Electronic Supplementary Material (ESI) for Chemical Communications

Near Infrared Photolysis of a Ru Polypyridyl Complex by Upconverting Nanoparticles

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Supporting Information

Experimental details

Materials

All chemical reagents, yttrium(III) acetate hydrate (99.9%), ytterbium(III) acetate tetrahydrate (99.9%), erbium(III) chloride hexahydrate (99,9%), thulium(III) acetate hydrate (99.9%),1-octadecene (technical grade, 90%), oleic acid (technical grade, 90%), sodium hydroxide (≥ 97%), ammonium fluoride (98%) and solvents were purchased from Sigma-Aldrich. Nanopure water was obtained using the Barnstead Nanopure Ultrapure Water Purification System.

Synthesis of oleate-capped $NaYF_4$:Yb^{3+}/Er^{3+}

The synthesis of oleate-capped $NaYF_4$:Yb^{3+}/Er^{3+} UCNPs was achieved by using a slightly modified version of the protocol reported by Boyer *et al.* [*Chem. Eur. J.* **2012**, *18*, 3122–3126]. The ratio of rare earth elements used during the synthesis was the following: Y/Yb/Er 78/20/2 mol%. The scale of the synthesis was 1.5 mmol.

In a 100 mL three-neck round-bottom flask equipped with a water-cooled condenser, yttrium(III) acetate hydrate (312 mg, 1.17 mmol), ytterbium(III) acetate tetrahydrate (127 mg, 0.30 mmol), erbium(III) chloride hexahydrate (11 mg, 0.03 mmol) were dissolved in 1-octadecene (22.5 mL) and oleic acid (14.0 mL). The reaction mixture was stirred and heated slowly to 120 °C under vacuum. By maintaining such conditions for 30 min, the lanthanide oleate complexes were formed and residual water and oxygen were removed by evaporation, observing a change in the solution, from turbid to transparent. The temperature was then lowered to 50 °C and the reaction flask placed under a gentle flow of nitrogen gas.

Successively, a solution of sodium hydroxide (150 mg, 3.75 mmol) and ammonium fluoride (222 mg, 6.0 mmol) in methanol (5 mL) was prepared and was added to the reaction flask, drop wise (1 mL/min).

The mixture was initially stirred for 30 min at 50 °C followed by stirring for a further 30 min at 70 °C in order to eliminate completely the excess methanol from the reaction vessel. The methanol-free reaction mixture was then heated up to 295 °C and maintained at this temperature for 90 min. During this period the solution became progressively clearer eventually forming a clear transparent solution at which point the reaction mixture was allowed to cool to ambient temperature.

The nanoparticles were obtained from the reaction mixtures via centrifugation at 4500 rpm at 20 °C for 15 minutes as a pellet. The pellet was dispersed in ethanol (30 mL) and centrifuged again. The new pellet was finally dispersed in THF (5 mL) and ethanol (25 mL) and collected via centrifugation. The resulting nanoparticles were dried under ambient conditions. In a typical preparation about 280 mg of product is obtained.

Synthesis of oleate-capped $NaYF_4$:Yb^{3+}/Tm^{3+}

The same protocol described above for oleate-capped Er-doped UCNPs was employed for $NaYF_4$:Yb^{3+}/Tm^{3+}nanocrystals. In the latter case, the reaction mixture was maintained at 295 °C for 60 min instead of 90 min to obtain NPs of smaller size. The ratio of rare earth elements used was Y/Yb/Tm 69.5/30/0.5 mol%. The scale of the synthesis was 1.5 mmol.

Synthesis of oleate-free $NaYF_4$: Yb^{3+}/Er^{3+} and oleate-free $NaYF_4$: Yb^{3+}/Tm^{3+}

The oleate-free nanoparticles were obtained using the procedure reported by N. Bogdan *et al.* [*Nano Lett.* **2011**, *11*, 835–840].

Synthesis of *cis*-$[Ru(bpy)_2(py)_2][Cl]_2$ (1)

The complex *cis*-$[Ru(bpy)_2(py)_2]^{2+}$ was synthesized as a ClO_4 salt following the method of Dwyer *et al.* [*Aust. J. Chem.* **1963**, *16*, 544–548] and then as chloride derivative following the procedure published by Borfecchia *et al.* [*Dalton Trans.* **2013**, *42*, 6564–6571].

Instrumentation

Transmission Electron Microscopy (TEM)

TEM was performed on a JEOL JEM-1400 PLUS-HC microscope operating at 120 kV. The TEM samples were prepared by dropping 2 µl sample solutions (0.1 mg/mL in THF or in water) onto a 400-mesh carbon coated copper grid (3 mm in diameter) followed by the evaporation of the solvent under vacuum. The nanoparticle sizes were estimated from over 100 nanoparticles.

Fourier Transform Infrared (FTIR)

FTIR spectra of oleic acid, oleate-capped UCNPs andoleate-free UCNPs were recorded on a Nicolet FTIR 6700 spectrometer preparing the KBr disc. The spectra were recorded in transmission mode with 32 scans.

X-Ray Photoelectron Spectroscopy (XPS)

XPS experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source Aluminum Kα line of 1486.6 eV energy and a power applied of 350 W and calibrated using the $3d_{5/2}$ line of Ag with a full width at half maximum (FWHM) of 1.0 eV. The selected resolution for the detailed spectra of the different elements was 5 eV of Pass Energy and 0.15 eV/step. All measurements were made in an ultra high vacuum (UHV) chamber at a pressure below $5 \cdot 10^{-8}$ mbar.

Nuclear Magnetic Resonance (NMR)

^{1}H NMR and ^{1}H-^{1}H COSY 2D NMR spectra of *cis*-$[Ru(bpy)_2(py)_2]Cl_2$ (**1**) in D_2O were recorded on a AVANCE III Bruker 500 NMR spectrometer. Chemical shifts were reported in parts-per-million (δ, ppm) and referenced to TMS.

UV–Vis absorption spectroscopy (UV-vis)

All spectra of *cis*-$[Ru(bpy)_2(py)_2]Cl_2$ (**1**) were acquired in aqueous solution using a Varian Cary 5000 spectrophotometer.

Emission spectroscopy

Upconverted emission spectra of Er-doped and Tm-doped UCNPs were collected on a Fluorometer Fluorolog-TSPC (Horiba-JovineIvone) coupled with a 980 nm laser diode (CNI, MDL-N-980). Oleate-capped NPs were dissolved in THF (2mg/mL) while oleate-free NPs in water (2mg/mL).

Photolysis of *cis*-$[Ru(bpy)_2(py)_2][Cl]_2$ (1) with and without UCNPs

Aqueous solutions of **1** were photoirradiated under visible (450 nm and 520 nm) and near infrared (980 nm) light.

A KiloArc light source was employed in the case of visible light irradiation, providing 1.5 mW·cm^{-2} for 450 nm excitation or 2 or 6 mW·cm^{-2} for 520 nm excitation. Aqueous solution of **1** (50 μM for UV-Vis and 150 μM for NMR) were placed in a cuvette under constant stirring and the evolution of the photoreaction was followed by UV-Vis or NMR.

For NIR photolysis experiments, a 980 nm laser diode (CNI, MDL-N-980) was used to irradiate (25–37.5 W·cm^{-2}) aqueous solutions of **1** (50 μM for UV-Vis and 150 μM for NMR) in the presence of UCNPs (15 mg/mL). Typically suspensions containing **1** and UCNPs were placed in a cuvette under constant stirring and the irradiation of **1** was followed by UV-Vis and NMR. Before acquisition of spectra, the suspension was centrifuged for 5 min at 12500 rpm to remove NPs and improve the quality of measurements. The surnatant was used to record UV-Vis or NMR spectra and afterwards was used to re-dissolve the UNCP pellet to obtain the initial suspension used for irradiation experiments.

