Electronic Supplementary Information

Near-Infrared Triggered Generation of Reactive Oxygen Species from Upconverting Nanoparticles Decorated with an Organoiridium Complex

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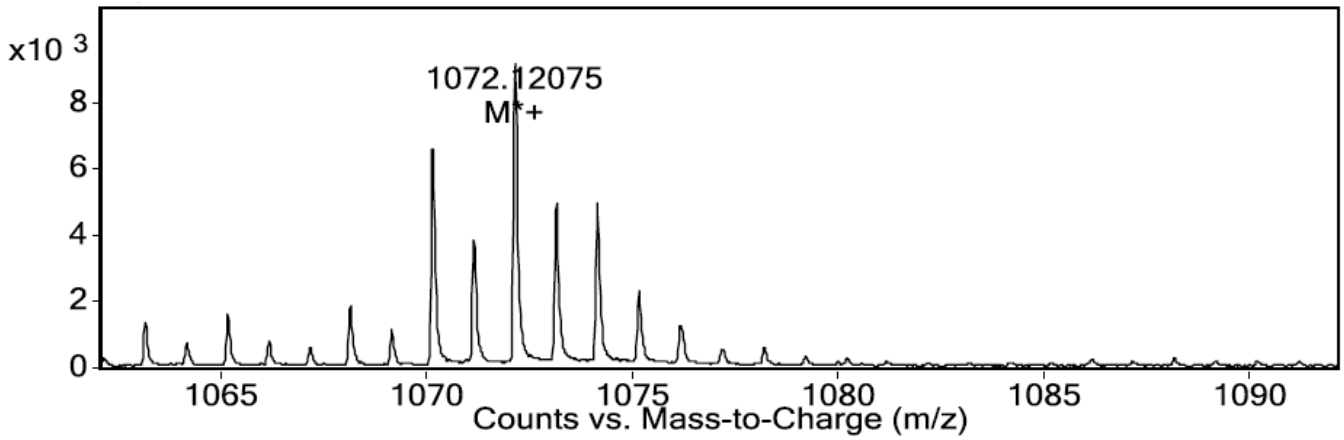
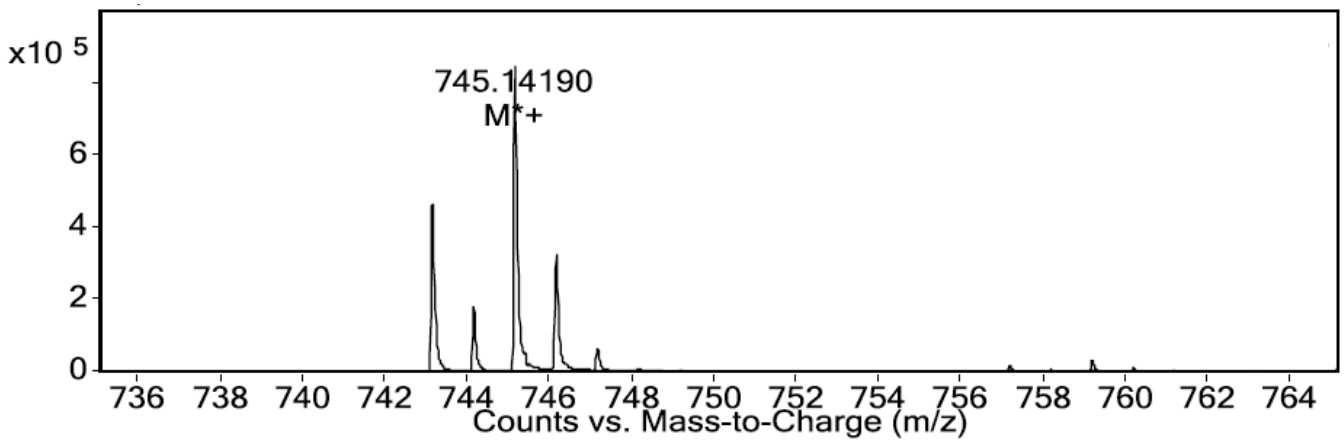
Contents:



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
M*+	C44H32Cl2[193Ir]2N4	9279.3	1072.12075	1072.1257	-4.62



