

Supporting Information

Small Upconversion-Ruthenium Nanohybrids for Cancer Theranostics

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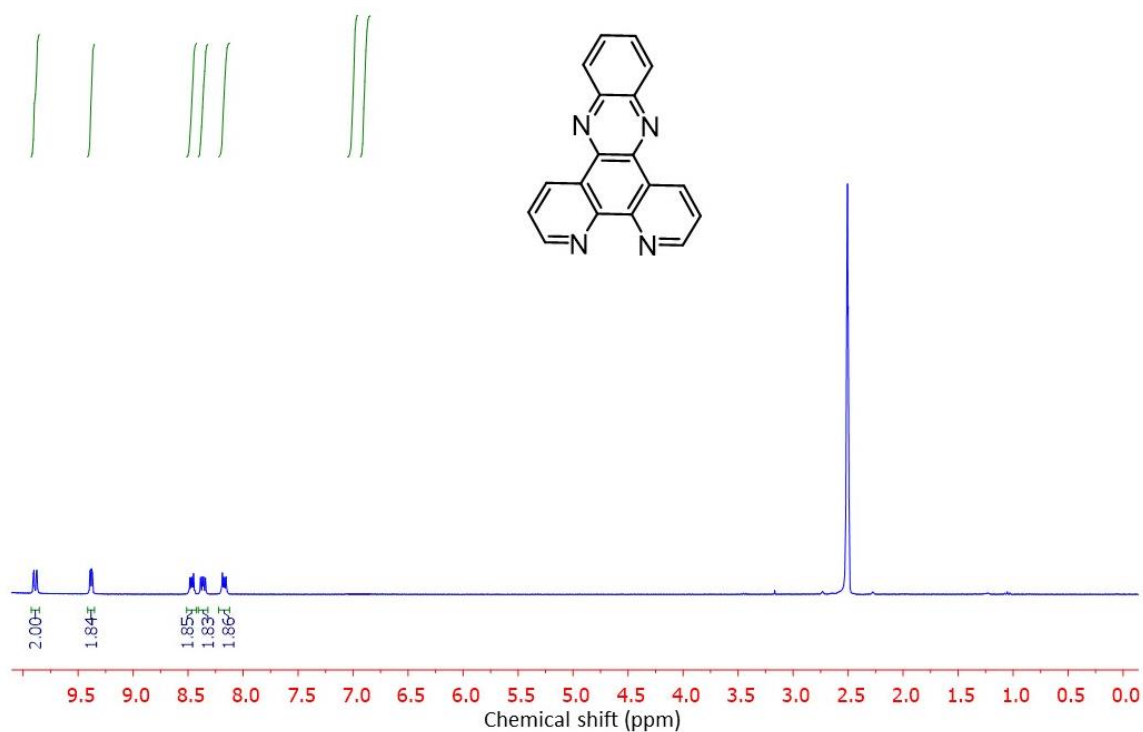


Figure S1: ¹H NMR spectrum (DMSO-d₆) of DPPZ.