Results

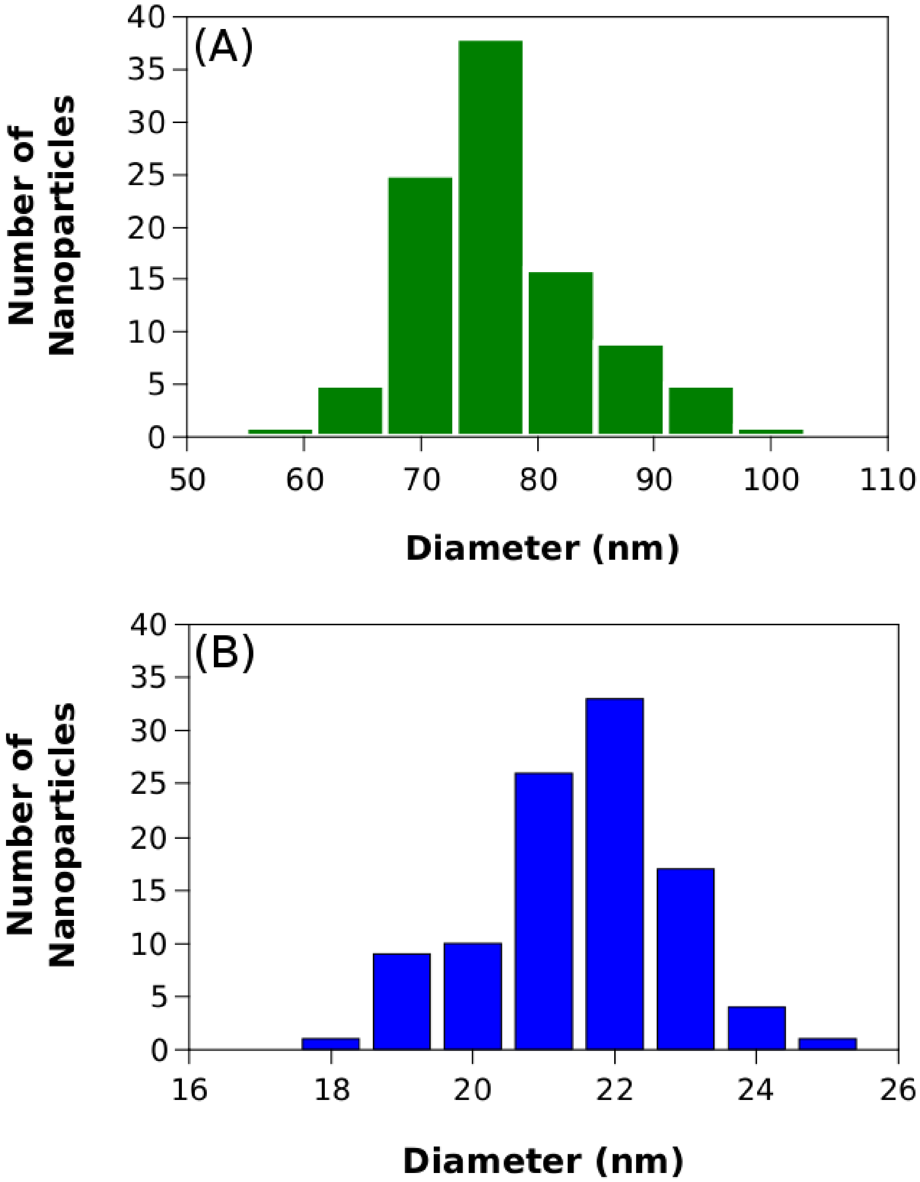

Figure S1 Size distribution of (A) $NaYF_4:Yb^{3+}/Er^{3+}$ and (B) $NaYF_4:Yb^{3+}/Tm^{3+}$ nanoparticles. Diameter of $NaYF_4:Yb^{3+}/Er^{3+}$ = 80 ± 9 nm. Diameter of $NaYF_4:Yb^{3+}/Tm^{3+}$ = 22 ± 1 nm. The nanoparticle sizes were estimated from over 100 nanoparticles using Gaussian fitting.

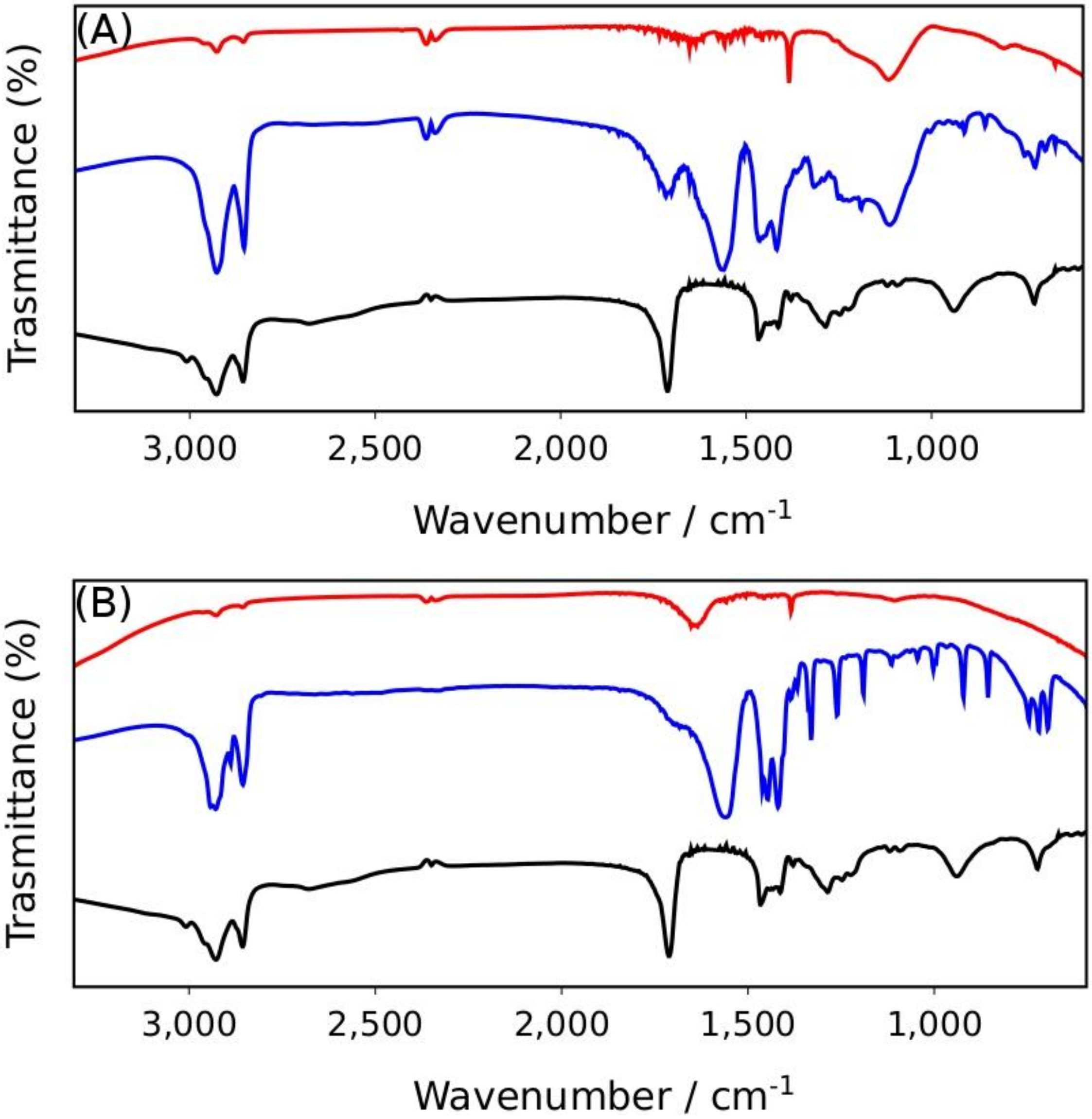

Figure S2 FT-IR spectra of (A) $NaYF_4:Yb^{3+}/Er^{3+}$ and (B) $NaYF_4:Yb^{3+}/Tm^{3+}$ nanoparticles. Colour code: black = oleic acid, blue = oleic acid capped NPs and red = oleate-free NPs.

