Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information for

Lutetium(III) porphyrinoids as effective triplet photosensitizers for photon upconversion based on triplet-triplet annihilation (TTA)

Zi-Shu Yang, Yingying Ning, Hao-Yan Yin and Jun-Long Zhang*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

Email: zhangjunlong@pku.edu.cn

Contents

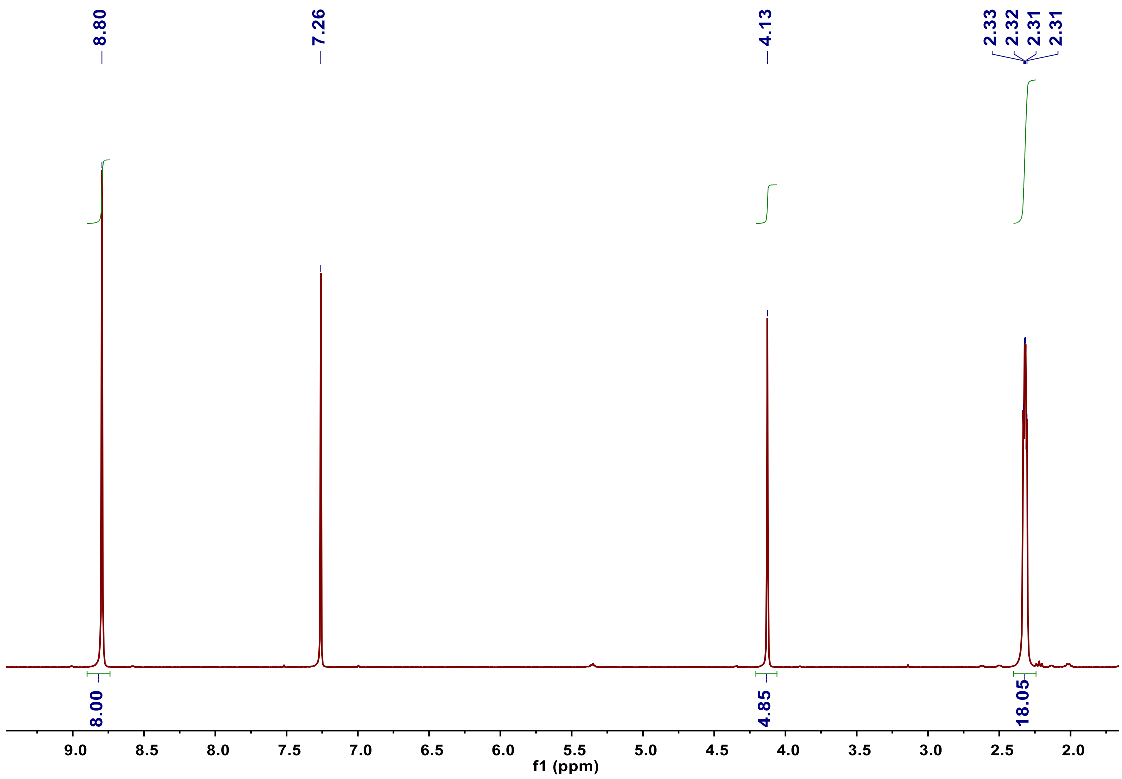


Fig. S1 ^{1}H NMR spectrum of **Lu-1** (400 MHz, $CDCl_3$).

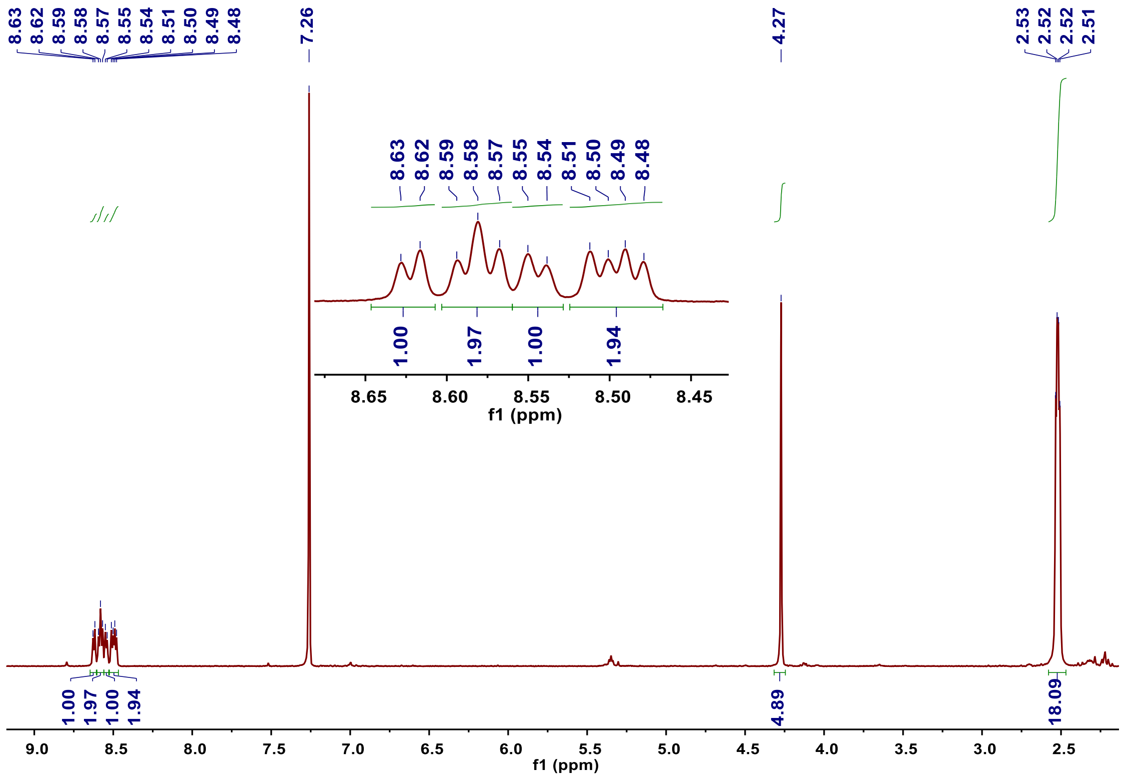


Fig. S2 ^{1}H NMR spectrum of **Lu-2** (400 MHz, $CDCl_3$).

