

## Supporting information

# *NIR-triggered photooxygenation of $\alpha$ -terpinene with upconversion nanohybrids*

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## Index

Materials and methods .....	2
Fig. S1 TEM image of UC@OA .....	6
Fig. S2 Thermogravimetric analyses of UC@OA, UC@RB and RB .....	6
Fig. S3 Emission spectra ( $\lambda_{\text{exc}} = 522 \text{ nm}$ ) of UC@RB2 .....	7
Fig. S4 Kinetic profiles of UC@RB nanohybrids ( $\lambda_{\text{exc}} = 560 \text{ nm}$ , $\lambda_{\text{em}} = 580 \text{ nm}$ ) .....	7
Table S1 RB emission lifetimes in UC@RB nanohybrids ( $\lambda_{\text{exc}} = 560 \text{ nm}$ , $\lambda_{\text{em}} = 580 \text{ nm}$ ) .....	7
Fig. S5 UC quenching efficiency.....	8
Fig. S6 Emission kinetic profiles of UC@RB NHs ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ) .....	8
Table S2 Emission lifetimes of UC@RB NHs ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ) .....	9
Fig. S7 Emission lifetimes plots of UC@RB NHs ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ).....	9
Fig. S8 UCQY .....	9
Fig. S9 Transient absorption spectra of UC@RB NHs and RB.....	10
Table S3 Transient absorption kinetics of UC@RB NHs and RB .....	10
Fig. S10 <sup>3</sup> RB phosphorescence .....	10
Fig. S11 Kinetic profiles of UC@RB ( $\lambda_{\text{exc}} = 560 \text{ nm}$ , $\lambda_{\text{em}} = 980 \text{ nm}$ ) .....	11
Table S4 Emission lifetimes of UC@RB ( $\lambda_{\text{exc}} = 560 \text{ nm}$ , $\lambda_{\text{em}} = 750 \text{ nm}$ ) .....	11
Fig. S12 Laser-induced emission spectra of UC@RB NHs and RB.....	11
Fig. S13 Emission lifetimes of UC@RB in the NIR ( $\lambda_{\text{exc}} = 560 \text{ nm}$ ) .....	12
Fig. S14 Kinetic profiles of UC@RB ( $\lambda_{\text{exc}} = 560 \text{ nm}$ , $\lambda_{\text{em}} = 980 \text{ nm}$ ) .....	12
Table S5 Emission lifetimes of UC@RB ( $\lambda_{\text{exc}} = 560 \text{ nm}$ , $\lambda_{\text{em}} = 980 \text{ nm}$ ) .....	13
Fig. S15 Kinetic profiles of UC@RB ( $\lambda_{\text{exc}} = 560 \text{ nm}$ , $\lambda_{\text{em}} = 1525 \text{ nm}$ ) .....	13
Table S6 Emission lifetimes ( $\lambda_{\text{exc}} = 560 \text{ nm}$ , $\lambda_{\text{em}} = 1525 \text{ nm}$ ).....	13
Fig. S16 ABDA emission spectra .....	14
Table S7 Kinetic rate constants of ABDA photoconsumption. ....	14
Fig. S17 Ascaridole conversion (%) with the reaction time. ....	14
Fig. S18 Absorption spectra of UC@RB, UC-RB, and supernatant .....	15
<sup>1</sup> H-NMR characterization .....	15
Calculation of the yield of photoproducts .....	15
Fig. S19 <sup>1</sup> H-NMR spectrum of photooxidation of $\alpha$ -terpinene .....	15
References .....	15

## Materials and methods

### Materials

The reactants for the synthesis of oleate-capped UCNPs were:  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  (AlfaAesar, 99.99 %),  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  (Acros Organics, 99.99 %), and  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$  (Sigma Aldrich, 99.9%), 1-octadecene (Alfa Aesar, 90%), oleic acid (Alfa Aesar, 90%), NaOH granules (Scharlau),  $\text{NH}_4\text{F}$  (Sigma Aldrich, 99.99%). Sodium salt of Rose Bengal (RB), 2-aminoethyl dihydrogen phosphate (AEP) (Sigma Aldrich), 6-bromohexanoic acid (Sigma Aldrich, 97%), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) (Sigma Aldrich,  $\geq 98\%$ ), N-hydroxysulfosuccinimide sodium salt (NHS), (Sigma Aldrich,  $\geq 98\%$ ), and the disodium salt of 9,10-anthracenediyl-bis(methylene)dimalonic acid (ABDA) were purchased from Sigma-Aldrich. The solvents used in this work are: *N,N*-Dimethylformamide  $\geq 99\%$  (DMF, Laboratory reagent grade, Fisher Scientific), chloroform  $\geq 99\%$  ( $\text{CHCl}_3$ , Laboratory reagent grade, Fisher Scientific), dimethyl sulfoxide (DMSO, reagent grade ACS, Schalarb), ethanol absolute (Essent Q<sup>®</sup>, Scharlab), acetonitrile  $\geq 99,5\%$  (ACN, reagent grade ACS, Thermo Scientific Chemicals), and  $\text{DMF-}d_7$  (99,50% D, Eurisotop). All the products and solvents were used as received without further purification.

$\alpha$ -terpinene (Thermo Scientific Chemicals,  $>90\%$ ) was previously purified by column chromatography on Merck silica gel 60 (230-400 mesh) with *n*-hexane as eluent to obtain  $>97\%$  purity. The separation was monitored using TLC on silica gel plated aluminium sheets and  $\text{KMnO}_4$  basic solution was used for detection.

### Methods

#### **Synthesis of oleate-coated $\beta\text{-NaYF}_4\text{:Yb}^{3+}$ (20%), $\text{Er}^{3+}$ (2%) UCNPs (UC@OA)**

UC@OA were synthesized following a previously reported protocol<sup>1</sup> with some modifications. 15 mL of 1-octadecene were combined with 8 mL of oleic acid in a round-bottom flask. Then, 2 mL of a solution containing 1 mmol of lanthanides (comprising 0.78 mmol  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.20 mmol  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ , and 0.02 mmol  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ ) in MeOH was added and the mixture was kept under  $\text{N}_2$  atmosphere and continuous stirring. The reaction mixture was heated to  $160^\circ\text{C}$  until dissolution of the salts. Then, the solution was cooled down to  $60^\circ\text{C}$  and a methanolic solution containing NaOH (2.5 mmol) and  $\text{NH}_4\text{F}$  (4 mmol) was added at once. After MeOH evaporation by heating the solution at  $125^\circ\text{C}$ , the reaction temperature was rapidly raised and kept for 1.5 hours. The mixture was allowed to cool to room temperature. The UCNPs were recovered by centrifugation of the reaction mixture at 7000 g for 7 minutes. Then, the white pellet was purified by redispersion in various solvents followed by centrifugation (7000 g, 7 min). First, the pellet was washed three times with a mixture of chloroform:ethanol (1:3) and then three times with a mixture of cyclohexane:acetone (1:3). Finally, the precipitate was redispersed in 3 mL of cyclohexane and centrifuge at 1000 g for 2 minutes, retaining the supernatant in order to discard any large UCNP agglomerate.