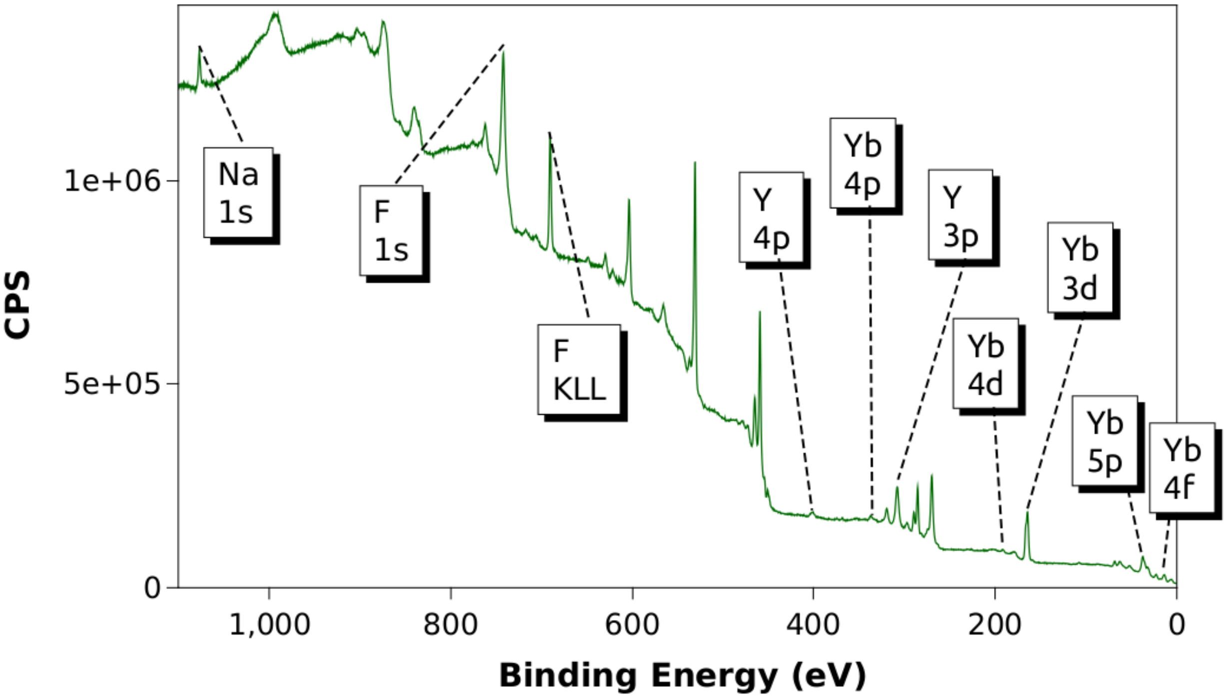

Figure S3 XPS spectrum of $NaYF_4:Yb^{3+}/Er^{3+}$ nanoparticles. Displayed peaks are assigned to the 1s level of Na, 1s level of F, 4p 3p 3d of Y, 4p 4d 5p 4f of Yb.

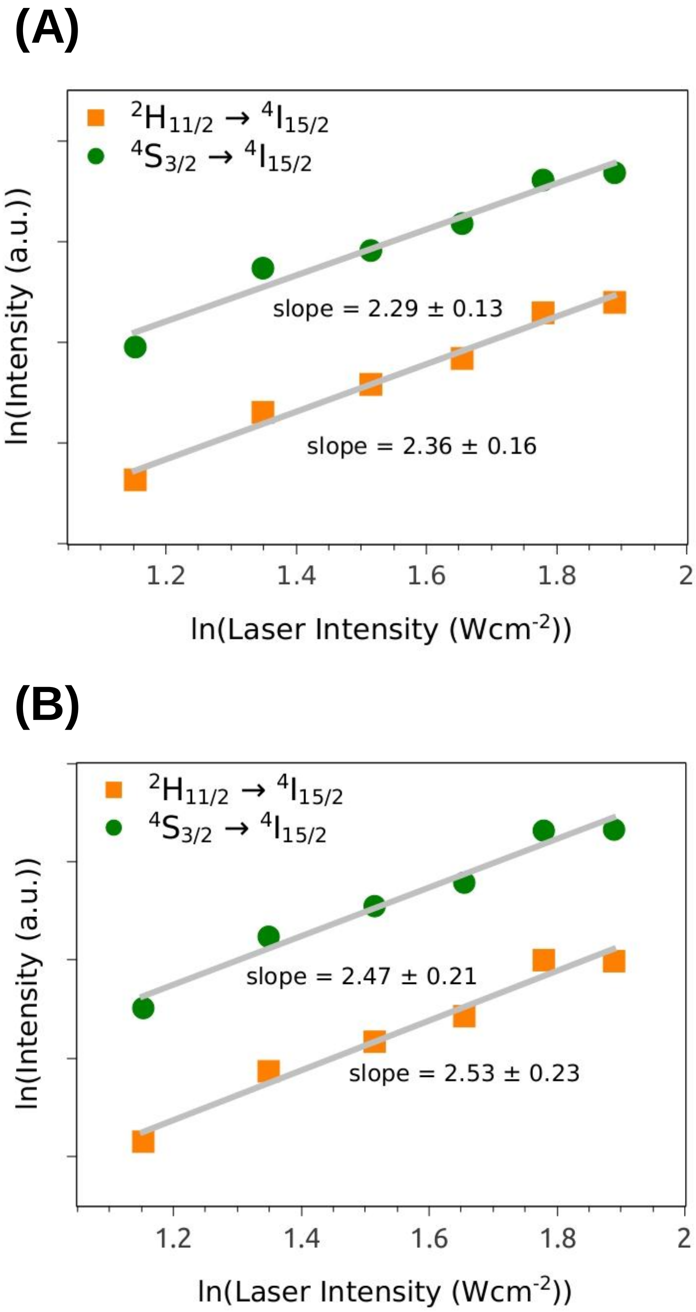

Figure S4 Power dependence of the upconverted emissions of (A) oleate-capped $NaYF_4$:Yb^{3+}/Er^{3+} and (B) oleate-free $NaYF_4$:Yb^{3+}/Er^{3+} nanocrystals in THF (0.4 mg/mL) excited at 980 nm.

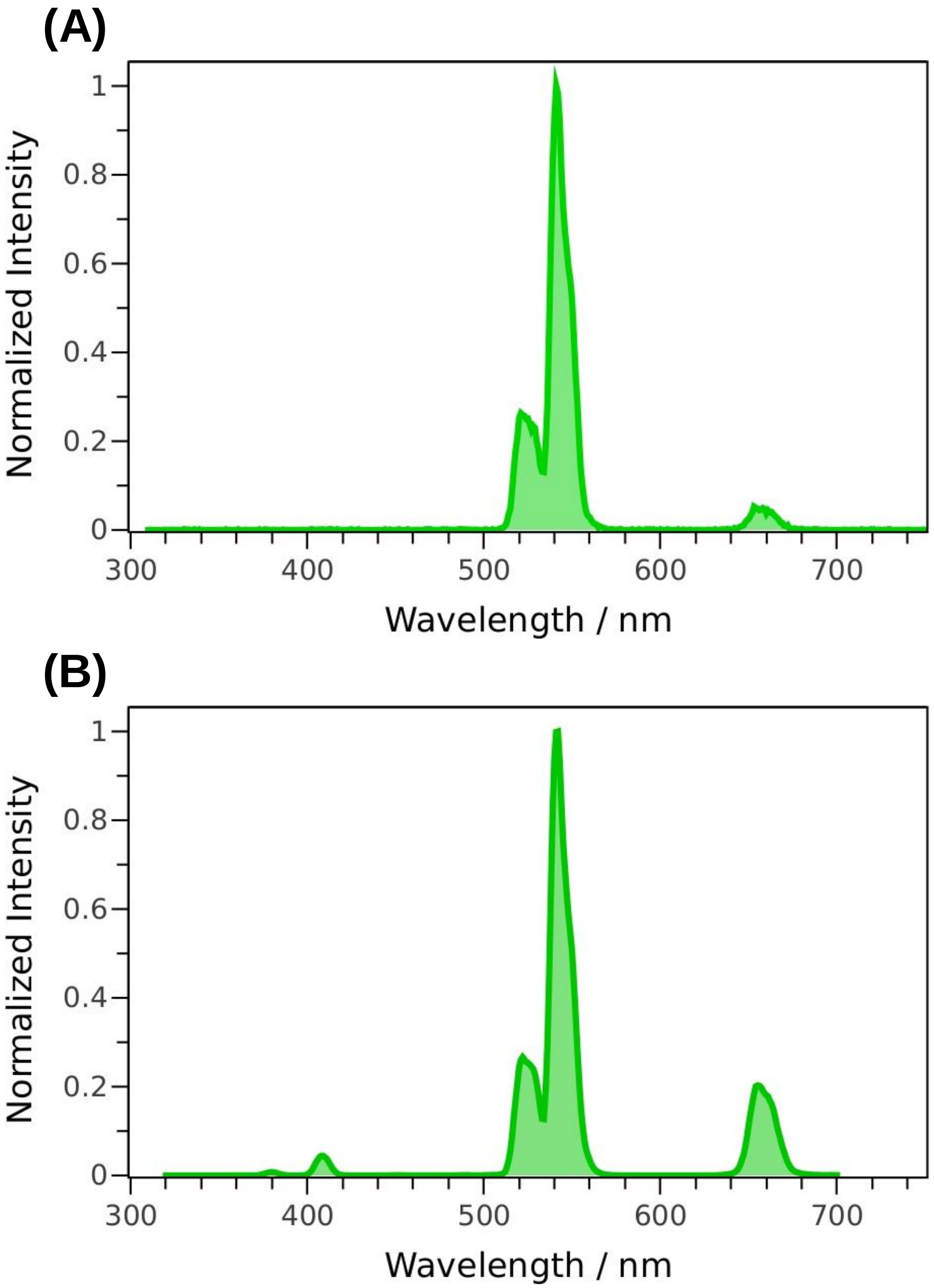

Figure S5 Upconversion emission spectra of (A) oleate-capped $NaYF_4:Yb^{3+}/Er^{3+}$ (2 mg/mL in THF) and (B) oleate-free $NaYF_4:Yb^{3+}/Er^{3+}$ (2 mg/mL in H_2O) upon NIR excitation (λ_{exc} = 980 nm, P = 4.2 $W\cdot cm^{-2}$).