MS Spectrum Peak List

Ion	Ion Formula	Abund	*Expe. m/z*	*Calc. m/z*	Diff(ppm)
M*+	C34H24[193Ir]N4O4	856737.3	745.1419	745.14213	-0.31

Fig. S1. Mass spectra of the dimeric iridium precursor complex $[(ppy)_2Ir(\mu\text{-}Cl)]_2$ (top) and the final iridium complex $[(ppy)_2Ir(dcbpy)]^+$ PF_6^- (bottom) showing molecular ion peaks at *m/z*: 1072 and 745, respectively.

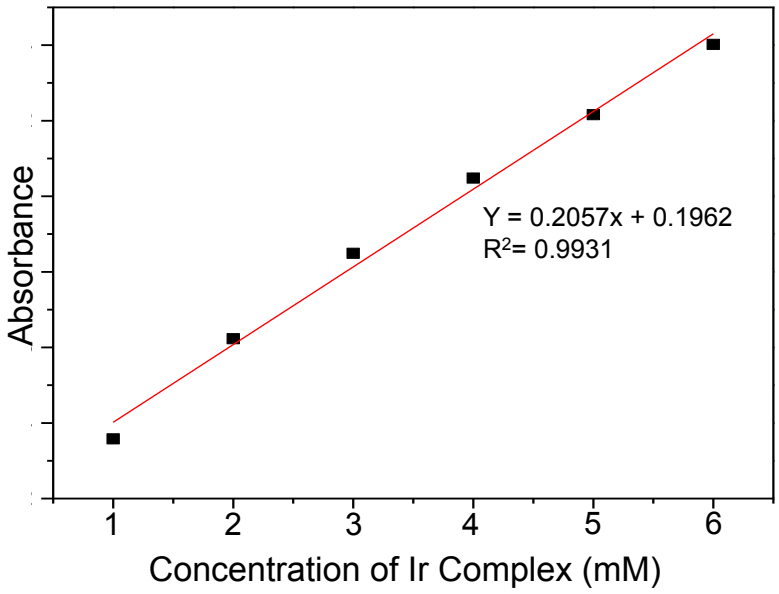


Fig. S2. Loading of the Ir complex on the SiO_2 coated $LiYF_4:Tm^{3+}$, Yb^{3+} UCNPs. The loading percentage was calculated to be 60.71% Increased loading showed increased absorbance confirming the successful encapsulation of the Ir complex on the surface of SiO_2.