#### **Synthesis of $\text{BF}_4^-$ stabilized UCNPs**

The removal of oleate ligands from the UCNP surface was achieved by using a previously described procedure.<sup>2</sup> Briefly, DMF was added in the same ratio as the desired amount of UC@OA dispersion in cyclohexane. Solid  $\text{NOBF}_4$  was added in an amount slightly higher than that of UCNP in the initial dispersion. The reaction was vigorously shaken and kept under stirring for 2 hours at  $40^\circ\text{C}$ . After that, the DMF phase was isolated, and an excess of chloroform was added. The mixture was centrifuged at 7000 g for 7 minutes. Two washing steps were performed by redispersing the precipitate in a small amount of DMF followed by the addition of an excess

chloroform, and centrifuging (10000 g, 10 min). Finally, the transparent precipitate was redispersed in 5 mL of DMF.

#### **Synthesis of amino-functionalized UCNPs**

The UCNP surface was modified with 2-aminoethyl dihydrogen phosphate (AEP) following a slightly modified reported protocol.<sup>3</sup> Firstly, 10 mL of a solution of AEP (200 mg) in milli-Q water and ethanol in a 3:2 ratio was prepared. Then, 20 mg of UC@BF<sub>4</sub> in DMF (113  $\mu$ L) was slowly added under vigorous stirring. The mixture was stirred for 48 h at room temperature. The UC@AEP nanohybrids were isolated by centrifugation (10000 g, 10 minutes) and redispersed in 5 mL of milli-Q water.

#### **Synthesis of covalently linked UC-RB nanohybrids**

For the covalent modification of UCNPs with RB, the RB hexanoic acid ester (RB-HA) was first synthesized by reacting RB and 6-bromohexanoic acid as previously described.<sup>4</sup> After that, a mixture containing 7.8 mg of RB-HA, 20 mg of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), and 20 mg of N-hydroxysulfosuccinimide sodium salt (NHS) in 5 mL DMF was stirred at room temperature for 2 h.<sup>5</sup> Subsequently, 10 mg of UC@AEP (2 mL) in water were added and vigorously stirred during 24 h. The reaction mixture was centrifuged (10000 g, 10 minutes) and the obtained pellet was washed with 2 mL of water followed by centrifugation (10000 g, 10 minutes). Then, 3 cycles of washing with 2 mL of DMSO and centrifugation (7000 g, 7 minutes) to remove the free RB-HA. Finally, the resultant UC-RB nanohybrids were redispersed in 2 mL of DMF.

#### **Selection of DMF as solvent**

DMF as solvent ensures the dispersibility of UC@RBn NHs<sup>6</sup> and facilitates the analysis of the reaction mixture. Three aprotic polar solvents were tested for singlet oxygen generation (ACN, DMF and DMSO). Among them, DMF was selected even if it ranks as hazardous<sup>7</sup> because DMSO generated additional radical reactions and ACN afforded lower conversion and lower selectivity towards ascaridole than DMF.

Ethanol was also evaluated as solvent for ABDA photocomsumption because it would have been a greener option.<sup>7</sup> However, the UC@RBn NHs did not remained dispersed for 8 h to perform the photocatalytic reaction.

#### **NIR-irradiation set up for photocatalytic reactions and ABDA photocomsumption**

An AB2 series spectrofluorometer equipped with a 5W NIR laser diode with an excitation wavelength of 980 nm, was utilized. The laser beam was focused onto the cuvette using a collimator lens, achieving a power density of 308 W/cm<sup>2</sup>. To ensure a consistent temperature during irradiation, the setup included a cooling system to maintain the sample holder at a stable temperature.

#### **Absorption spectroscopy**

Attenuation/absorption spectra were recorded with a Perkin Elmer Lambda 1050 UV-vis-NIR spectrophotometer using quartz cuvettes (10 x 10 mm). The absorption spectra of UC@RB nanohybrids in DMF (1 mg·mL<sup>-1</sup>) were registered from 250 to 2000 nm using a step size of 2 nm. The obtained spectra were corrected by subtraction of an artificial scattering baseline as described previously.<sup>6</sup>

### ***Steady-state (SS) photoluminescence***

SS photoluminescence spectra were registered using nanohybrids dispersions in DMF (1 cm light-path quartz cuvettes) on an FLS1000 spectrophotometer (Edinburgh Instruments). For UC measurements, a 980 nm CW laser (2W, PSU-III-LED, CNI Optoelectronics Technology Co. Ltd.) was used to irradiate 1 mg·mL<sup>-1</sup> dispersions. For RB signals recording, samples with an absorption of 560 nm of 0.1 were prepared and excited with a Xe arc lamp (150 W). A PMT-980 photomultiplier (Edinburgh Instruments) was used to detect emissions in the visible (excitation and emission bandwidth of 1 nm). For the phosphorescence acquisition, a 645 nm long pass filter was placed in the detection path. For the obtention of the NIR emission signals exciting with the Xe lamp, nanohybrids dispersions of 5 mg·mL<sup>-1</sup> in DMF were prepared, a standard 645 nm long pass filter was placed in the detection path, and a PMT 1700 H10330C-75 photomultiplier (Hamamatsu Photonics, K.K.) was used (excitation and emission bandwidth of 10 nm). To achieve a nitrogen atmosphere, a sealed cuvette containing the solution to be measured was bubbled with a nitrogen flow for at least 10 minutes.

### ***Time-resolved (TR) photoluminescence***

TR emission spectra were recorded also in 10 x 10 mm quartz cuvettes on the FLS1000 photoluminescence spectrometer (Edinburgh Instruments). Different configurations were used as detailed below.

For the acquisition of the kinetic profiles at 580 nm, a nanosecond supercontinuous pulsed laser (SuperK Extreme EXU-6, NKT Photonics) at a frequency of 5.5 MHz was used to excite the samples at 560 nm (excitation bandwidth: 1 nm). The signals were registered using a visible photomultiplier (MCP-900, Edinburgh Instruments; emission bandwidth: 2 nm). The dispersions were prepared in DMF adjusting to 0.1 the absorbance at 560 nm.

For the collection of the TR phosphorescence ( $\lambda_{em}=750$  nm) and NIR emissions ( $\lambda_{em}=980$  nm and  $\lambda_{em}=1525$  nm) spectra, we employed a microsecond Xe 60 W flash lamp ( $\mu$ F2, Edinburgh Instruments) operating at a frequency of 100 Hz and with an excitation bandwidth of 7 nm. A standard 645 nm long pass filter was placed in the detection path and an emission bandwidth of 7 nm was set up. We used a visible photomultiplier (PMT-980, Edinburgh Instruments) and a sensitive NIR photomultiplier (PMT 1700 – H10330C-75, Hamamatsu Photonics, K.K.) for visible and NIR emissions, respectively. The nanohybrids samples were prepared in DMF at a concentration of 5 mg·mL<sup>-1</sup>.

UC kinetic profiles were registered upon excitation with a continuous wave laser 980 nm coupled with a pulsed variable electronic laser controller (pulse width: 100  $\mu$ s; PM2 box, Edinburgh Instruments). A visible photomultiplier (PMT-980, Edinburgh Instruments) was used to collect the signals with an excitation bandwidth of 7 nm. 1 mg·mL<sup>-1</sup> dispersions in DMF were used.

To get a nitrogen atmosphere, a sealed cuvette containing the solution to be measured was bubbled with a nitrogen flow for at least 10 minutes. The fitting of kinetics curves was done using Fluoracle software.