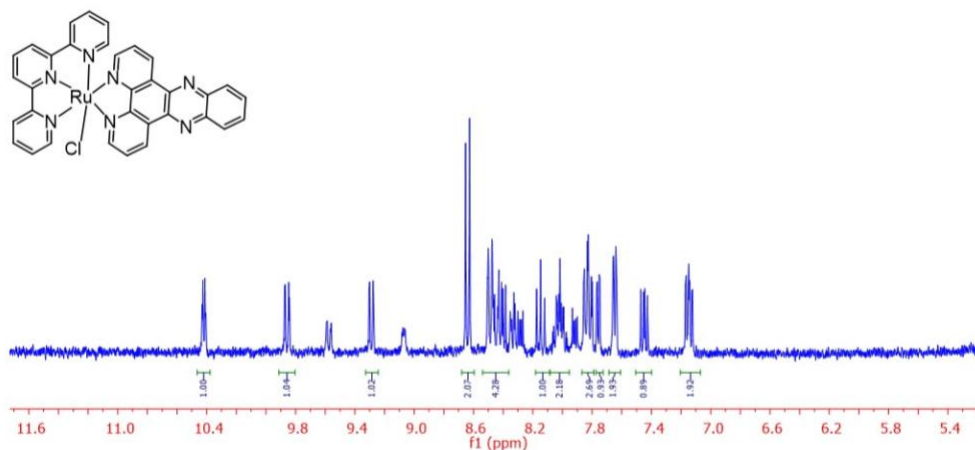


Figure S2. ¹H NMR spectrum (MeOD) of [Ru(tpy)DPPZ(Cl)]Cl⁻

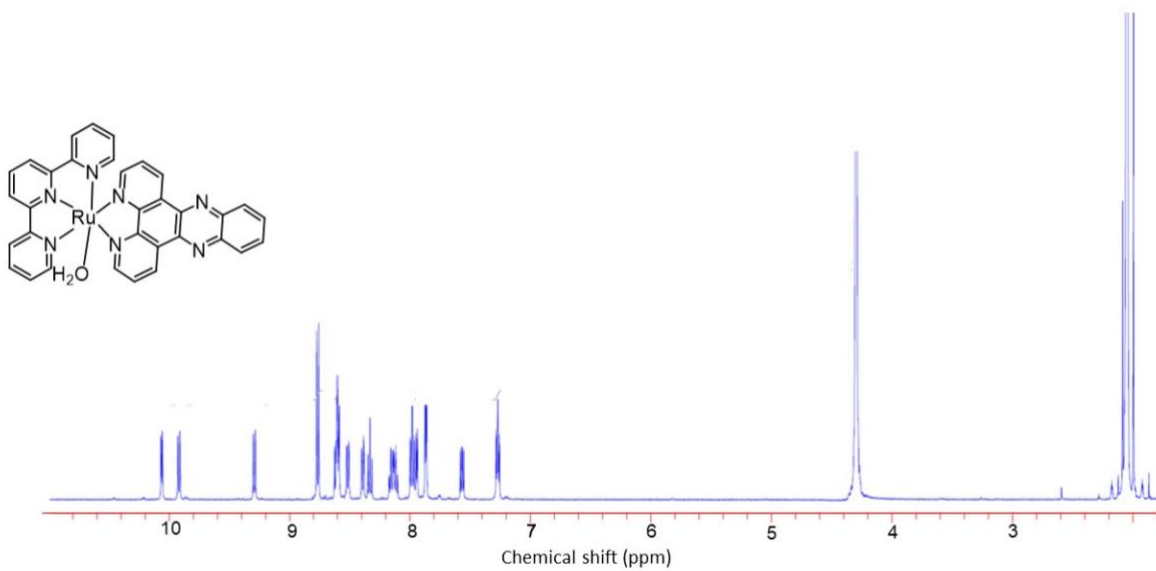


Figure S3. ¹H NMR spectrum (MeOD) of [Ru(tpy)DPPZ(H₂O)](PF₆)₂

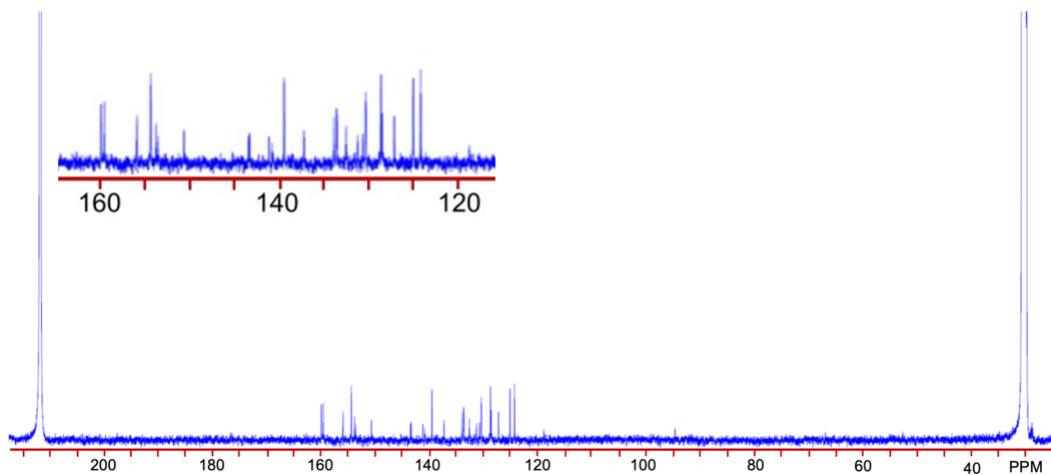


Figure S4. ^{13}C NMR spectrum (CD_3COCD_3 , 125 MHz) of $[\text{Ru}(\text{tpy})\text{DPPZ}(\text{H}_2\text{O})](\text{PF}_6)_2$