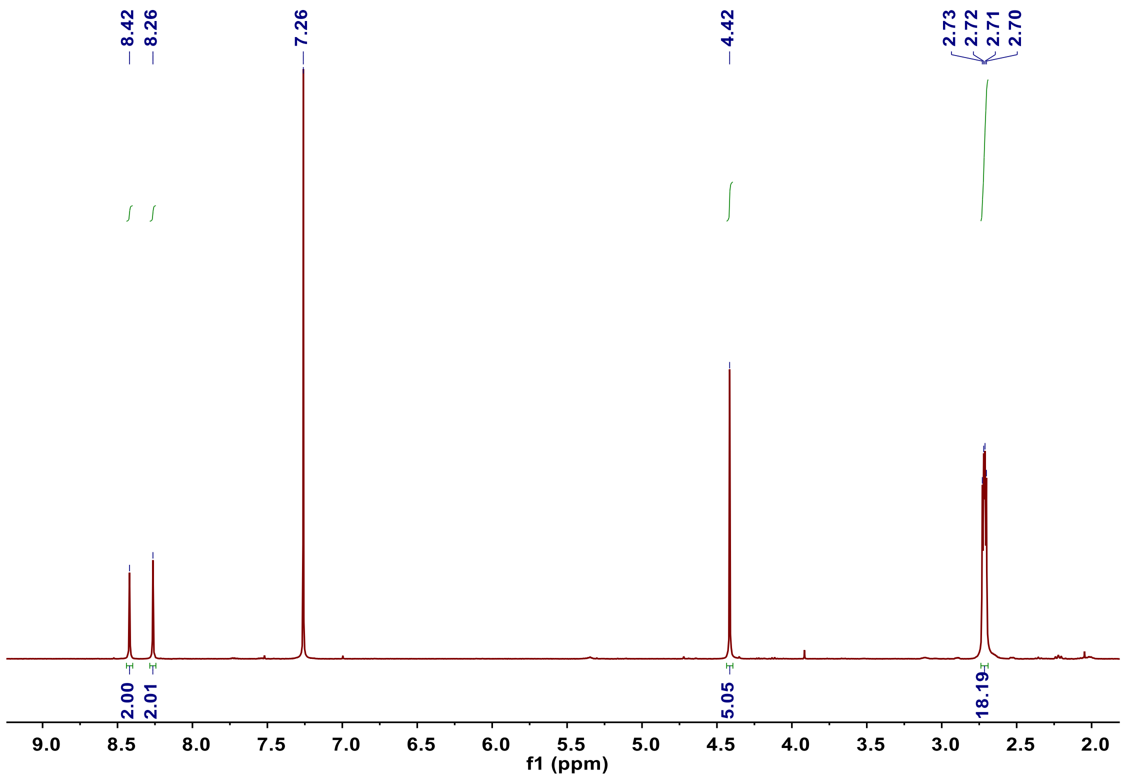


Fig. S3 ^{1}H NMR spectrum of **Lu-3** (400 MHz, $CDCl_3$).

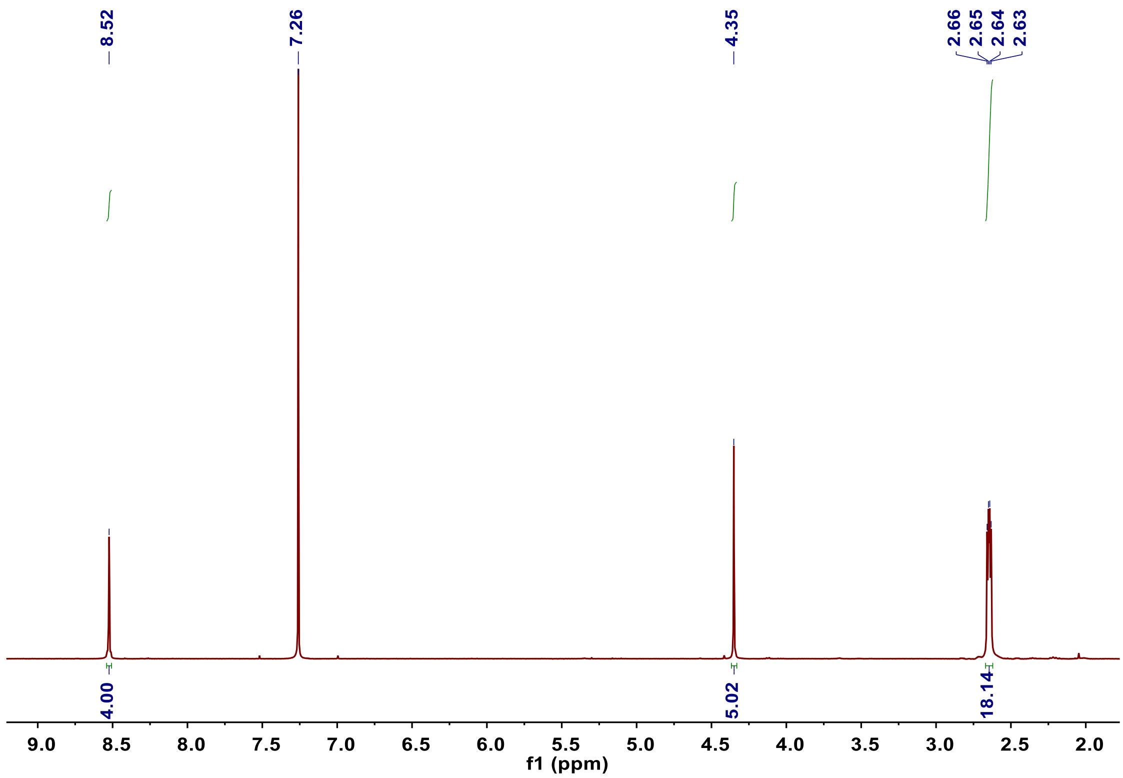


Fig. S4 ^{1}H NMR spectrum of **Lu-4** (400 MHz, $CDCl_3$).