### ***Quantum yield (QY) and upconversion quantum yield (UCQY)***

Absolute quantum yield measurements were conducted in sealed-tube quartz cuvettes with a 1 cm optical path length and using a Quantaury QY Plus (C13534-11, Hamamatsu Photonics K.K.) equipped with a NIR photoluminescence measurement unit (C13684-01, Hamamatsu Photonics K.K.). Two excitation sources were employed: the integrated Xe lamp and a 980 nm continuous wave laser (2.5 W, MDL-III-980, CNI Optoelectronics Technology Co. Ltd.). For UCQY, the laser power was adjusted utilizing a variable neutral density disk. Excitation irradiance was

determined based on the laser spot size provided by the manufacturer and the measured laser power using a power meter (PD300-3W, Ophir Optronics Solutions Ltd.) within the integration sphere.

#### ***Transient absorption spectroscopy (TAS)***

TAS measurements were performed in 1 cm septum-stoppered quartz cuvettes (standard cross-beam geometry) on a laser flash photolysis spectrometer (LP980-KS, Edinburgh Instruments). The spectrometer was equipped with a Quanta-Ray INDI Nd:YAG laser (Spectra Physics) featuring a parametric optical oscillator (primoScan BB, Spectra Physics). The laser output power was set at 3 mJ. Spectral measurements were recorded using an ICCD camera (Andor DH320T) with an integration time of 500 ns (gate width) relative to the specified delay of the laser pulse (pump), alongside a 150W Xe pulsed lamp. Kinetic measurements were obtained with a photomultiplier detector and the pulsed Xe lamp. Kinetic fittings were made with L900 software (Edinburgh Instruments). Solutions/dispersions of RB and UC@RB in DMF were prepared with an absorbance of 0.28 at 560 nm.

#### ***Laser-induced fluorescence***

Emission measurements of spectral transient species were performed in septum-stoppered 1 cm quartz cuvettes with a standard sample holder, within the same laser flash photolysis spectrometer but with the Xe lamp turned off. The ICCD camera (Andor DH320T) was used as a detector, integrating over 100  $\mu$ s (gate width) for the specified delay of the laser pulse.

#### ***Transmission Electron Microscopy (TEM)***

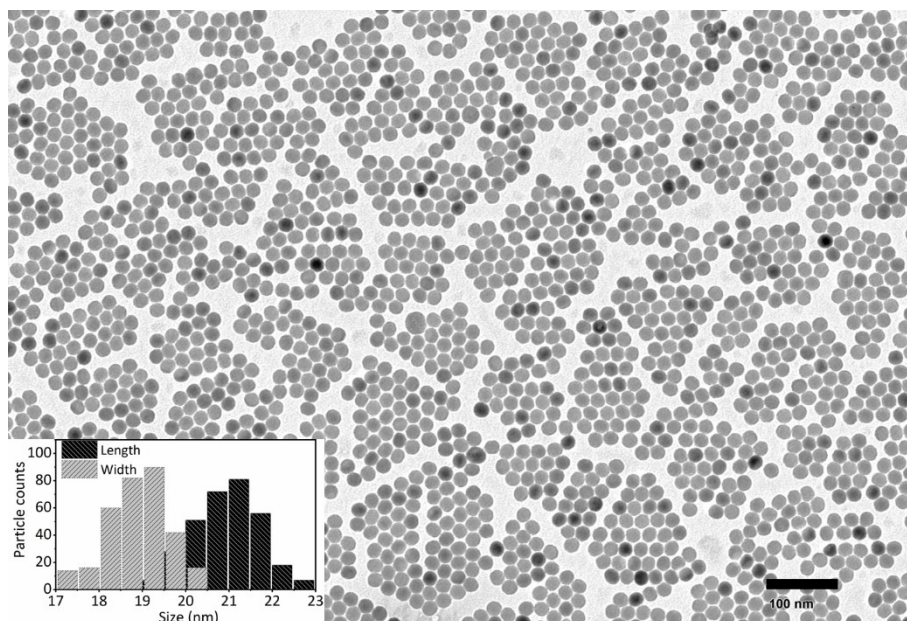
TEM images were recorded using a high contrast JEOL jem 1010 transmission electron microscope operating at 100 kV equipped with an 8 Mpx digital camera AMT RX80. The samples were prepared by deposition of the UC@OA dispersion in cyclohexane (10  $\mu$ L, 0.5 mg/mL) on a formvar/carbon film supported on a 300-mesh copper grid.

#### ***NMR spectroscopy***

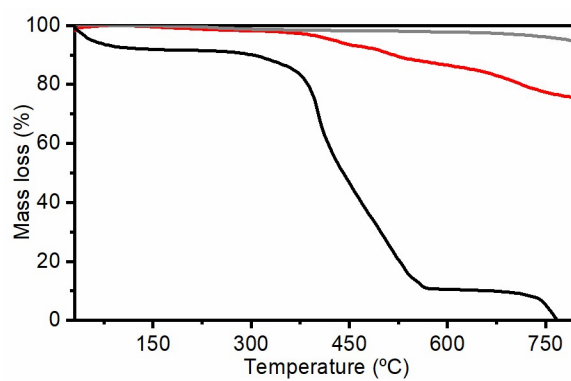
$^1$ H-NMR spectroscopy was performed on a 500 MHz Bruker instrument. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to TMS ( $\delta = ^1\text{H} = 0.0$  ppm). The chemical shift range for each spectrum was calibrated using the residual solvent signals as an internal reference at  $\delta$  8.03 for the  $^1\text{H}$  spectrum. Abbreviations used in the NMR experiments are: s, singlet; d, doublet; q, quartet; m, multiplet. Coupling constants are in Hz.

#### ***Thermogravimetric analysis (TGA)***

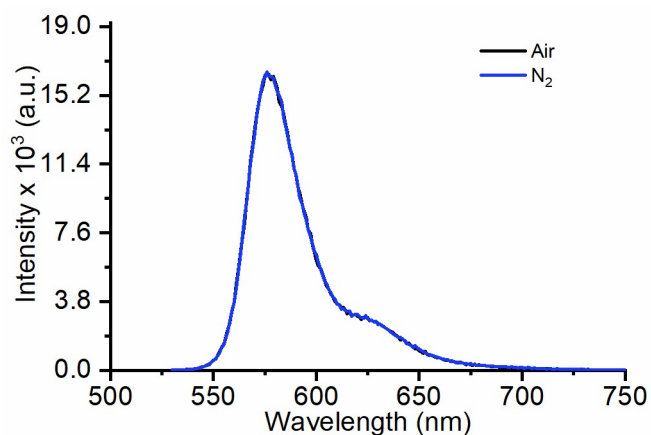
TGA analyses were conducted using a TGA 550 instrument from TA Instruments, operating under a nitrogen atmosphere within a temperature ranging from 25 to 950  $^{\circ}\text{C}$  and a heating rate of 10  $^{\circ}\text{C}\cdot\text{min}^{-1}$ .