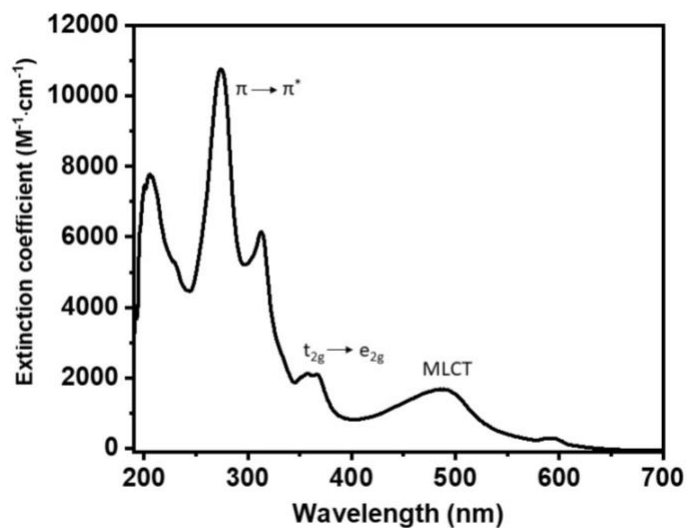


Figure S5. Absorption spectrum of $\text{Ru}(\text{tpy})\text{DPPZ}$ in MeOH . The intense UV band at ~ 270 nm comprises the $\pi \rightarrow \pi^*$ intra ligand transitions, the band at 352 nm corresponds to the $t_{2g} \rightarrow e_g$ metal centered state, and the band at 487 is indicative of the low-level MLCT of $\text{Ru}(\text{II})$.

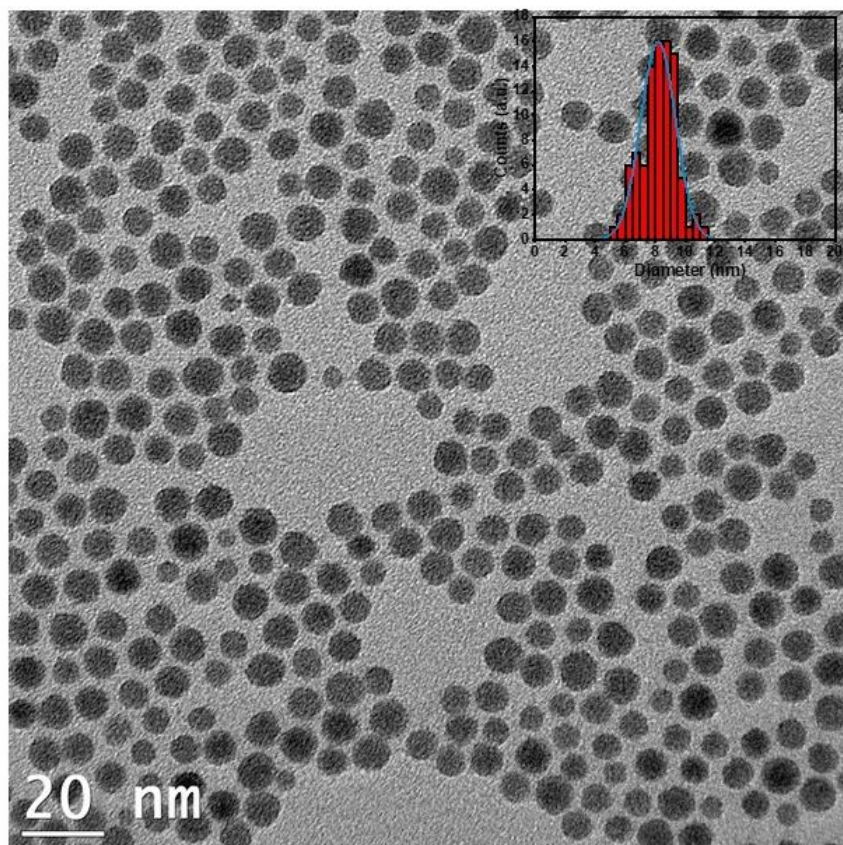


Figure S6. TEM micrograph of NaGdF₄: 25% Yb³⁺, 1% Nd³⁺, 0.5% Tm³⁺ UCNPs. The inset displays the size distribution indicating a size of 8.2 ± 1.6 nm.