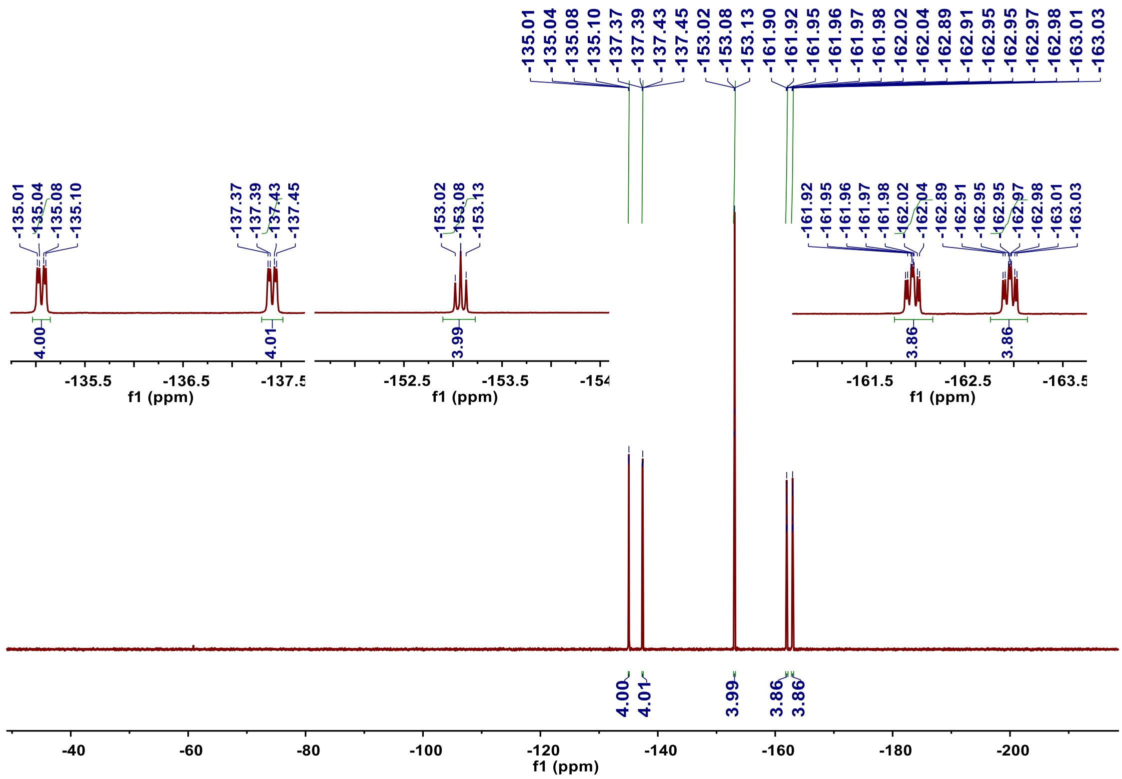


Fig. S5 ^{19}F NMR spectrum of **Lu-1** (377 MHz, $CDCl_3$).

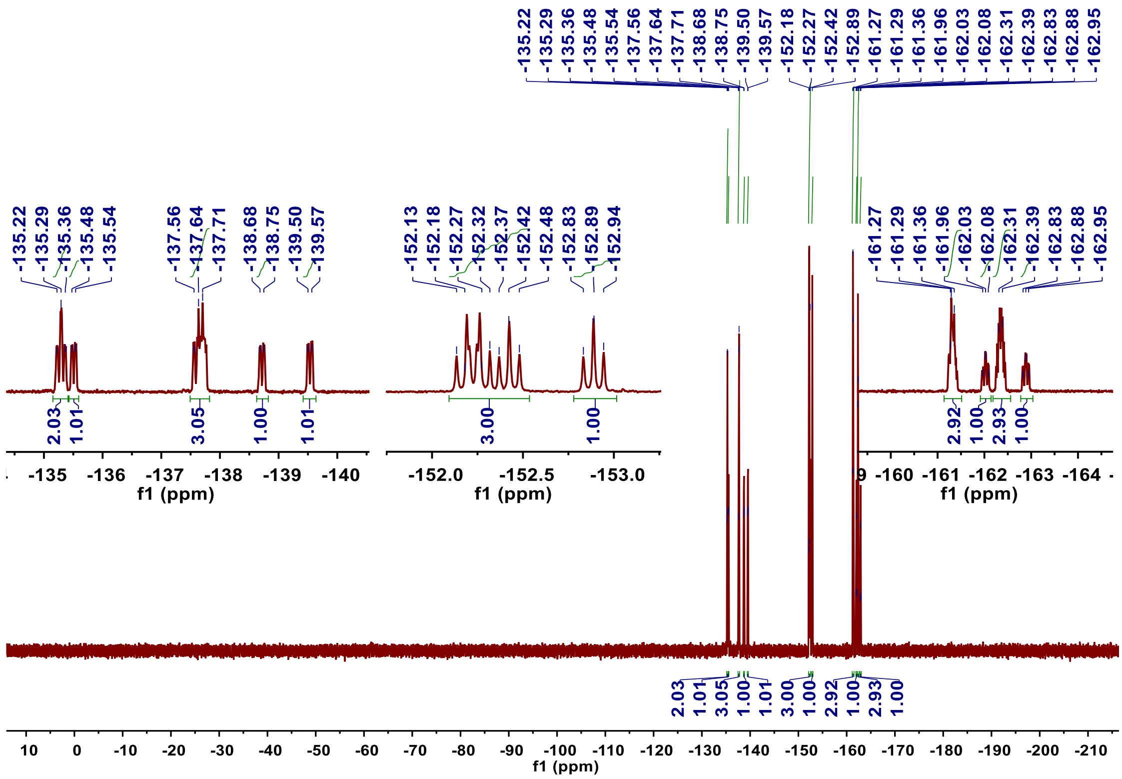


Fig. S6 ^{19}F NMR spectrum of **Lu-2** (377 MHz, $CDCl_3$).