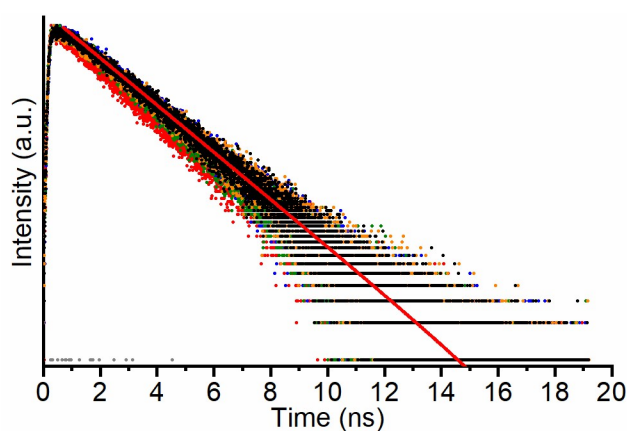
**Fig. S1** TEM image of UC@OA. Scale bar: 100 nm. Inset: Histogram displaying the size distribution of the synthesized UC@OA. The UC@OA were hexagonal prisms with a size of  $(21.0 \pm 0.8) \times (18.9 \pm 0.7)$  nm.



**Fig. S2** Thermogravimetric analyses of UC@RB1 (red line), UC@OA (grey line) and RB (black line).



**Fig. S3** Emission spectra of UC@RB2 dispersions ( $\lambda_{\text{exc}} = 522$  nm) under air (black line) and nitrogen (blue line) in DMF ( $A_{560} = 0.1$ ).

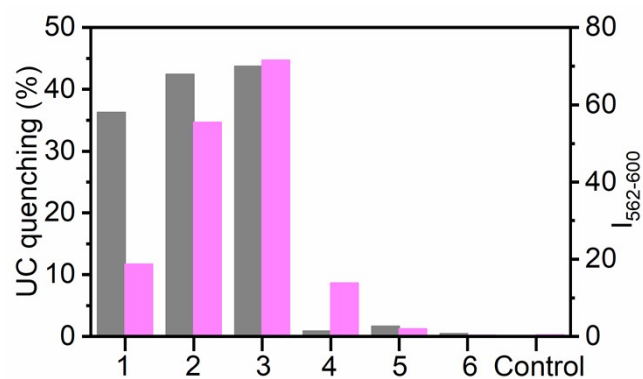


**Fig. S4** Kinetic profiles of UC@RBn ( $\lambda_{\text{exc}} = 560$  nm,  $\lambda_{\text{em}} = 580$  nm) in DMF: UC@RB1 (red), UC@RB2 (blue), UC@RB3 (green), and UC@RB4 (orange). UC@OA (grey) and RB (black) are added for comparative purposes.

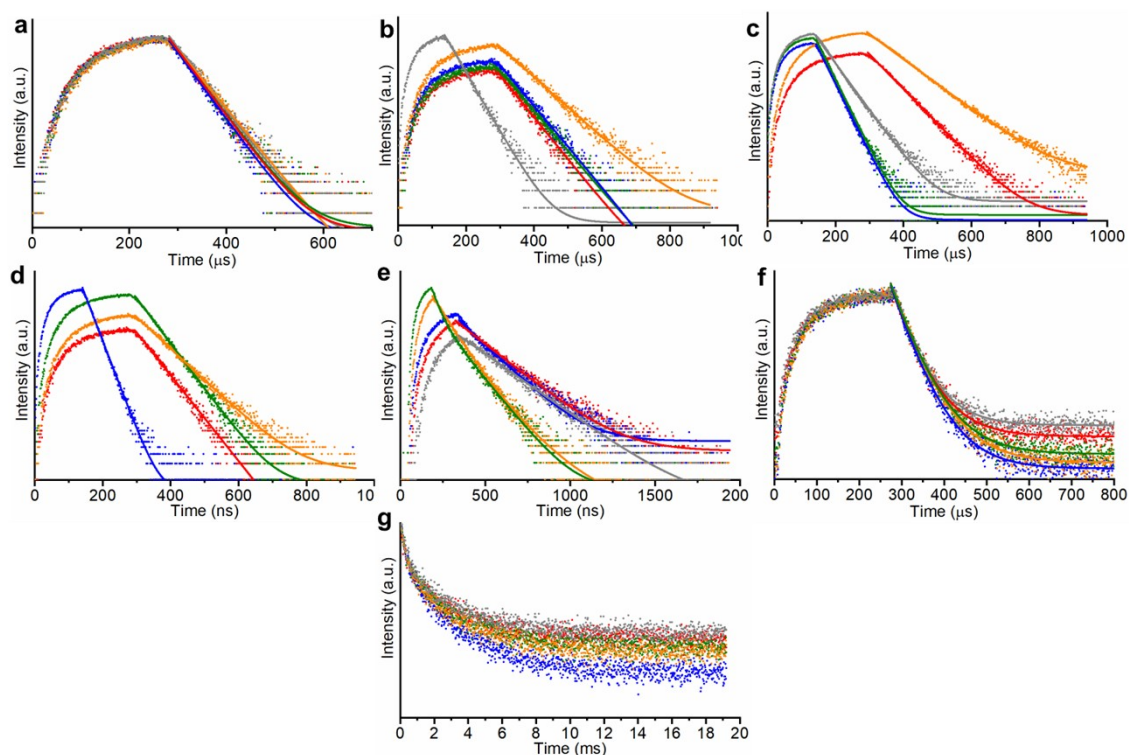
**Table S1** Fitting parameters of the kinetics obtained for UC@RB nanohybrids in DMF ( $\lambda_{\text{em}} = 580$  nm) upon excitation at 560 nm.

Sample	Air			Nitrogen		
	$\tau_{580}$ (ns)	SD* (ns)	$\chi^2$	$\tau_{580}$ (ns)	SD* (ns)	$\chi^2$
UC@RB1	2.0	0.004	0.8927	2.1	0.004	0.8840
UC@RB2	2.2	0.004	0.9025	2.2	0.004	0.8816
UC@RB3	2.1	0.004	0.8375	2.1	0.004	0.8567
UC@RB4	2.3	0.004	0.8917	2.3	0.004	0.8762
UC@RB5	2.3	0.004	0.9184	2.3	0.004	0.88
UC@RB6	2.1	0.01	0.6778	2.1	0.01	0.6964
RB (control)	2.2	0.004	0.8851	2.3	0.004	0.8779

\*SD: fitting standard deviation.



**Fig. S5** Grey columns: UC quenching efficiency calculated from the green emission bands in the SS emission spectra ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ) and using UC@OA as control. Pink columns: Integrated area of the emission spectra ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ) between 562 and 600 nm corresponding to the RB emission.



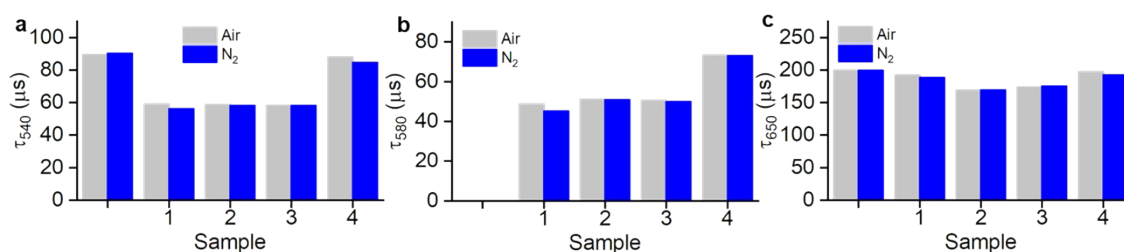
**Fig. S6** Emission kinetic profiles ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ) of UC@RBn dispersions ( $1 \text{ mg}\cdot\text{mL}^{-1}$ ) in DMF: UC@RB1 (red), UC@RB2 (blue), UC@RB3 (green), and UC@RB4 (orange), UC@OA (grey line) at a) 408 nm, b) 525 nm, c) 540 nm, d) 580 nm, e) 650 nm, f) 1050 nm, and g) 1550 nm.