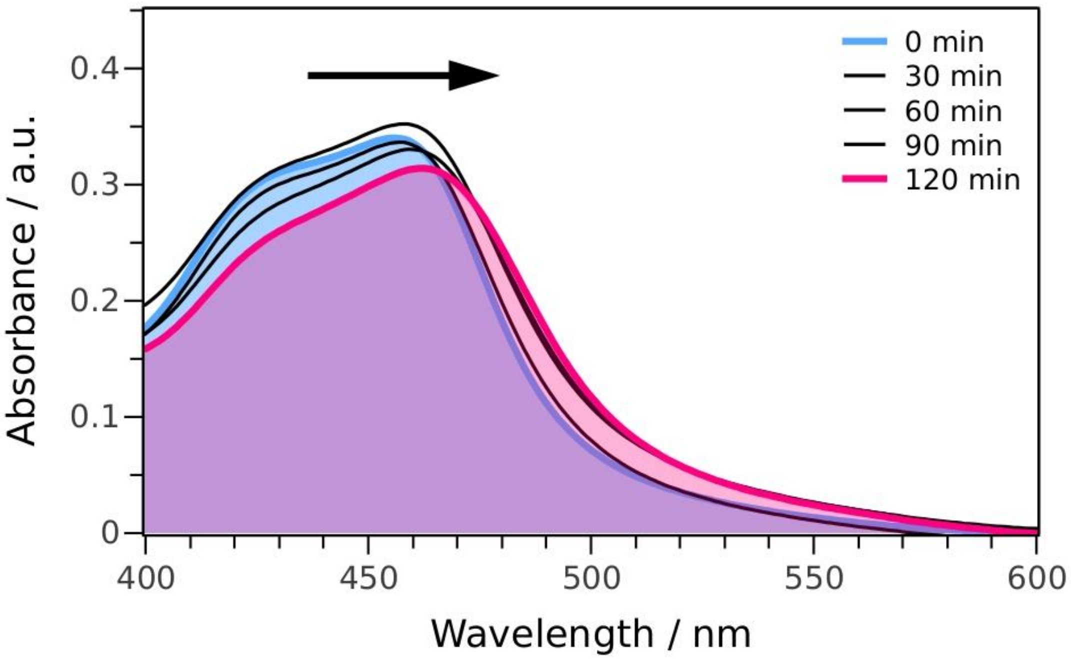

Figure S6 Changes in the electronic absorption spectrum of *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (**1**) in aqueous solution (50 μM) upon NIR excitation (λ_{exc} = 980 nm,25 W·cm^{-2}) in the presence of oleate-free NaYF$_4$:Yb^{3+}/Er^{3+} UCNPs (15 mg/mL).

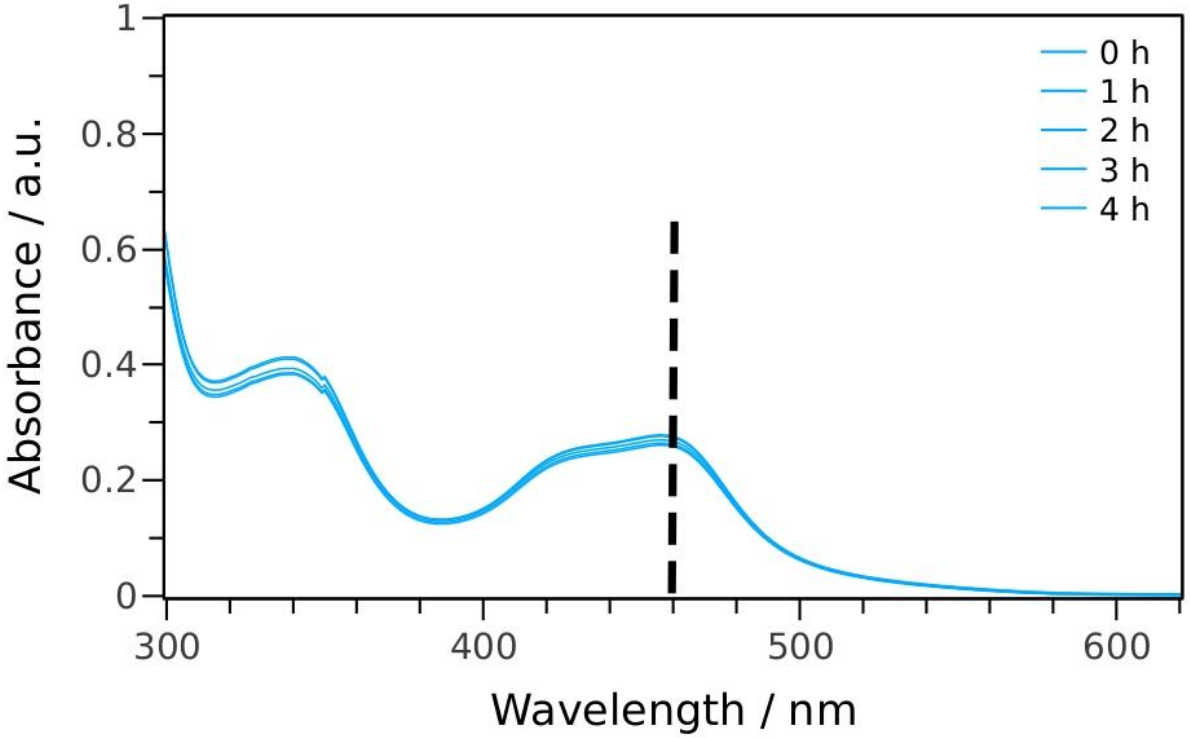

Figure S7 NIR irradiation (λ_{exc} = 980 nm, laser power = 3 W) of *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (**1**) (50 μM) in aqueous solution followed by UV-Vis. The dotted line is put in correspondence of the MLCT maximum of **1** to highlight the absence of any shift in the absorption band under NIR irradiation.