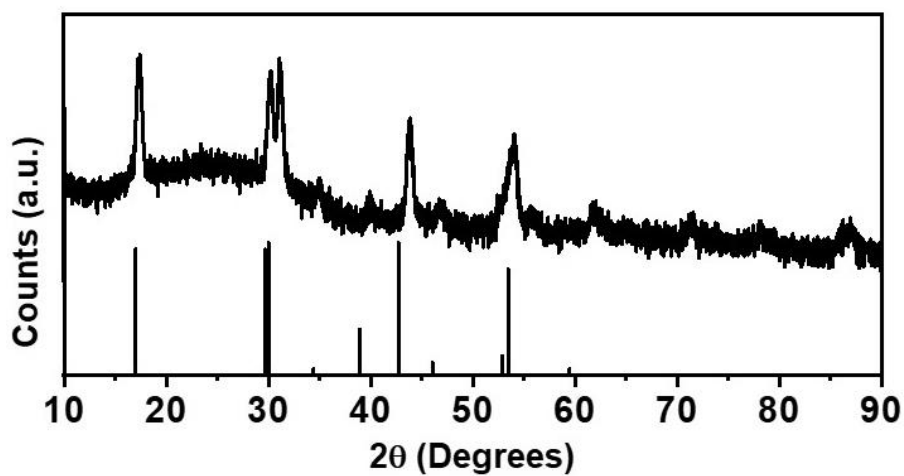


Figure S7. XRD diffraction pattern of OA-coated NaGdF₄ UCNPs (top) compared to (β-NaGdF₄) PDF card 27-0699 (bottom). The diffractions are assigned to the hexagonal β-phase.

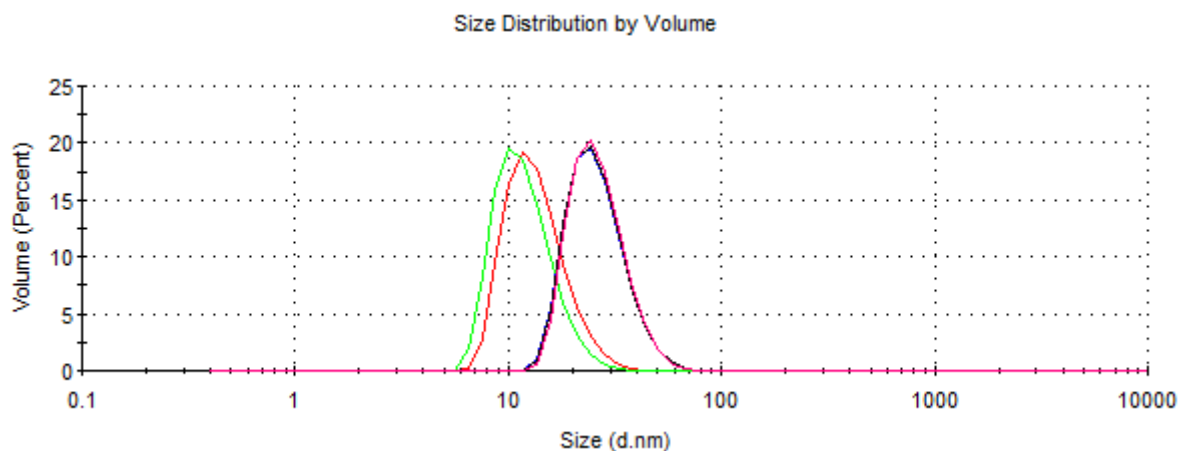


Figure S8. DLS spectra showing the hydrodynamic diameter (D_h) of OA-coated UCNPs (green), mSiO₂-UCNPs (red), azo-mSiO₂ UCNPs (purple) and Ru(tpy)DPPZ-loaded azo-mSiO₂-UCNPs (blue).

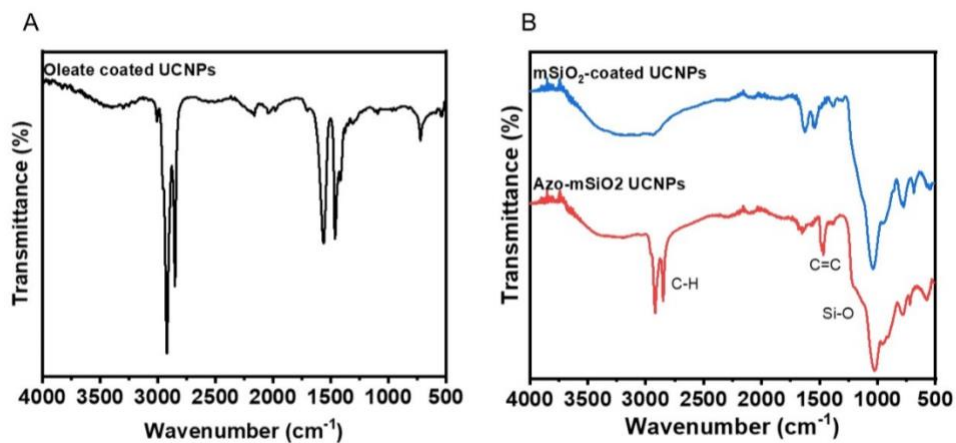


Figure S9. FT-IR spectra of **A:** OA-coated UCNPs and **B:** mSiO₂-UCNPs and azo-mSiO₂-UCNPs.