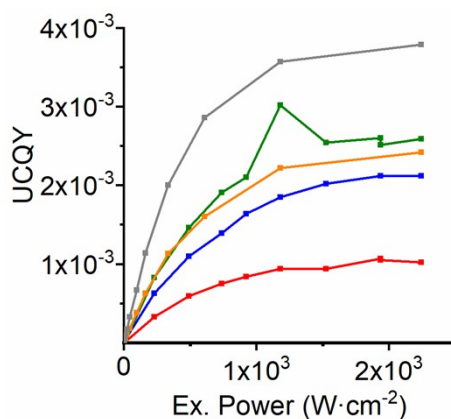
**Table S2** Emission lifetimes of UC@RB nanohybrids ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ) in DMF.

Sample	$\lambda_{\text{em}}$ (nm)	Air			Nitrogen		
		$\tau$ ( $\mu\text{s}$ )	$SD^*$ ( $\mu\text{s}$ )	$\chi^2$	$\tau$ ( $\mu\text{s}$ )	$SD^*$ ( $\mu\text{s}$ )	$\chi^2$
UC@RB1	540	58.8	0.3	0.9163	56.2	0.3	1.037
	580	48.5	1	0.7040	45.2	1	0.7039
	650	191.7	0.9	1.2366	188.5	1.2	1.0052
UC@RB2	540	58.7	0.3	1.0528	58.1	0.25	1.2589
	580	51.1	0.3	0.9694	50.8	0.3	0.9975
	650	65.3 (25.9%) 204.5 (74.1%)	3 3.1	1.0707	79.8 (34.8%) 217.4 (65.2%)	2.9 3.9	1.0052
UC@RB3	540	58.2	0.3	1.0763	58.2	0.25	1.2535
	580	50.4	0.3	0.8876	49.9	0.3	0.9954
	650	76.0 (38.2%) 233.3 (61.8%)	1.9 2.7	0.7072	74.1 (32%) 222.6 (68%)	2.7 3.6	1.1199
UC@RB4	540	76.2 (74%) 149 (26%)	1 4.2	1.1371	74.18 (86.1%) 150.24 (13.9%)	0.7 5.7	0.98
	580	73.3	0.4	0.9882	73.1	0.4	1.0527
	650	165.8 (63.4%) 251.5 (36.6%)	11 23.9	0.8441	192.2	0.8	1.0855
UC@OA (control)	540	71.7 (71%) 132.6 (29%)	1.5 5.1	0.8382	72.4 (1.1%) 140 (26.3%)	1.1 4.4	0.982
	650	199.2	1.3	0.948	199.6	1.1	1.1602

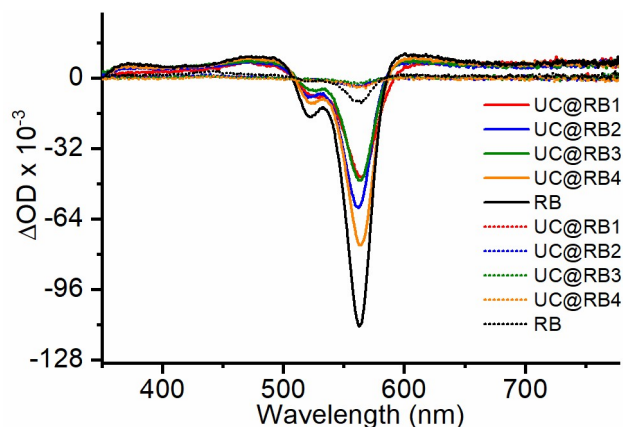
\*SD: fitting standard deviation.



**Fig. S7** Emission lifetimes of UC@RBn ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ) under air (grey) and nitrogen (blue) at 540 nm (a), 580 nm (b), and 650 nm (c).



**Fig. S8** UCQY of UC@RBn dispersions in DMF ( $\lambda_{\text{exc}} = 980 \text{ nm}$ ): UC@RB1 (red), UC@RB2 (blue), UC@RB3 (green), and UC@RB4 (orange); and UC@OA (grey).



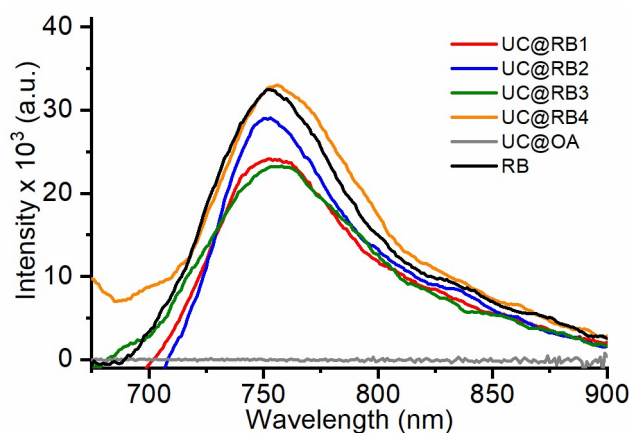
**Fig. S9** Transient absorption spectra of UC@RB1 (red), UC@RB2 (blue), UC@RB3 (green), and UC@RB4 (orange), and RB (black) recorded 20 ns (straight line) and 550  $\mu$ s (dotted line) after the laser pulse ( $\lambda_{exc} = 560$  nm). All samples had an absorbance of 0.24 at 560 nm.

**Table S3** Fitting parameters of the transient absorption kinetics obtained for UC@RB

Sample	$\lambda_{abs}$ ( $\mu$ s)	Air			Nitrogen		
		$\tau$ ( $\mu$ s)	SD*	$\chi^2$	$\tau$ ( $\mu$ s)	SD*	$\chi^2$
UC@RB1	560	0.9	0.3	3.264	50.6 (15%) 267.9 (85%)	1.4 3.7	0.783
UC@RB2	560	0.7	0.3	10.961	25.9 (7.1%) 222.6 (92.9%)	0.7 1.6	0.971
UC@RB3	560	0.2	0.9	10.113	65.5 (34.6%) 297.3 (65.4%)	0.5 2.9	1.078
UC@RB4	560	0.01	0.7	6.007	54.3 (26.5%) 231.5 (73.5%)	0.6 2.0	1.043
RB	560	0.7	0.006	4.256	293.45	0.6	1.044

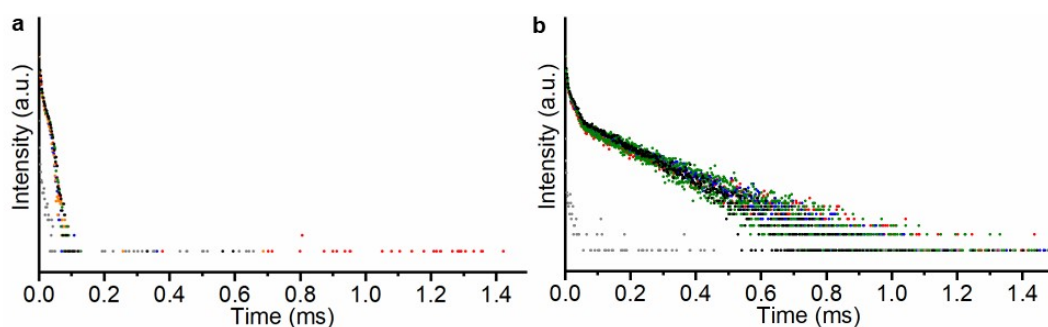
nanohybrids and RB in DMF ( $A_{560} = 0.24$ ).