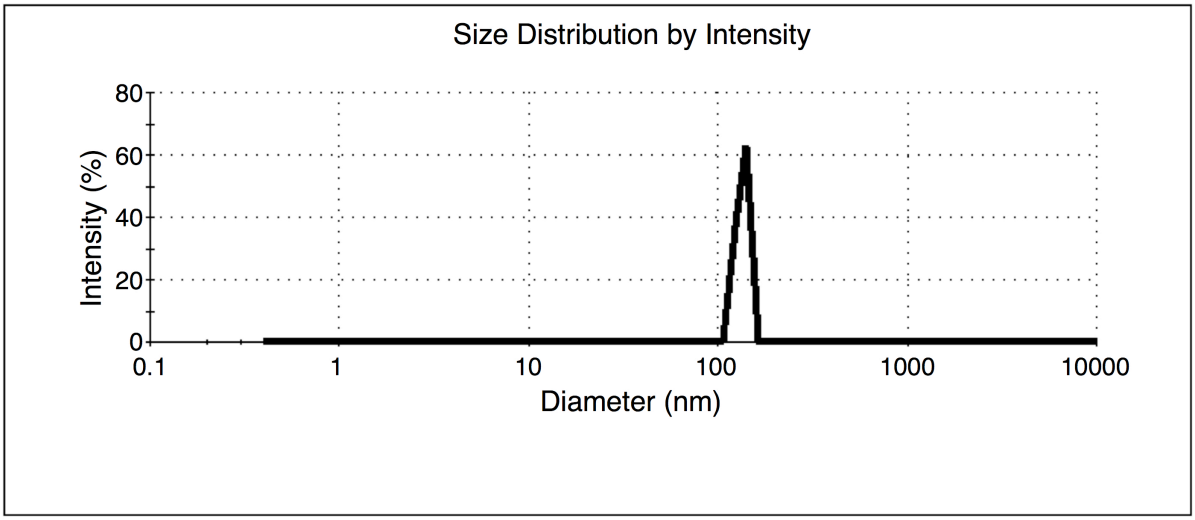


Fig. S3. DLS results of the $LiYF_4$: Tm^{3+}, Yb^{3+}@SiO_2@Ir nanostructures. Average particle diameter was determined to be 135 nm. Note: All DLS measurements were performed in PBS buffer solution and the $LiYF_4$: Tm^{3+}, Yb^{3+}@SiO_2@Ir nanostructures were highly stable.

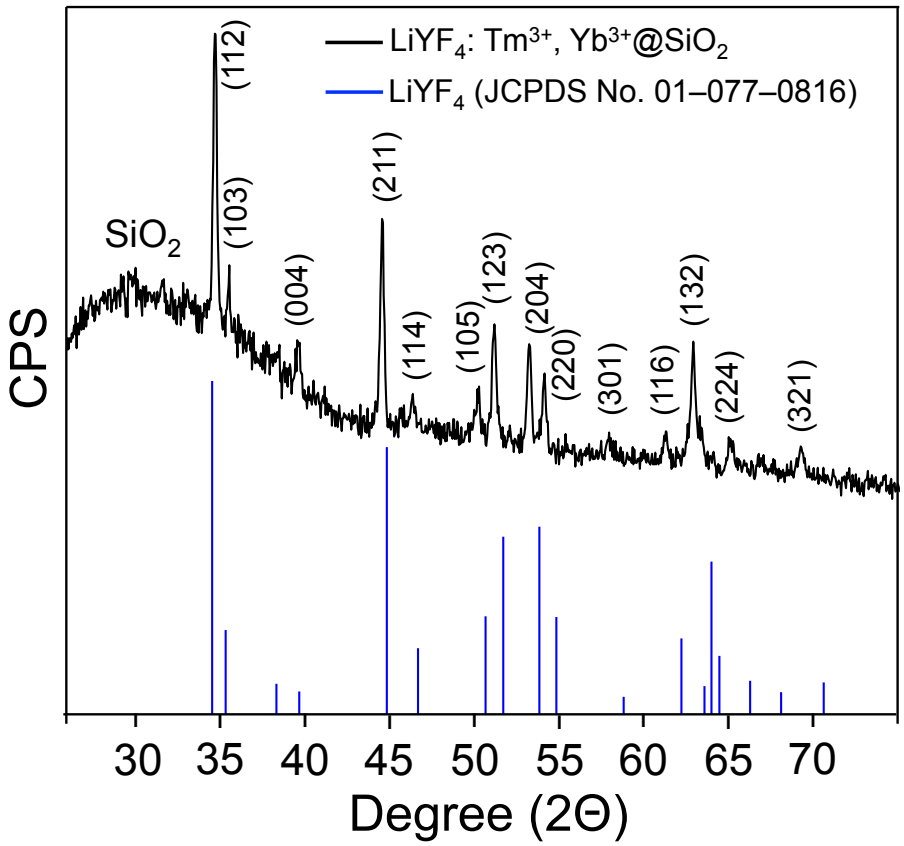


Fig. S4. XRD pattern of $LiYF_4$:Tm^{3+}, Yb^{3+}@SiO_2 UCNPs along with the corresponding reference pattern for $LiYF_4$ crystals (JCPDS-01-077-0816).