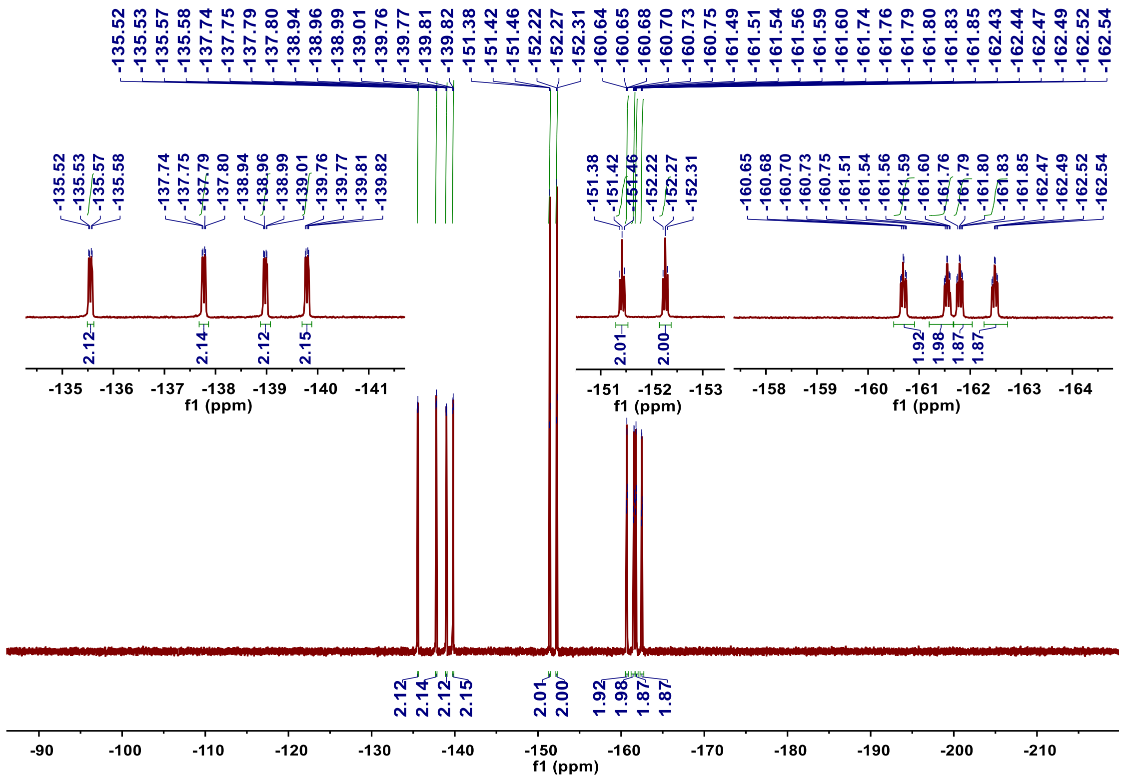


Fig. S7 ^{19}F NMR spectrum of **Lu-3** (471 MHz, $CDCl_3$).

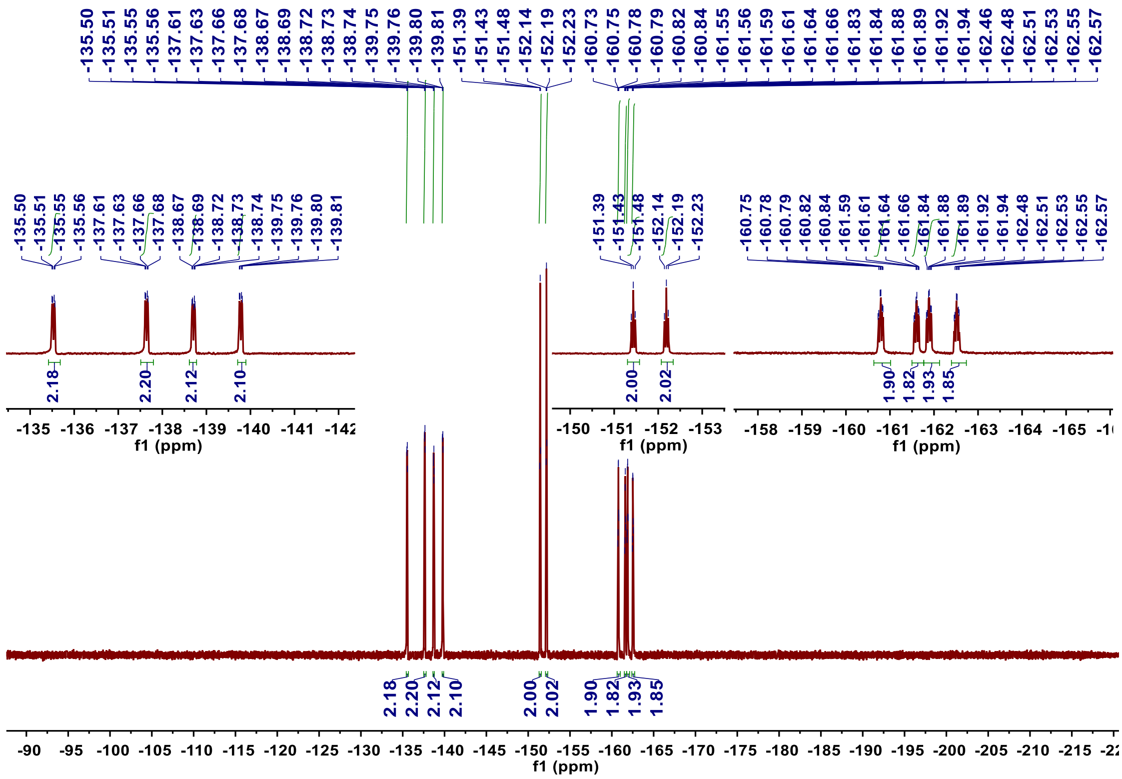


Fig. S8 ^{19}F NMR spectrum of **Lu-4** (471 MHz, $CDCl_3$).