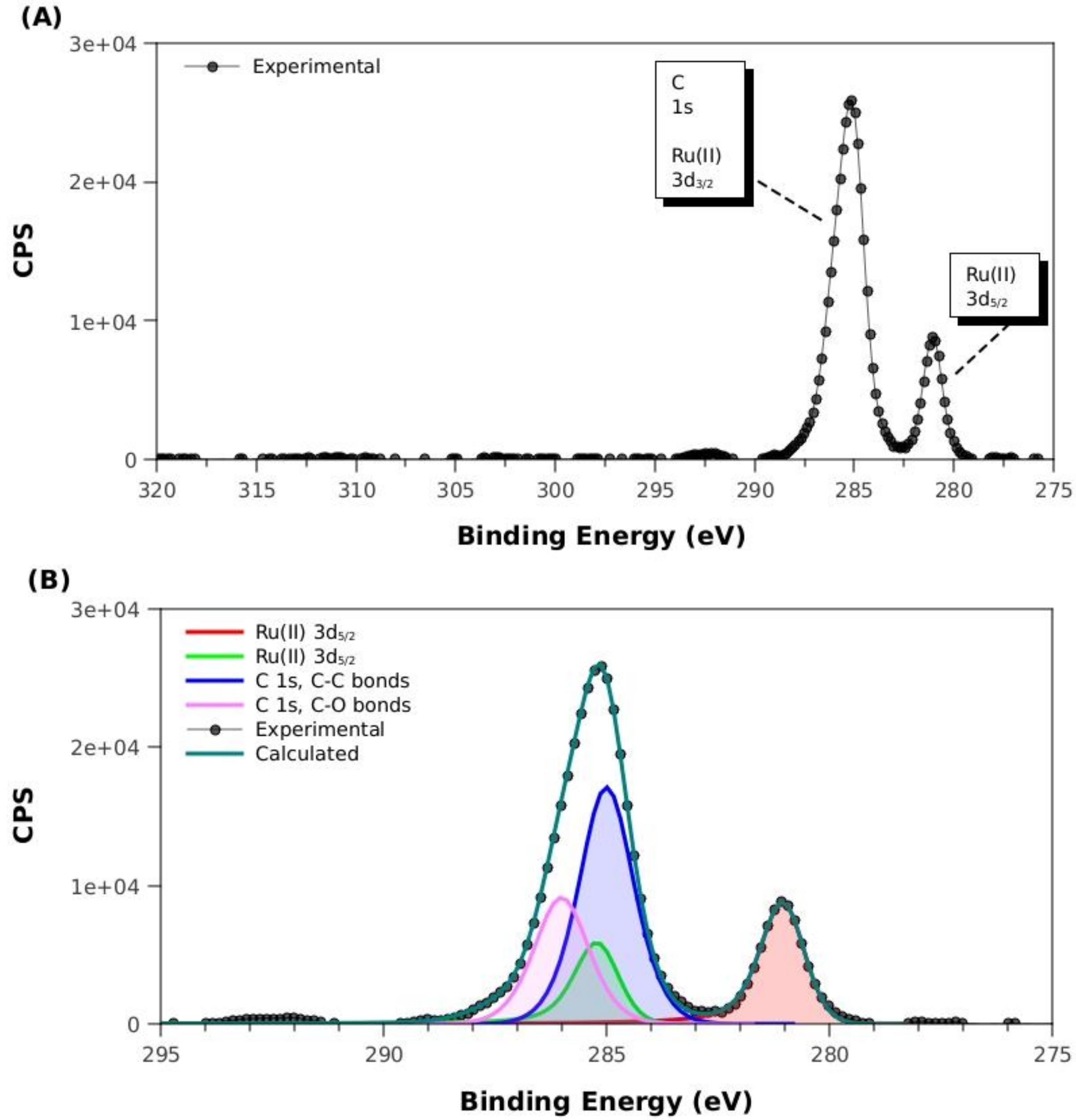

Figure S8 XPS C 1s and Ru 3d spectrum (A) and fitted spectra (B) for *cis*-$[Ru(bpy)_2(py)_2]Cl_2$ (**1**) as a solid. The Ru $3d_{3/2}$ peak overlaps with the C 1s peak.

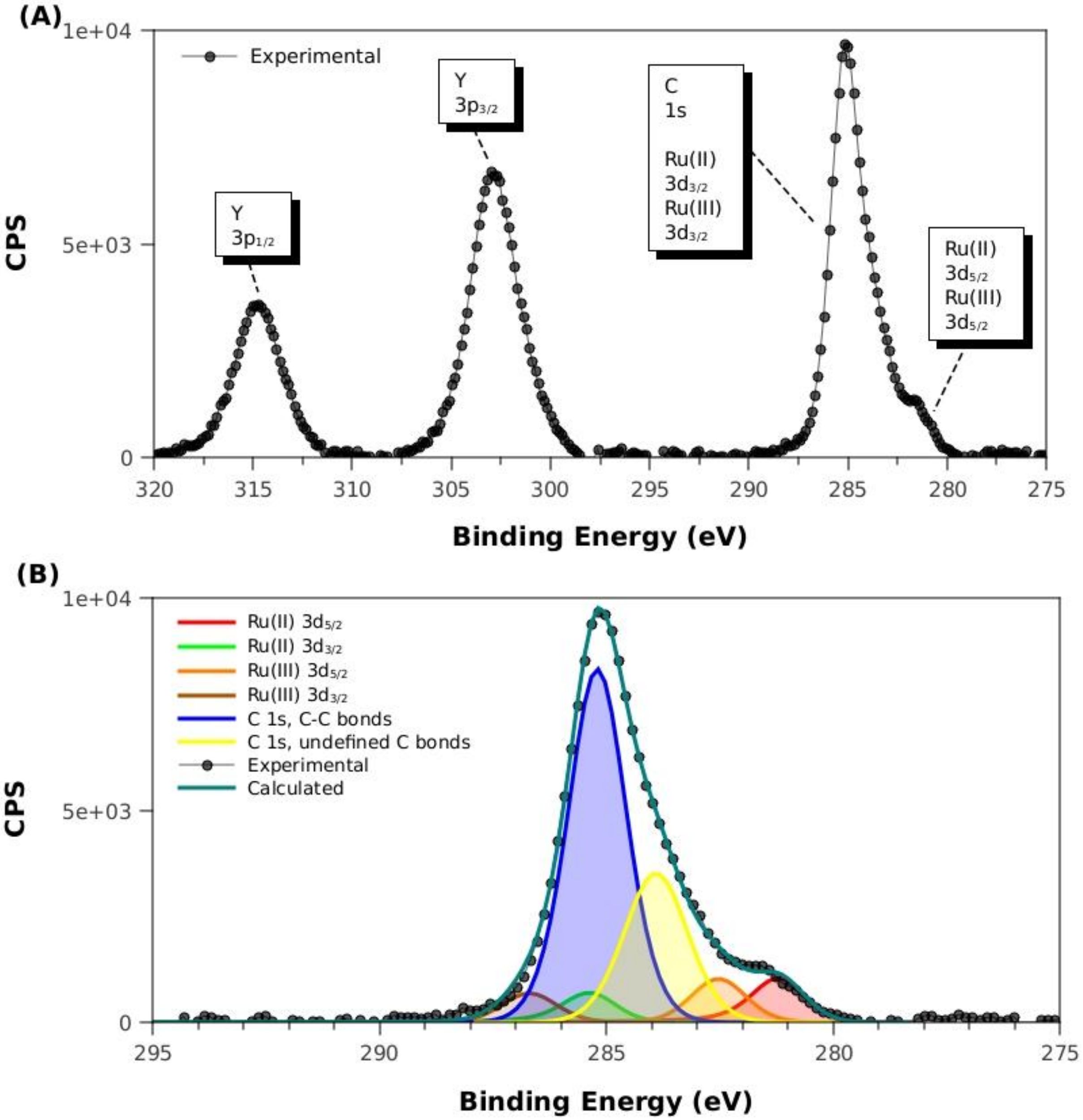

Figure S9 XPS Y 3d, C 1s and Ru 3d spectrum for the oleate-capped Er-doped UCNP-**1** sample (A) together with corresponding C 1s and Ru 3d fitted spectra (B). The Ru $3d_{3/2}$ peaks overlap with the C 1s peak. Based on peak areas, Ru/Y for the sample is 0.087.