\*SD: fitting standard deviation.



**Fig. S10**  $^3$ RB phosphorescence of UC@RBn dispersions ( $\lambda_{exc} = 560$  nm) with 0.1 absorption at 560 nm: UC@RB1 (red line), UC@RB2 (blue line), UC@RB3 (green line), and UC@RB4 (orange line),

UC@OA (grey line), and RB (black line). A 645 nm long-pass filter was used to remove the contribution of excitation beam.

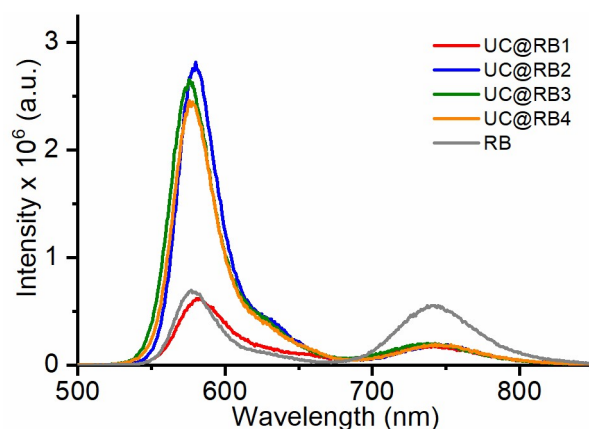


**Fig. S11** Kinetic profiles of UC@RBn ( $\lambda_{\text{exc}} = 560$  nm,  $\lambda_{\text{em}} = 750$  nm) in DMF under air (a) and nitrogen (b); UC@RB1 (red line), UC@RB2 (blue line), UC@RB3 (green line), and UC@RB4 (orange line). UC@OA (grey) and RB (black) are added for comparative purposes.

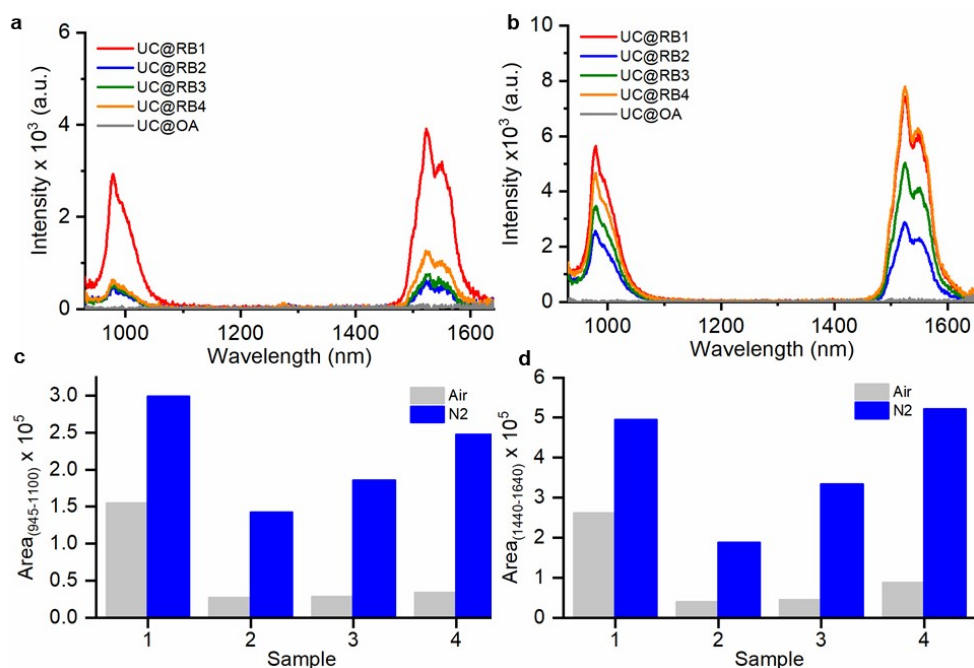
**Table S4** Fitting parameters of the kinetics obtained for UC@RB nano hybrids in DMF ( $\lambda_{\text{em}} = 750$  nm) upon excitation at 560 nm with a microsecond Xe 60 W flash lamp.

Sample	Nitrogen		
	$\tau_{750}$ ( $\mu\text{s}$ )	SD* ( $\mu\text{s}$ )	$\chi^2$
UC@RB1	158.9	1.6	0.8914
UC@RB2	151.3	1.4	0.7502
UC@RB3	129.2	1.3	0.8266
UC@RB4	159.5	1.4	0.9571

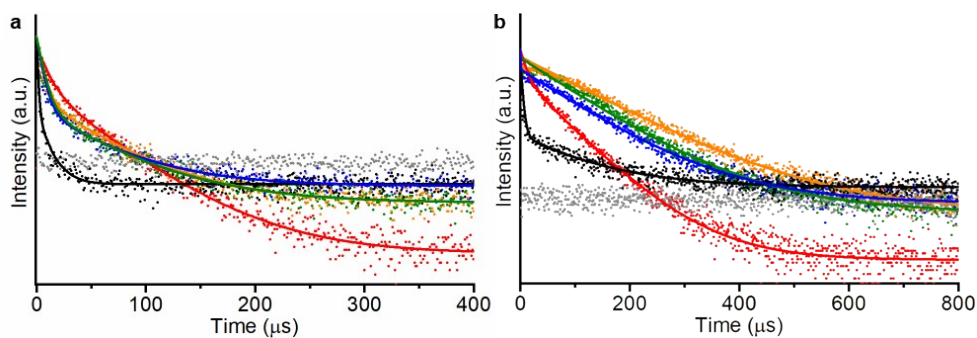
\*SD: fitting standard deviation.



**Fig. S12** Laser-induced emission spectra of UC@RB1 (red), UC@RB2 (blue), UC@RB3 (green), and UC@RB4 (orange), and RB (black) recorded 100 ns after the laser pulse ( $\lambda_{\text{exc}} = 560$  nm). All samples had an absorbance of 0.24 at 560 nm.



**Fig. S13** Emission spectra ( $\lambda_{\text{exc}} = 560$  nm) in the NIR window of the UC@RB nanohybrids in DMF at  $5 \text{ mg}\cdot\text{mL}^{-1}$  in air (a) and nitrogen atmosphere (b) for UC@RB1 (red line), UC@RB2 (pink line), UC@RB3 (orange line), UC@RB4 (yellow line), and UC@OA (grey line). Comparison of the integrated area of the emissive bands between 945 and 1100 (c) and between 1440-1640 nm (d) in air (grey) and nitrogen (blue).