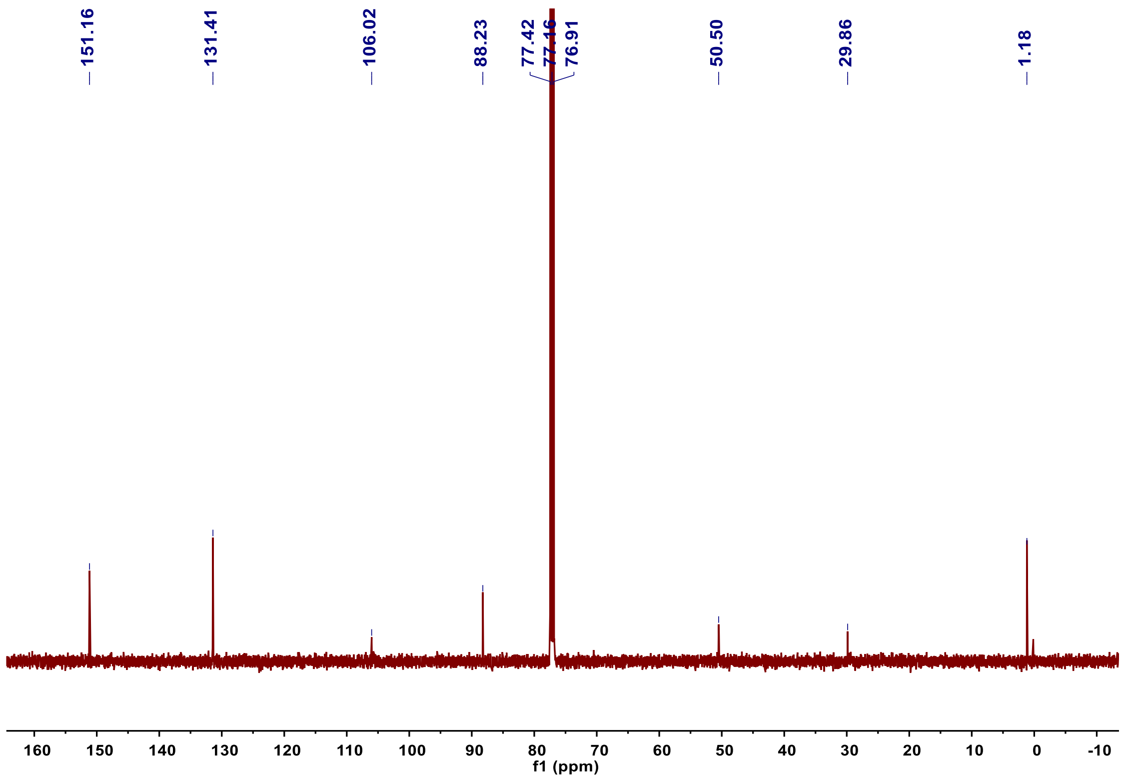


Fig. S9 ^{13}C NMR spectrum of **Lu-1** (126 MHz, $CDCl_3$).

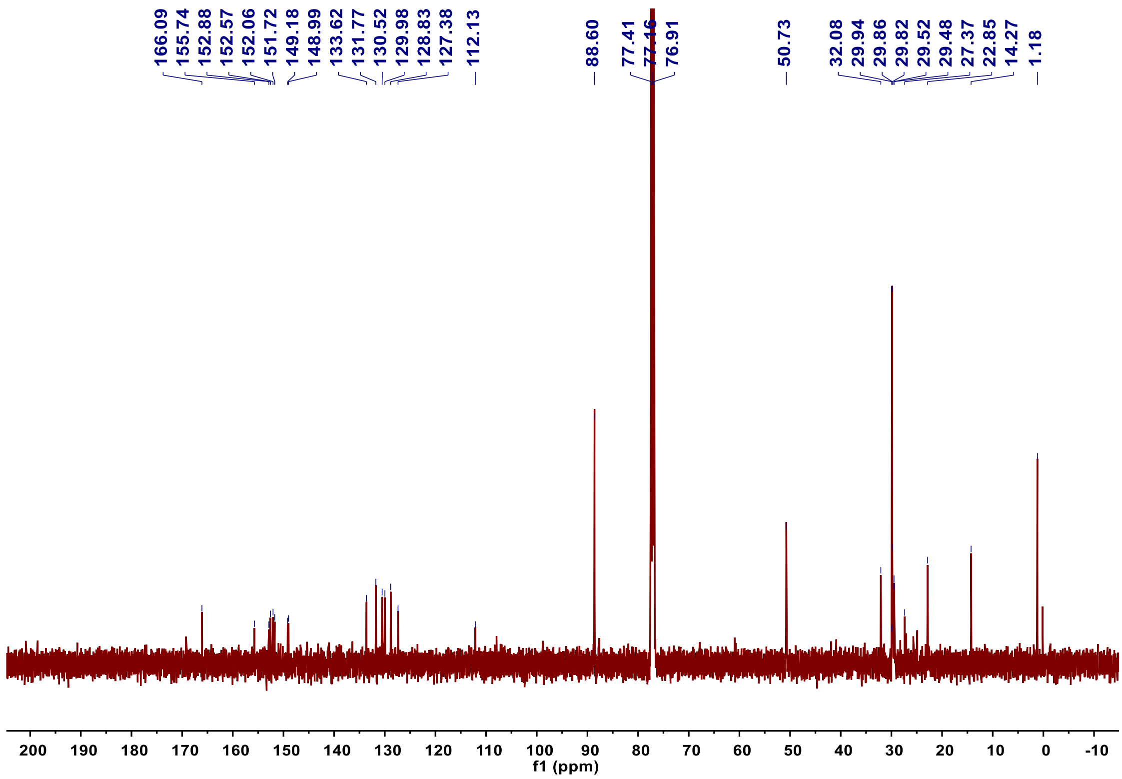


Fig. S10 ^{13}C NMR spectrum of **Lu-2** (126 MHz, $CDCl_3$).

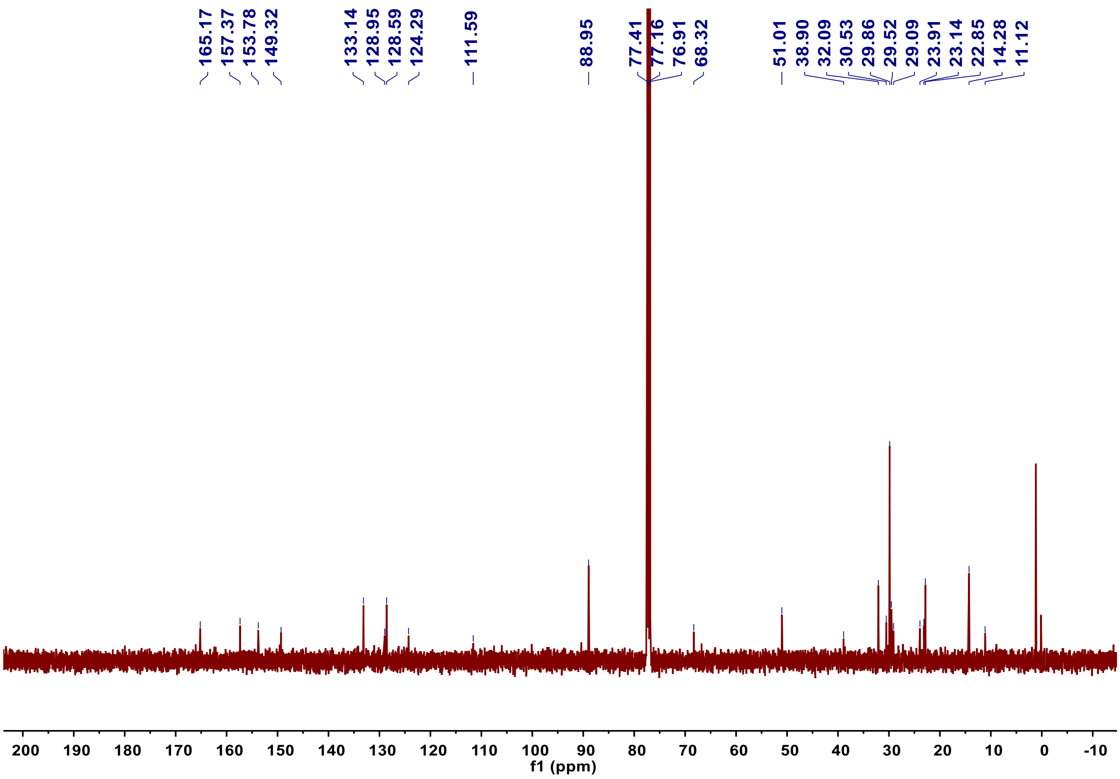


Fig. S11 ^{13}C NMR spectrum of **Lu-3** (126 MHz, $CDCl_3$).