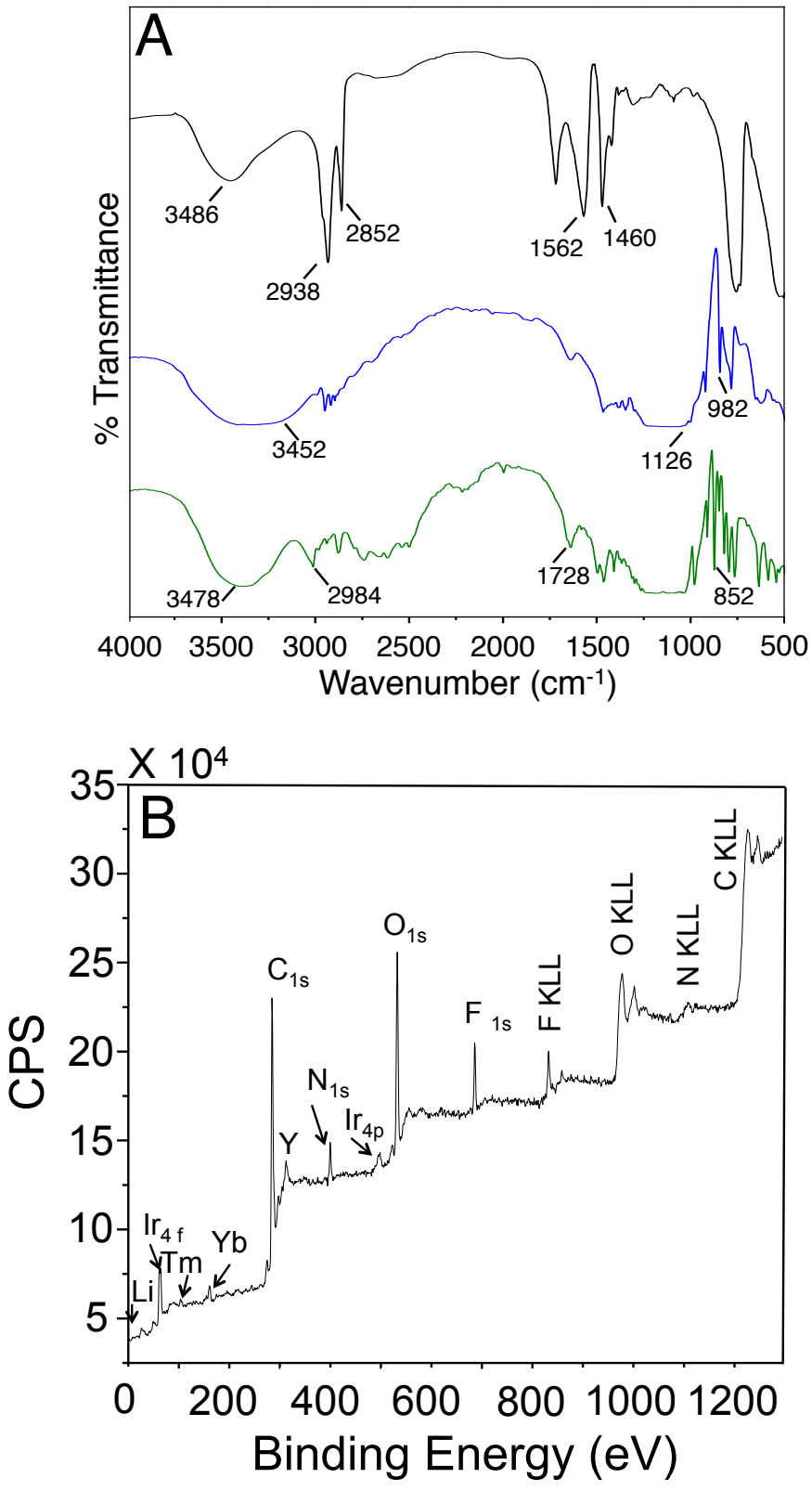


Fig. S5 (A) FTIR spectra of the parent oleate-capped $LiYF_4$:Tm^{3+}, Yb^{3+} UCNPs (black line), UCNPs@SiO_2 (blue line) and UCNPs@SiO_2@Ir nanostructures (green line). (B) XPS spectrum of the $LiYF_4$: Tm^{3+}, Yb^{3+}@SiO_2@Ir nanostructures.