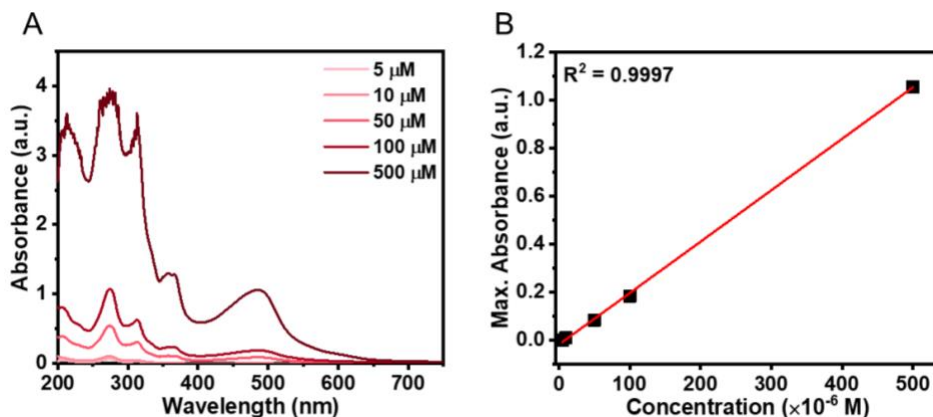


Figure S10. A: Absorption spectra for Ru(tpy)DPPZ. **B:** Calibration curve to quantify the concentration of for Ru(tpy)DPPZ embedded in azo-mSiO₂-UCNPs.

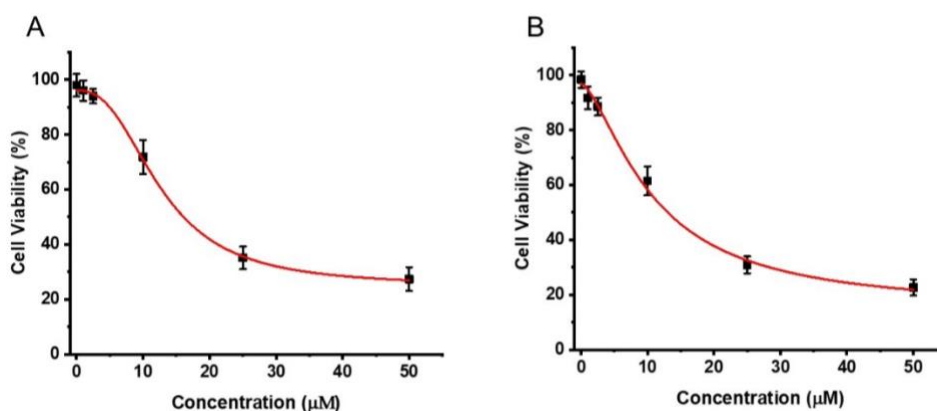


Figure S11. Cytotoxicity of Ru(tpy)DPPZ (**A**) and cisplatin (**B**) in MCF-7 cancer cell lines. IC₅₀ values were calculated using GraphPad software (Prism 7.0). Data are expressed as mean ± SD from a representative of three independent experiments

Table S1. Volume-weighted DLS particle size distributions (D_h) for azo-mSiO₂-UCNPs and Ru(tpy)DPPZ loaded azo-mSiO₂-UCNPs, incubated in DMEM supplemented with 10% fetal bovine serum. All measurements were done in triplicates. Errors present standard deviations.

UCNP samples	Particle size (D_h) in nm (PDI) ^[a]				
	as synthesized	+24 h	+48 h	+72 h	+7 days
azo-mSiO ₂ -UCNPs	26.8 ± 2.3 (0.18) ^a	32.4 ± 1.2 (0.19) ^a	36.4 ± 2.4 (0.21) ^a	36.4 ± 3.1 (0.20) ^a	38.8 ± 3.4 (0.24) ^a
Ru(tpy)DPPZ-loaded azo-mSiO ₂ -UCNPs	26.8 ± 2.5 (0.21) ^a	36.1 ± 2.6 (0.24) ^a	37.8 ± 2.8 (0.22) ^a	39.1.2 ± 3.6 (0.22) ^a	44.7 ± 4.2 (0.28) ^a

[a] PDI = polydispersity index