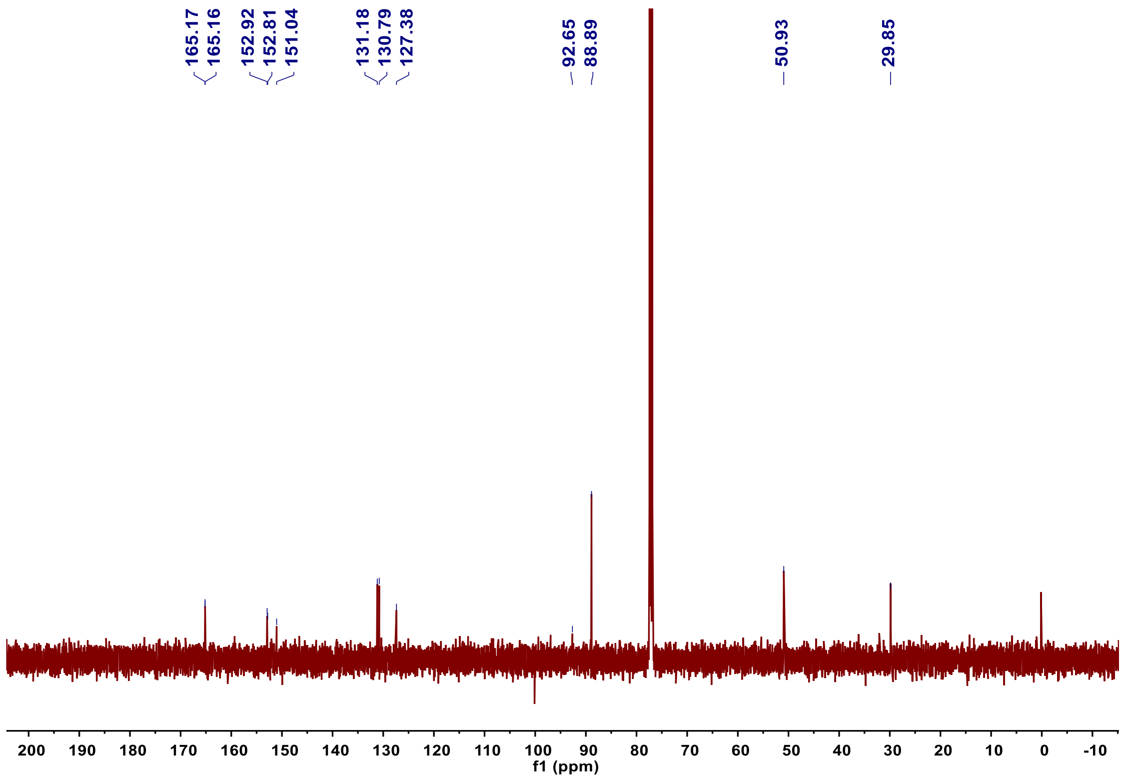


Fig. S12 ^{13}C NMR spectrum of **Lu-4** (126 MHz, $CDCl_3$).

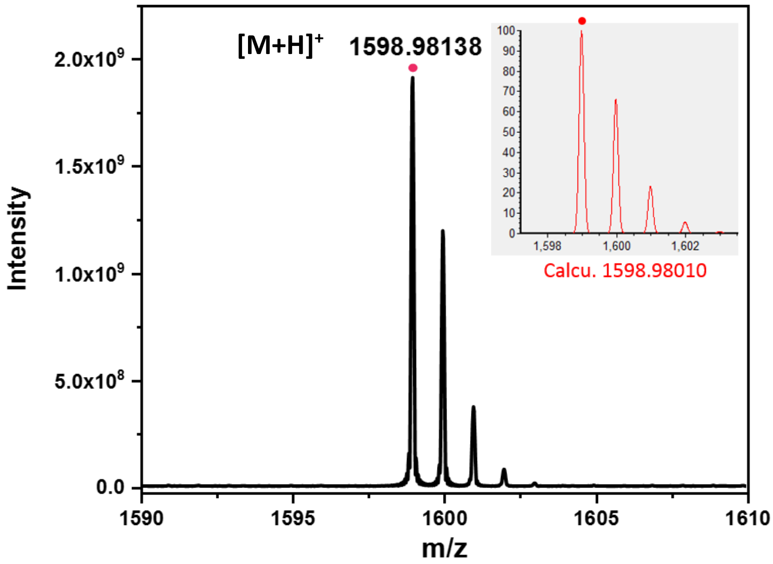


Fig. S13 HR ESI-MS spectrum of **Lu-1**. Inset presents the simulated spectrum.

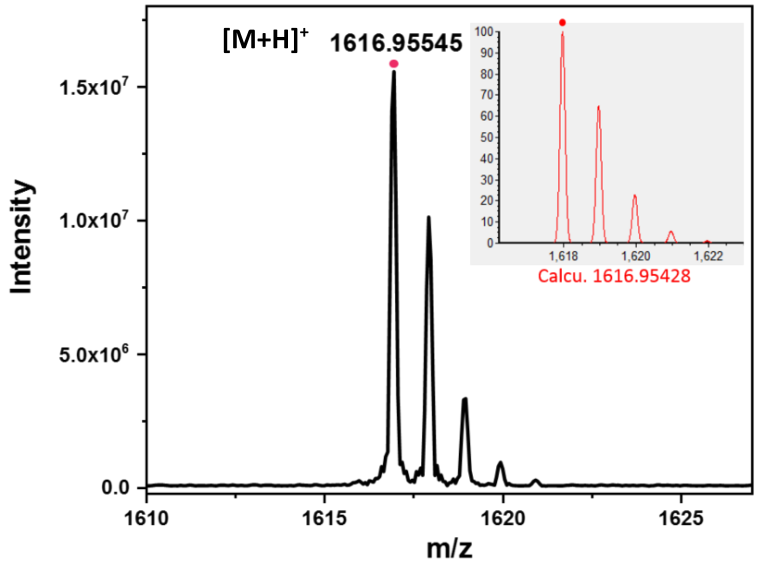


Fig. S14 HR ESI-MS spectrum of **Lu-2**. Inset presents the simulated spectrum.