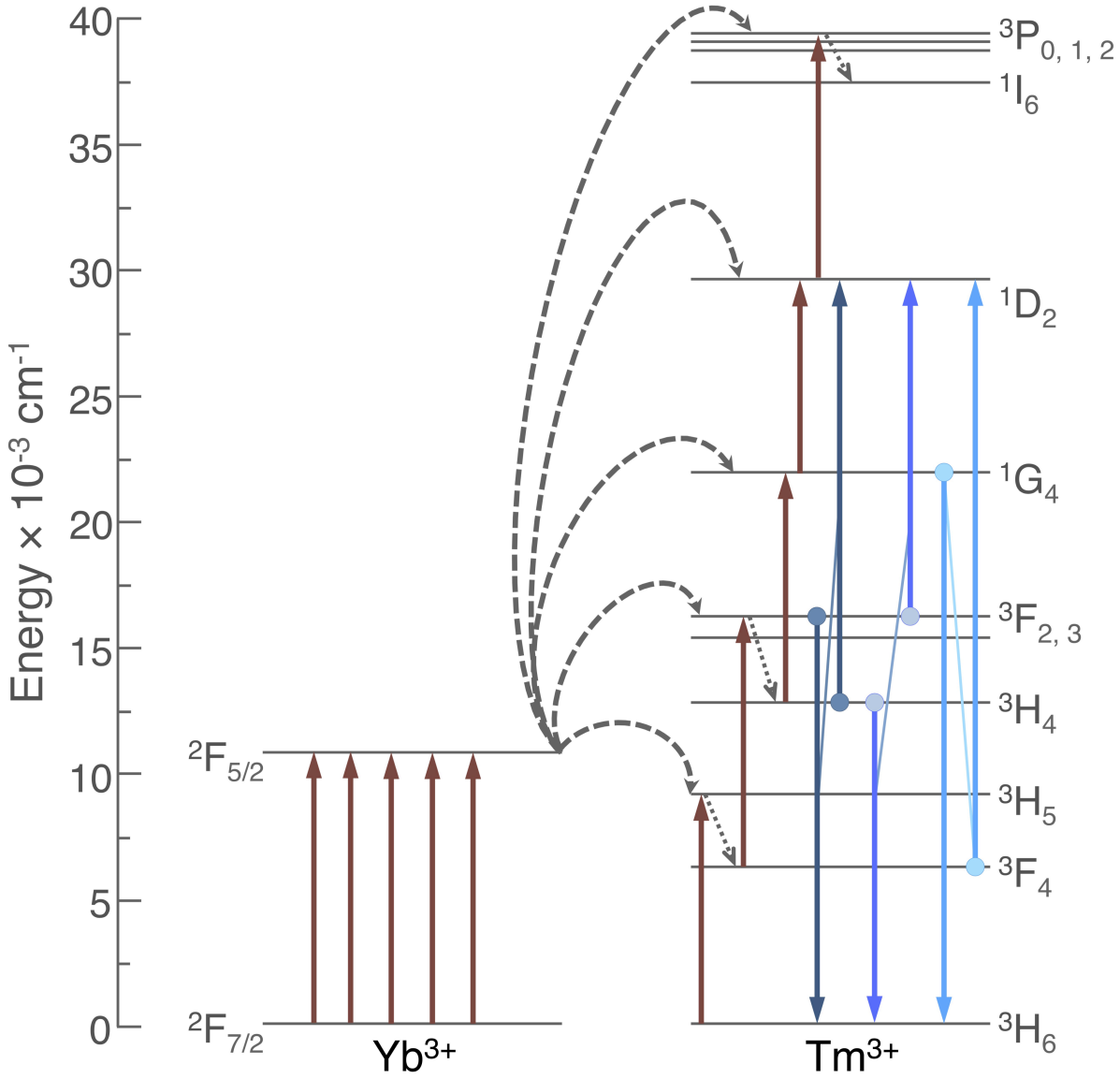


Fig. S6. Energy level diagrams of Yb^{3+} and Tm^{3+} ions showing the different mechanisms leading to the observed upconverted emissions following 980 nm excitation. Curved arrows indicate non-radiative energy transfer from excited Yb^{3+} ions to the Tm^{3+} ions sequentially populating the various excited states; The dotted arrows pointing downwards indicate multiphonon relaxation to the lower-lying levels; the connected arrows in various shades of blue show the cross-relaxation mechanisms possible for populating the $^1D_2$ state.