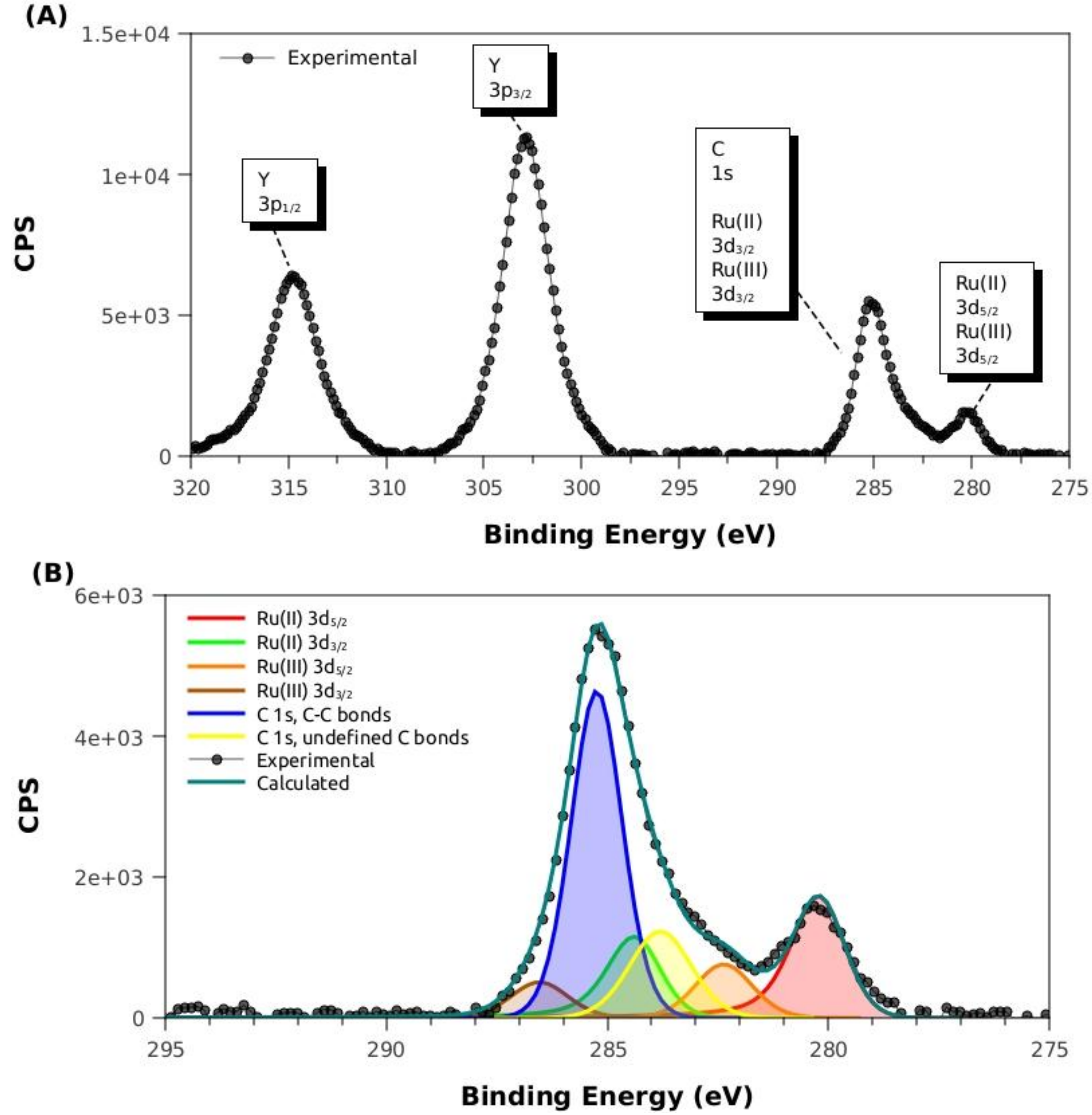

Figure S10 XPS Y 3d, C 1s and Ru 3d spectrum for the oleate-capped Er-doped UCNP-**1** sample after washing in water (A and C) together with corresponding C 1s and Ru 3d fitted spectra (B). The Ru $3d_{3/2}$ peaks overlap with the C 1s peak. Based on peak areas, Ru/Y for the sample is 0.063.

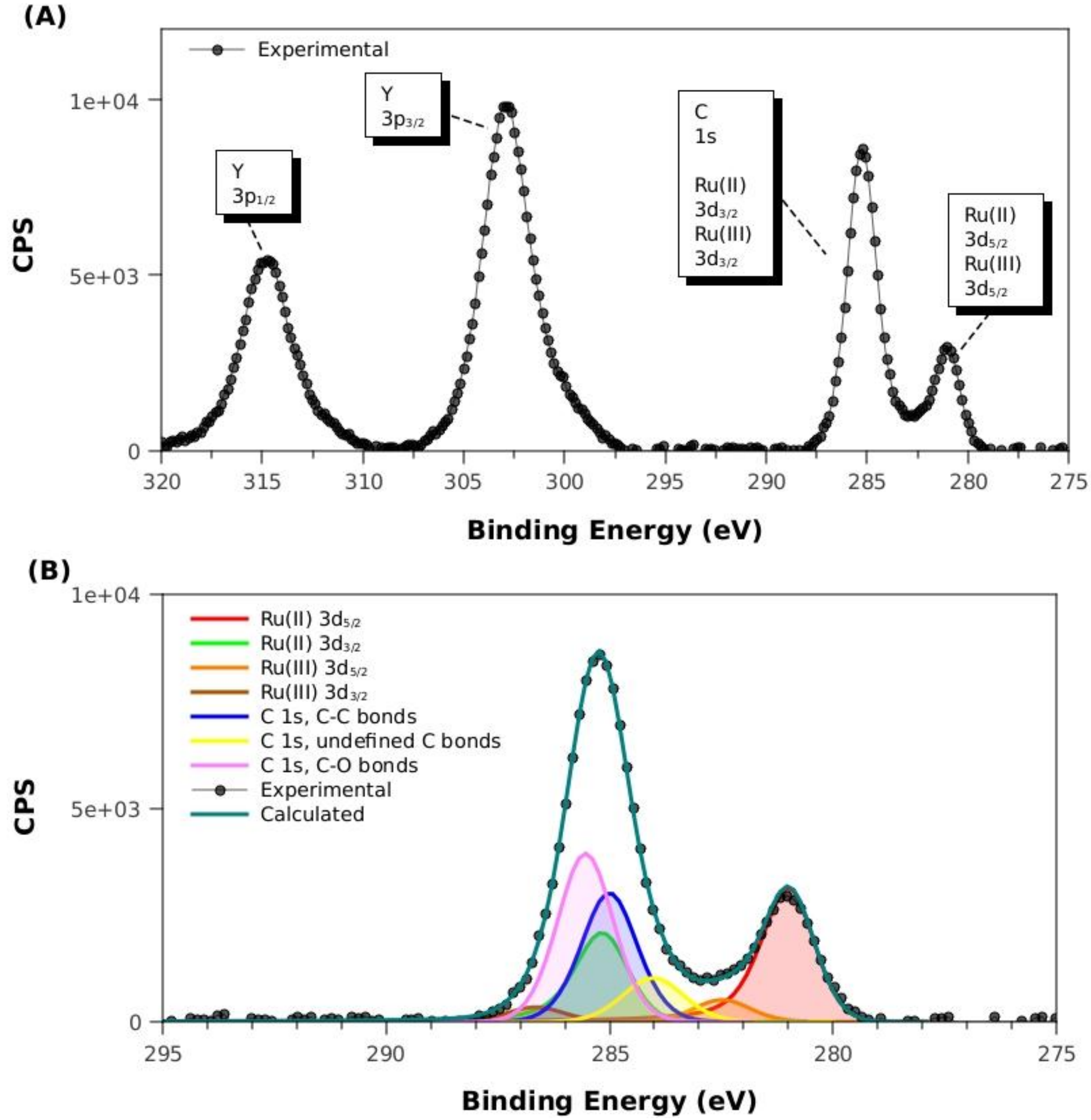

Figure S11 XPS Y 3d, C 1s and Ru 3d spectrum for the oleate-free Er-doped UCNP-**1** sample (A) together with corresponding C 1s and Ru 3d fitted spectra (B). The Ru 3d$_{3/2}$ peaks overlap with the C 1s peak. Based on peak areas, Ru/Y for the sample is 0.098.