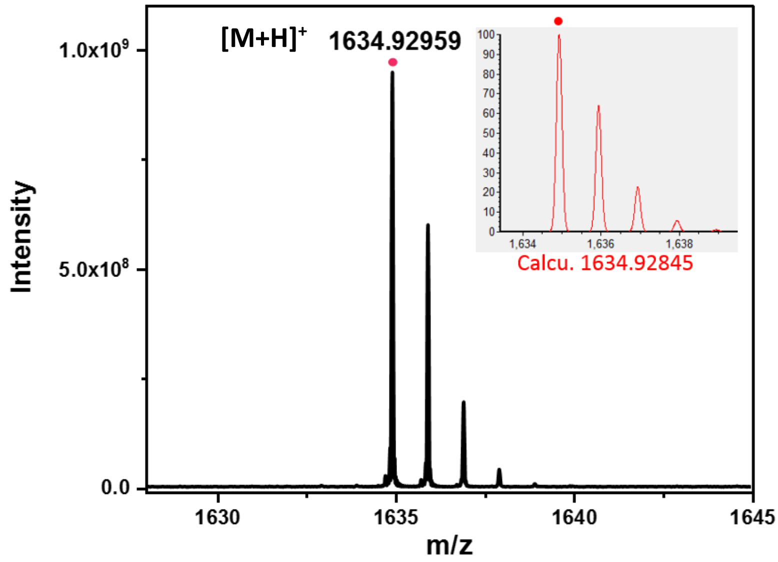


Fig. S15 HR ESI-MS spectrum of **Lu-3**. Inset presents the simulated spectrum.

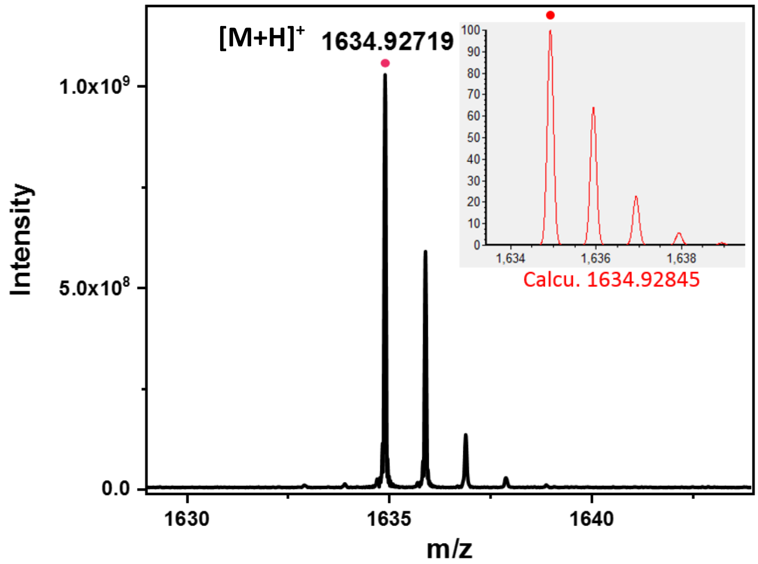


Fig. S16 HR ESI-MS spectrum of **Lu-4**. Inset presents the simulated spectrum.

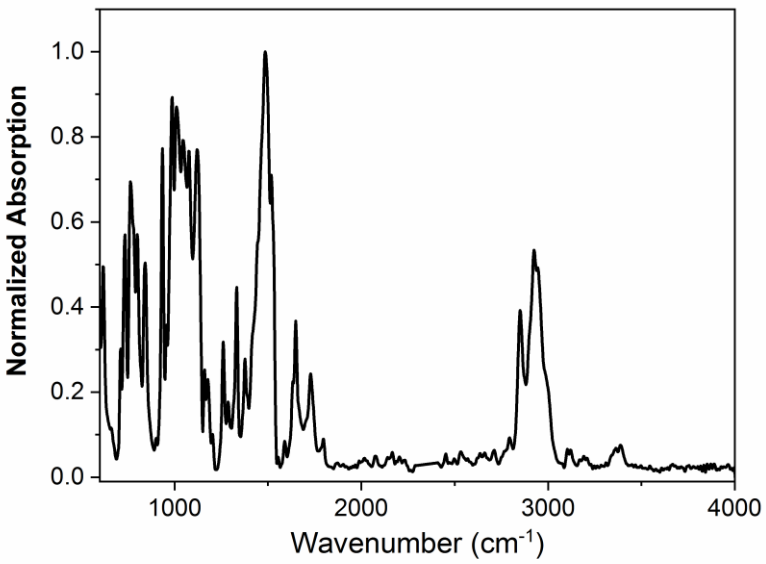


Fig. S17 Normalized FT-IR spectrum of **Lu-1**.

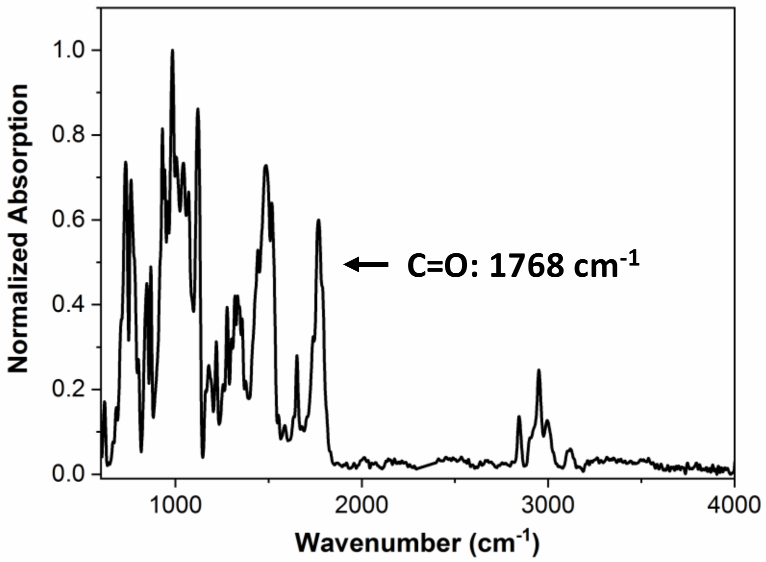


Fig. S18 Normalized FT-IR spectrum of **Lu-2**.