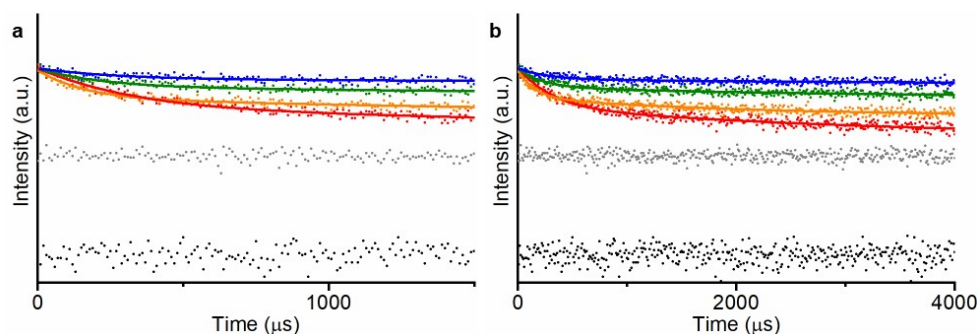


**Fig. S14** Kinetic profiles ( $\lambda_{\text{exc}} = 560$  nm,  $\lambda_{\text{em}} = 980$  nm) of the UC@RB in DMF ( $5 \text{ mg}\cdot\text{mL}^{-1}$ ) under air (a) and nitrogen (b); UC@RB1 (red line), UC@RB2 (pink line), UC@RB3 (orange line), UC@RB4 (yellow line). UC@OA (grey) and RB (black) are added for comparative purposes.

**Table S5** Lifetime fitting results ( $\lambda_{em} = 980$  nm) of the UC@RB nano hybrids in DMF upon excitation at 560 nm.

Sample	Air			Nitrogen		
	$\tau_{980}$ ( $\mu\text{s}$ )	SD* ( $\mu\text{s}$ )	$\chi^2$	$\tau_{980}$ ( $\mu\text{s}$ )	SD* ( $\mu\text{s}$ )	$\chi^2$
UC@RB1	8.9 (15%) 63.5 (85%)	0.6 1.1	1.0181	14.3 (7.6%) 93.9 (92.4 %)	1.3 1	1.0697
UC@RB2	5.7 (15.6%) 60.9 (84.4%)	0.4 2.0	1.0527	0.44 (33.7%) 134.9 (66.4%)	4.7 1.1	1.0656
UC@RB3	7.4 (16.5%) 69.7 (83.5%)	0.5 1.7	1.0269	115.4	2.2	1.1011
UC@RB4	5.6 (13.2%) 64.6 (86.8%)	0.4 1.3	1.0092	158.1	2.5	1.0522

\*SD: fitting standard deviation.

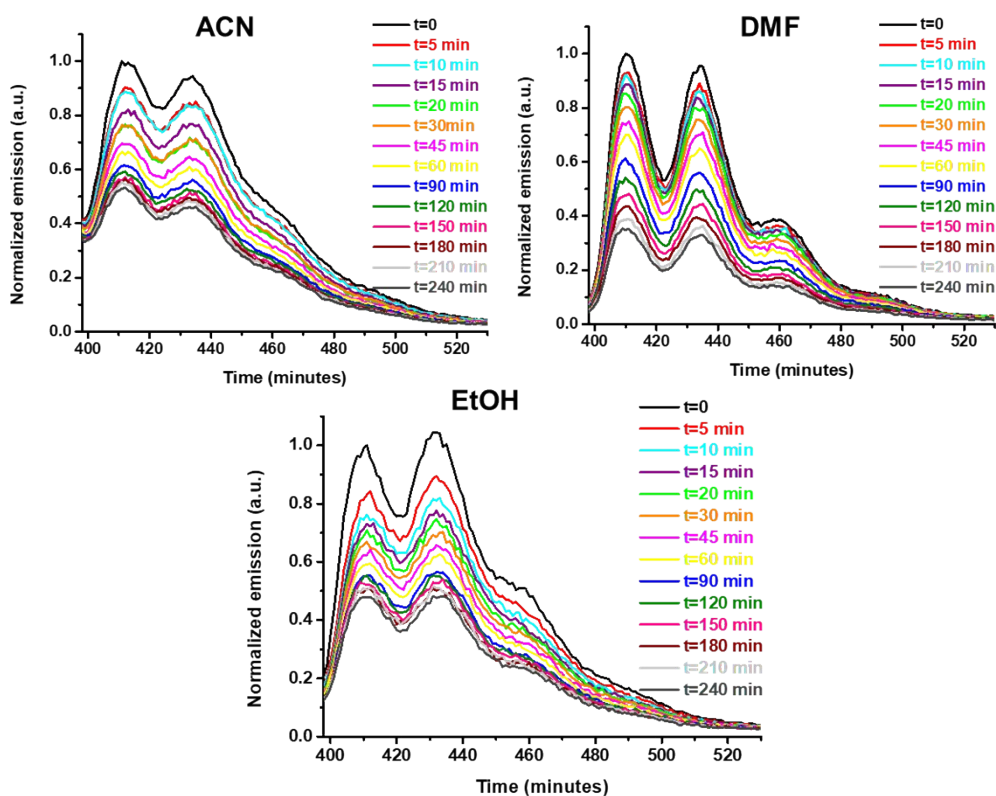


**Fig. S15** Kinetic profiles ( $\lambda_{exc} = 560$  nm,  $\lambda_{em} = 1525$  nm) of the UC@RB nano hybrids in DMF (5 mg·mL<sup>-1</sup>) under air (a) and nitrogen (b); UC@RB1 (red line), UC@RB2 (pink line), UC@RB3 (orange line), UC@RB4 (yellow line). UC@OA (grey) and RB (black) are added for comparative purposes.

**Table S6** Fitting parameters of the kinetics obtained for UC@RB nano hybrids in DMF ( $\lambda_{em} = 1525$  nm) upon excitation at 560 nm.

Sample	Air			Nitrogen		
	$\tau_{1525}$ ( $\mu\text{s}$ )	SD ( $\mu\text{s}$ )	$\chi^2$	$\tau_{1525}$ ( $\mu\text{s}$ )	SD ( $\mu\text{s}$ )	$\chi^2$
UC@RB1	272.4 (16%) 2789.6 (84%)	16.8 187.8	1.1217	352.4 (18.2%) 2598.3 (81.8%)	17.9 117.7	0.9657
UC@RB2	1103.8	91.3	0.9970	422.4 (13.9%) 3257.1 (86.1%)	41.4 339.7	1.0701
UC@RB3	250.7 (15.5 %) 2692.3 (84.5%)	36.4 451	0.9500	436.8 (17.2%) 2807.7 (82.8%)	33.7 216.12	1.0575
UC@RB4	127.8 (14.2%) 1760.5 (85.8%)	11.6 119.8	1.0113	425.9 (15.2%) 2512.1 (84.8%)	32.5 84.8	0.9675

\*SD: fitting standard deviation.

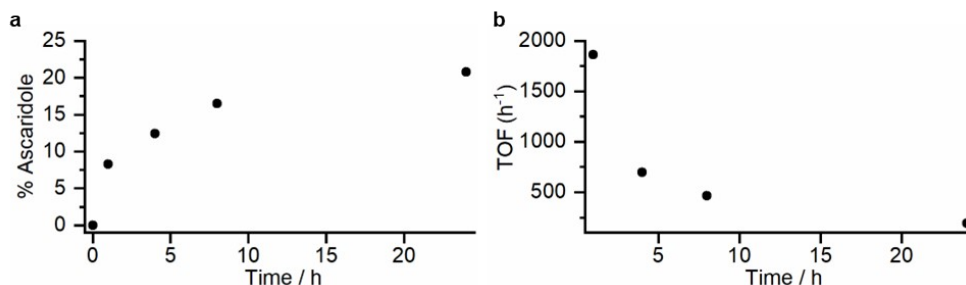


**Fig. S16** Emission spectra of ABDA ( $\lambda_{exc} = 378$  nm) upon irradiation at 980 nm of a UC@RB2 dispersion ( $[ABDA]=1.027 \cdot 10^{-5}$  M,  $[UC@RB2]=1$  mg·mL $^{-1}$ ) at different time intervals for up to 240 min in ACN, DMF, and EtOH.