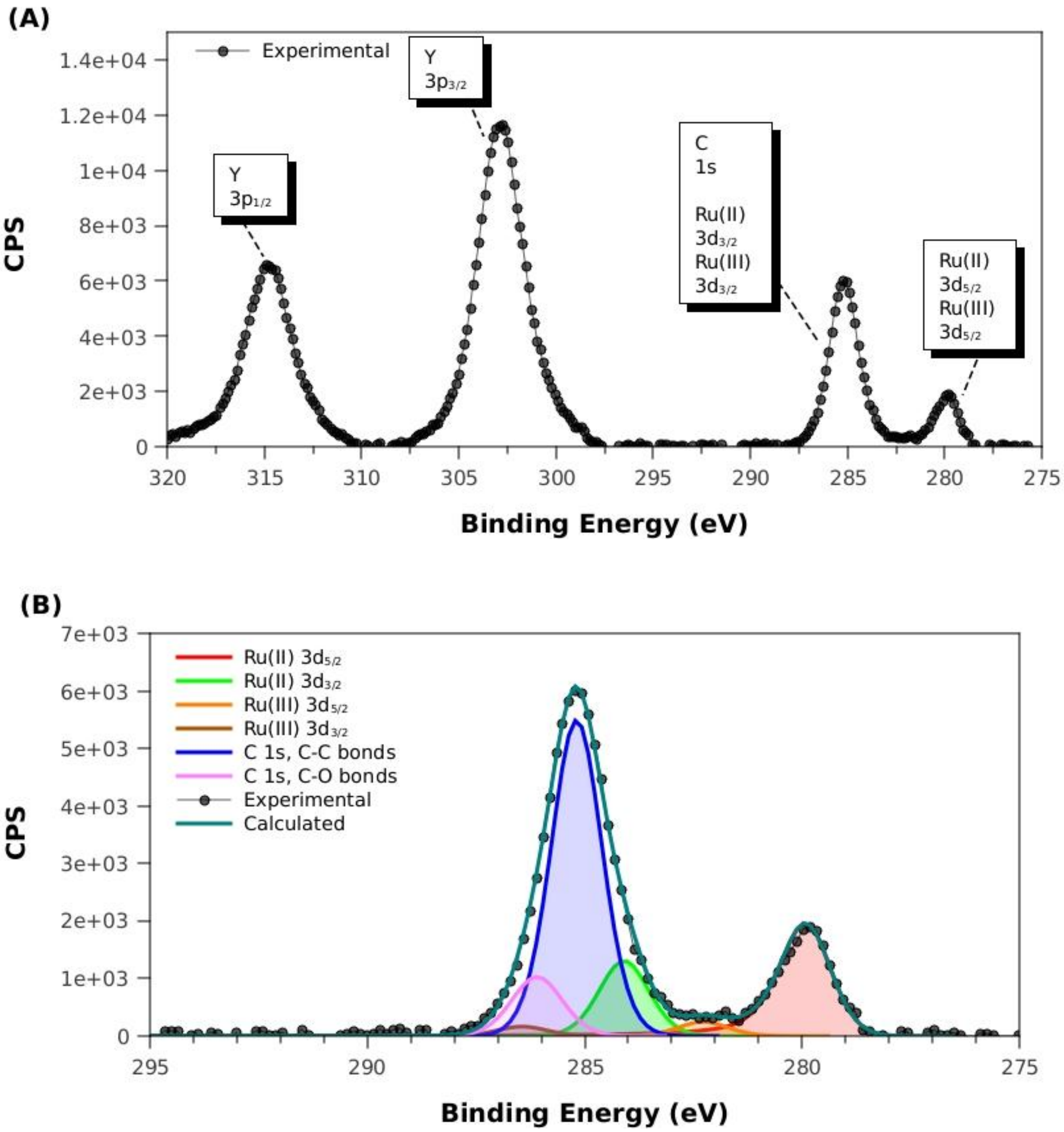

Figure S12 XPS Y 3d, C 1s and Ru 3d spectrum for the oleate-free Er-doped UCNP-**1** sample after washing in water (A) together with corresponding C 1s and Ru 3d fitted spectra (B). The Ru $3d_{3/2}$ peaks overlap with the C 1s peak. Based on peak areas, Ru/Y for the sample is 0.050.

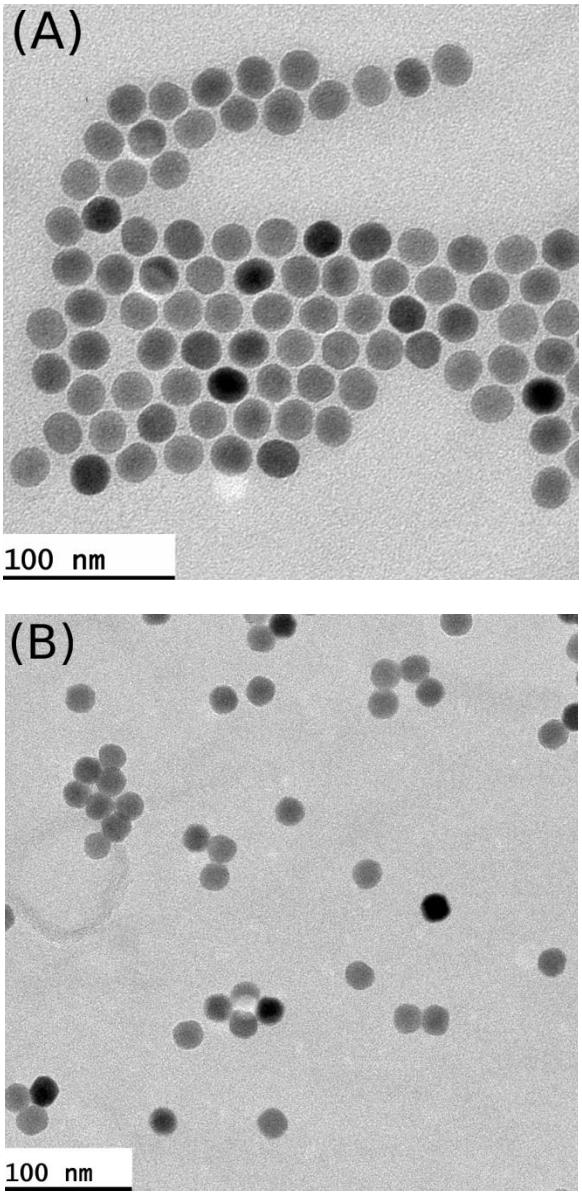

Figure S13 Transmission electron microscopy (TEM) images of (A) oleic acid capped (0.1 mg/mL in THF) and (B) oleate-free (0.1 mg/mL in H_2O) $NaYF_4$:Yb^{3+}/Tm^{3+} nanoparticles.

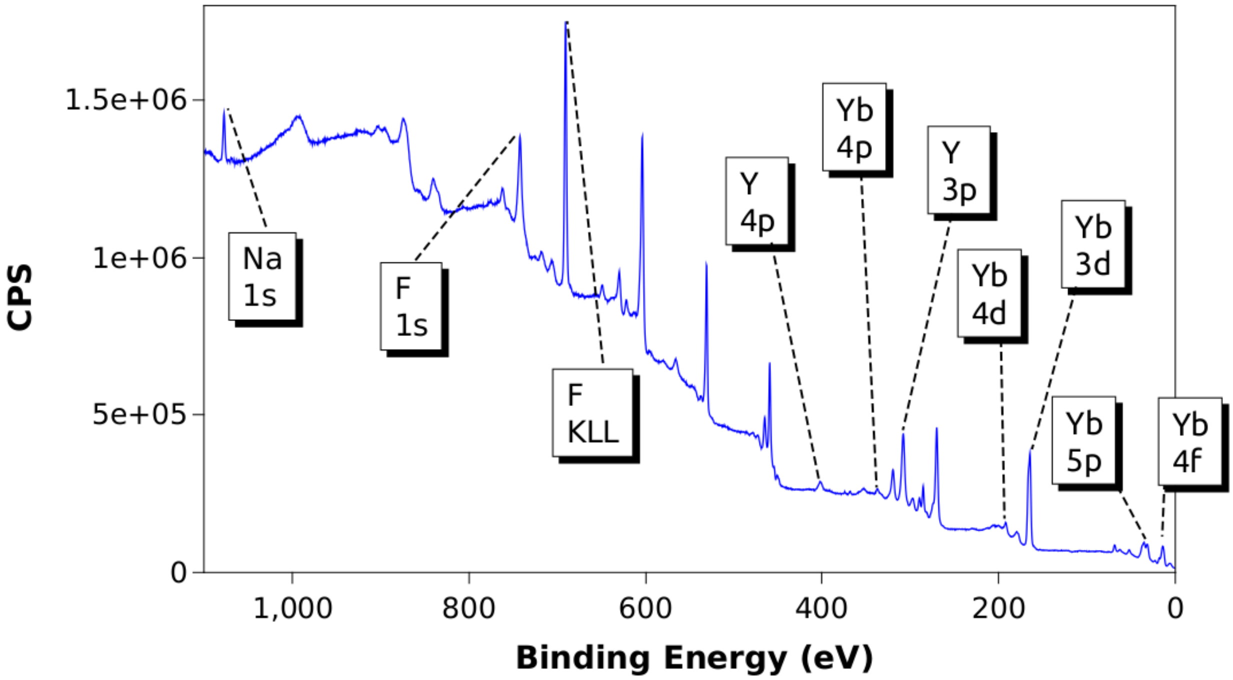

Figure S14 XPS spectrum of $NaYF_4$:Yb^{3+}/Tm^{3+} nanoparticles. Displayed peaks are assigned to the 1s level of Na, 1s level of F, 4p 3p 3d of Y, 4p 4d 5p 4f of Yb.

