrystals offers new opportunities in photodynamic therapy and 3D data storage. In these studies we have demonstrated that either ring-closing or ring-opening reactions can be triggered by the judicious choice of organic chromophore and UCNP.

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Supporting Information Available: Synthesis and characterizations of chromophores and UCNPs, switching in solid-state forms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) See Supporting Information for details.
- (11) The transitions responsible for the luminescence are given in the Supporting Information.
- (12) The inset of Figure S3b in the Supporting Information shows a digital photograph of the total upconversion luminescence of a dispersion of NaYF₄:ErYb when stimulated with a 980 nm diode laser.
- (13) See Figure S4 in the Supporting Information. Other solid-state versions (bulk gels and solvent-free films) of the composite material were prepared and exhibit similar photochemistry as shown in Figure S6.

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