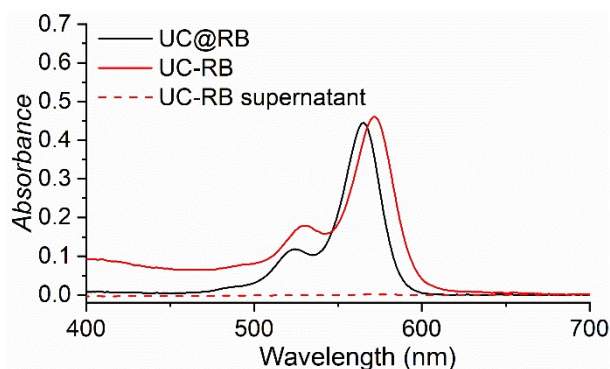
**Table S7** Kinetic rate constants of ABDA photoconsumption ( $y=A1 \cdot e^{-x/K_1} + A2 \cdot e^{-x/K_2} + y_0$ ) in different solvents.

Solvent	$K_1$ (min $^{-1}$ )	$K_2$ (min $^{-1}$ )	$SD_1$ (min $^{-1}$ )	$SD_2$ (min $^{-1}$ )	$R^2$
DMF	0.0054	0.0051	0.0286	0.0015	0.9982
ACN	0.0185	0.3167	0.0038	0.1341	0.9847
EtOH	0.2644	0.0140	0.0509	0.0027	0.9925

\*SD: fitting standard deviation.



**Fig. S17** a) Ascaridole conversion (%) and b) turnover rate with the reaction time.



**Fig. S18** Absorption spectra of UC@RB (black) and UC-RB (red) NHs at the reaction mixture concentrations and the supernatant (dashed line) obtained after centrifugation of the UC-RB sample.

### **<sup>1</sup>H-NMR characterization**

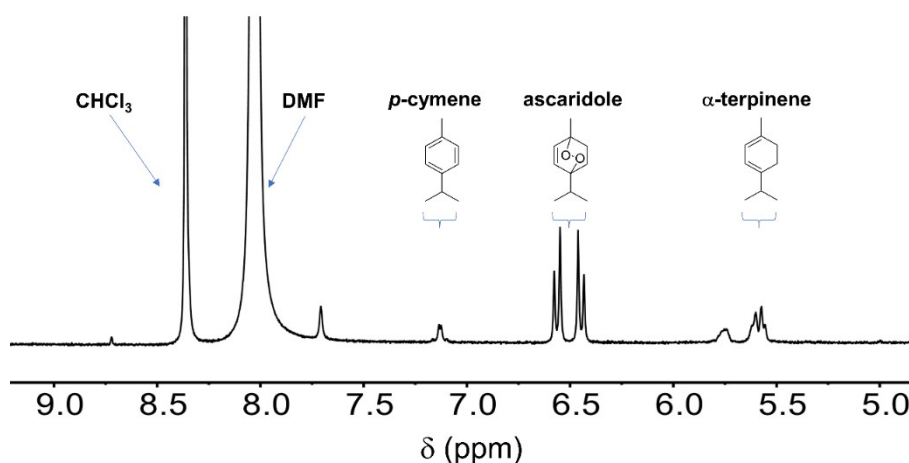
**$\alpha$ -terpinene:** <sup>1</sup>H NMR (500 MHz, DMF-*d*<sub>7</sub>)  $\delta$  5.61 (d, *J* = 5.4 Hz, 1H), 5.57 (d, *J* = 5.6 Hz, 1H), 2.37-2.20 (m, 1H), 2.07 (m, 4H), 1.74 (s, 3H), 1.00 (d, *J* = 6.8 Hz, 6H).

**ascaridole:** <sup>1</sup>H NMR (500 MHz, DMF-*d*<sub>7</sub>)  $\delta$  6.56 (d, *J* = 8.6 Hz, 1H), 6.45 (d, *J* = 8.6 Hz, 1H), 1.93-1.85 (m, 2H), 1.86-1.78 (m, 1H), 1.57 – 1.44 (m, 2H), 1.29 (s, 3H), 1.00 (d, 6H). NMR data matched with those reported in the literature.<sup>7</sup>

***p*-cymene:** <sup>1</sup>H NMR (500 MHz, DMF-*d*<sub>7</sub>)  $\delta$  7.13 (q, *J* = 8.0 Hz, 4H), 2.61 (m, 1H), 2.28 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 6H). NMR data matched with those reported in the literature.<sup>8</sup>

### **Calculation of the yield of photoproducts**

Yields were determined by <sup>1</sup>H-NMR analysis of the crude directly diluted in 430  $\mu$ L of DMF-*d*<sub>7</sub> and using CHCl<sub>3</sub> as internal standard. The yield was estimated by comparison between the signal integration of the CHCl<sub>3</sub> (8.36 ppm, 1H, s) with those of the olefinic protons of  $\alpha$ -terpinene (5.63-5.61 ppm, 1H, m; 5.59-5.57 ppm, 1H, m), ascaridole (6.56 ppm, 1H, d; 6.45 ppm, 1H, d) and the aromatic ones of *p*-cymene as shown in Figure S18.



**Fig. S19** <sup>1</sup>H-NMR spectrum of photooxidation of  $\alpha$ -terpinene catalysed by 5 mg/mL of UC@RB2.

### **References**

- 1 Z. Li and Y. Zhang, *Nanotechnology*, 2008, **19**, 345606.
- 2 A. Dong, X. Ye, J. Chen, Y. Kang, T. Gordon, J. M. Kikkawa and C. B. Murray, *J. Am. Chem. Soc.*, 2007, **129**, 12222-12223.



- Chem. Soc.*, 2010, **133**, 998–1006.
- 3 K. Song, X. Kong, X. Liu, Y. Zhang, Q. Zeng, L. Tu, Z. Shi and H. Zhang, *Chem. Commun.*, 2012, **48**, 1156–1158.
  - 4 J. J. M. Lamberts, D. R. Schumacher and D. C. Neckers, *J. Am. Chem. Soc.*, 1984, **106**, 5879–5883.
  - 5 K. Liu, X. Liu, Q. Zeng, Y. Zhang, L. Tu, T. Liu, X. Kong, Y. Wang, F. Cao, S. A. G. Lambrechts, M. C. G. Aalders and H. Zhang, *ACS Nano*, 2012, **6**, 4054–4062.
  - 6 J. Ferrera-González, M. González-Béjar and J. Pérez-Prieto, *Nanoscale*, 2023, **15**, 19792–19800.
  - 7 D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada and P. J. Dunn, *Green Chem.*, 2016, **18**, 288–296.
  - 8 F. Lévesque and P. H. Seeberger, *Org. Lett.*, 2011, **13**, 5008–5011.