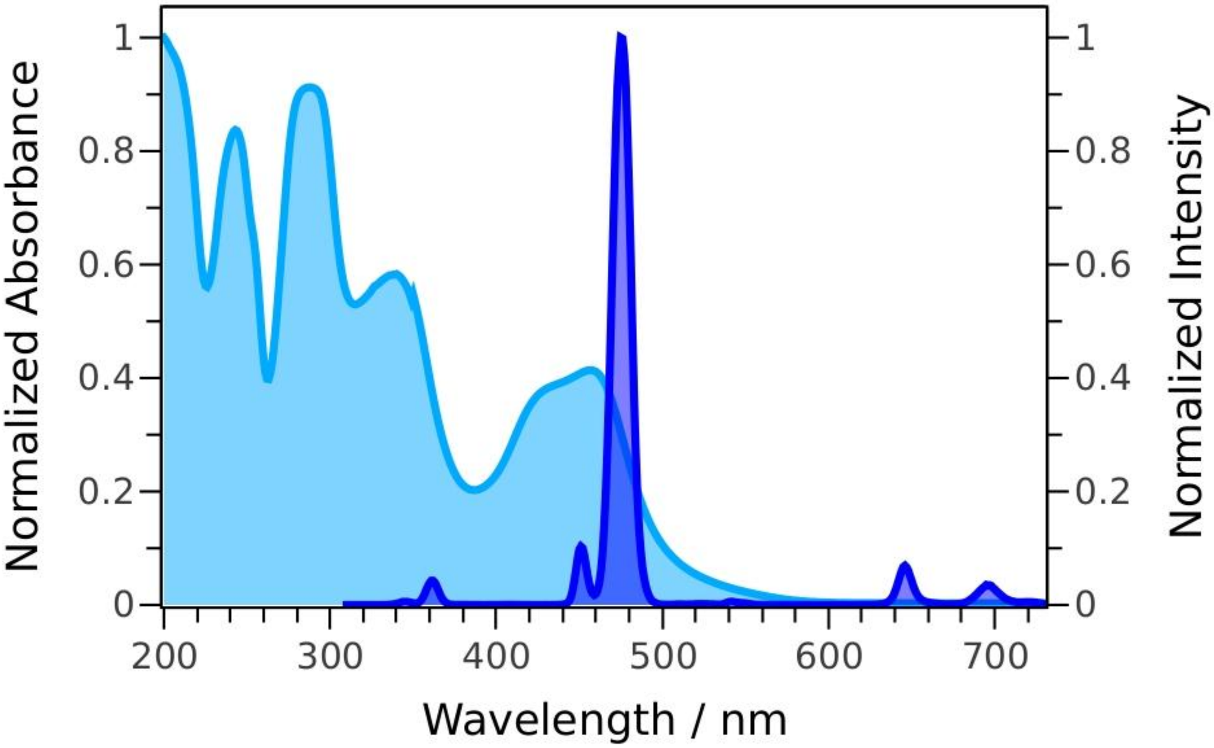

Figure S15 Overlapped absorption spectrum of *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (**1**) (light blue) and upconversion emission intensity (blue) of oleate-free (2 mg/mL in H$_2$O) NaYF$_4$:Yb^{3+}/Tm^{3+} nanoparticles (λ_{exc} = 980 nm).

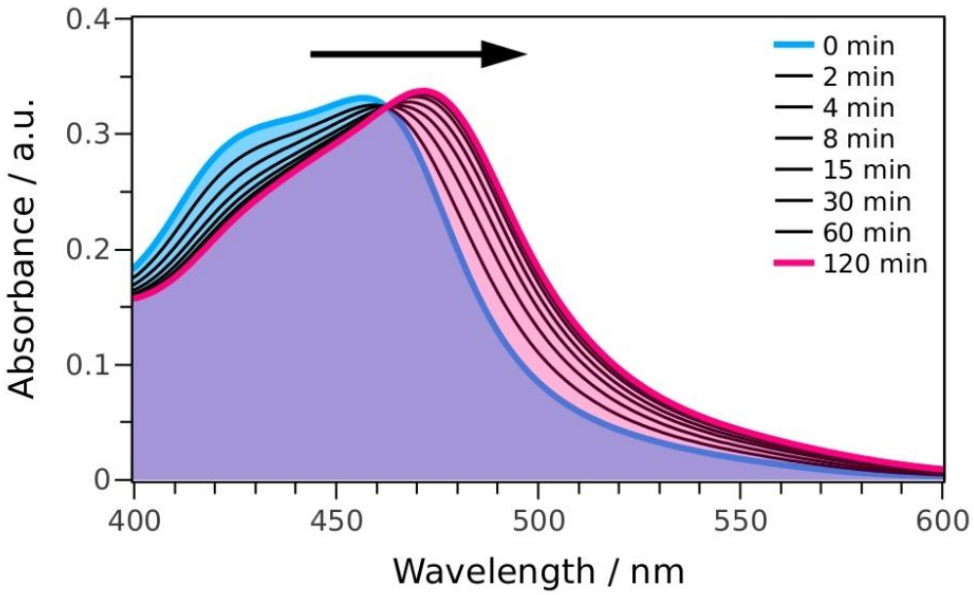

Figure S16 Photolysis (λ_{exc} = 450 nm, *ca.* 1.5 mW·cm^{-2}) of *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (**1**) (50 µM) in aqueous solution followed by UV-Vis.

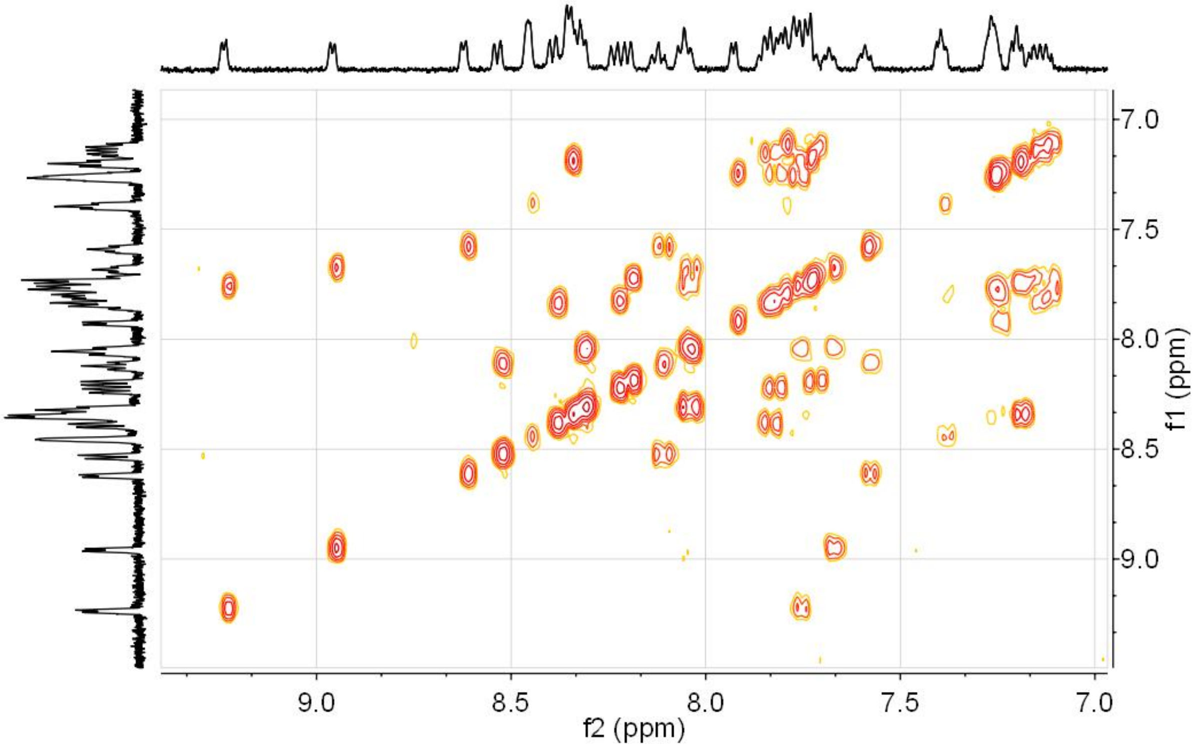

Figure S17 ^{1}H-^{1}H COSY 2D NMR spectrum for an irradiated solution of *cis*-[Ru(bpy)$_2$(py)$_2$]Cl$_2$ (**1**) (150 μM) in D$_2$O (aromatic region). Irradiation details: λ_{exc} = 520 nm (*ca.* 6 mW·cm^{-2}) at 310 K for 5 min.