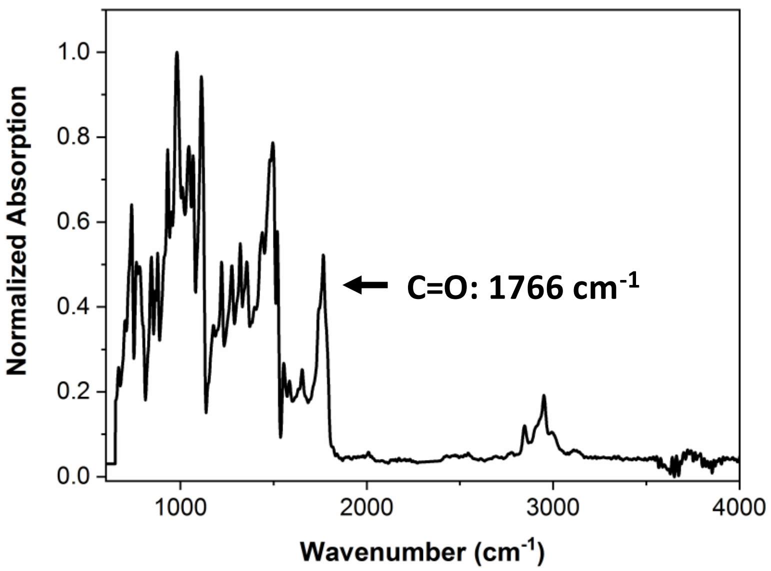


Fig. S19 Normalized FT-IR spectrum of **Lu-3**.

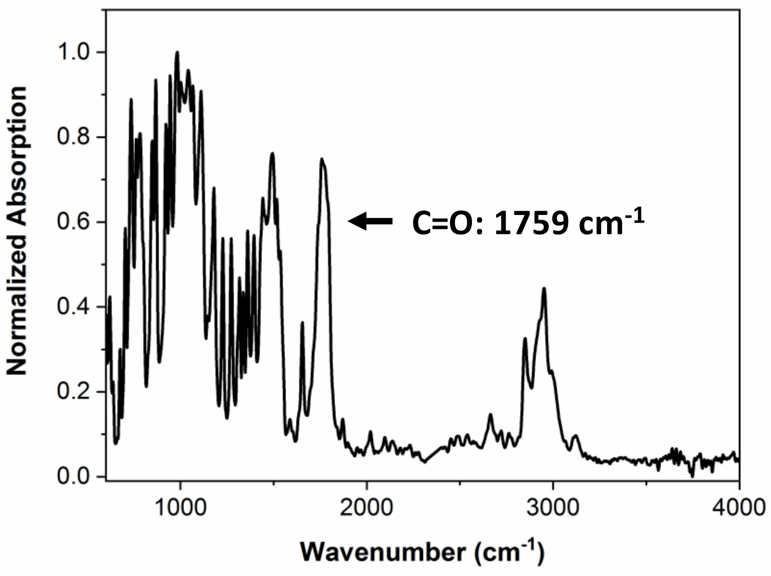


Fig. S20 Normalized FT-IR spectrum of **Lu-4**.

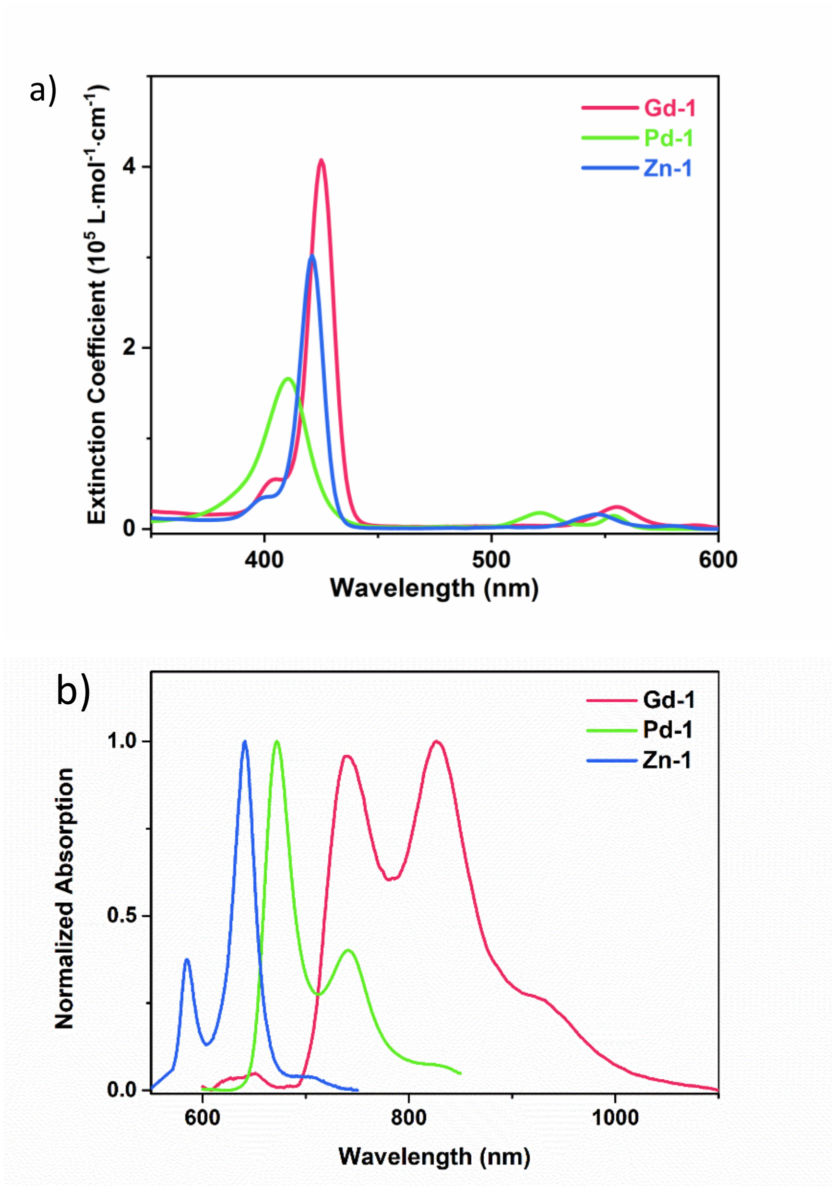


Fig. S21 (a) UV/Vis absorption spectra and (b) normalized emission spectra (excited at Soret bands) of **M-1** (M = Gd, Pd, Zn) in degassed toluene at room temperature.

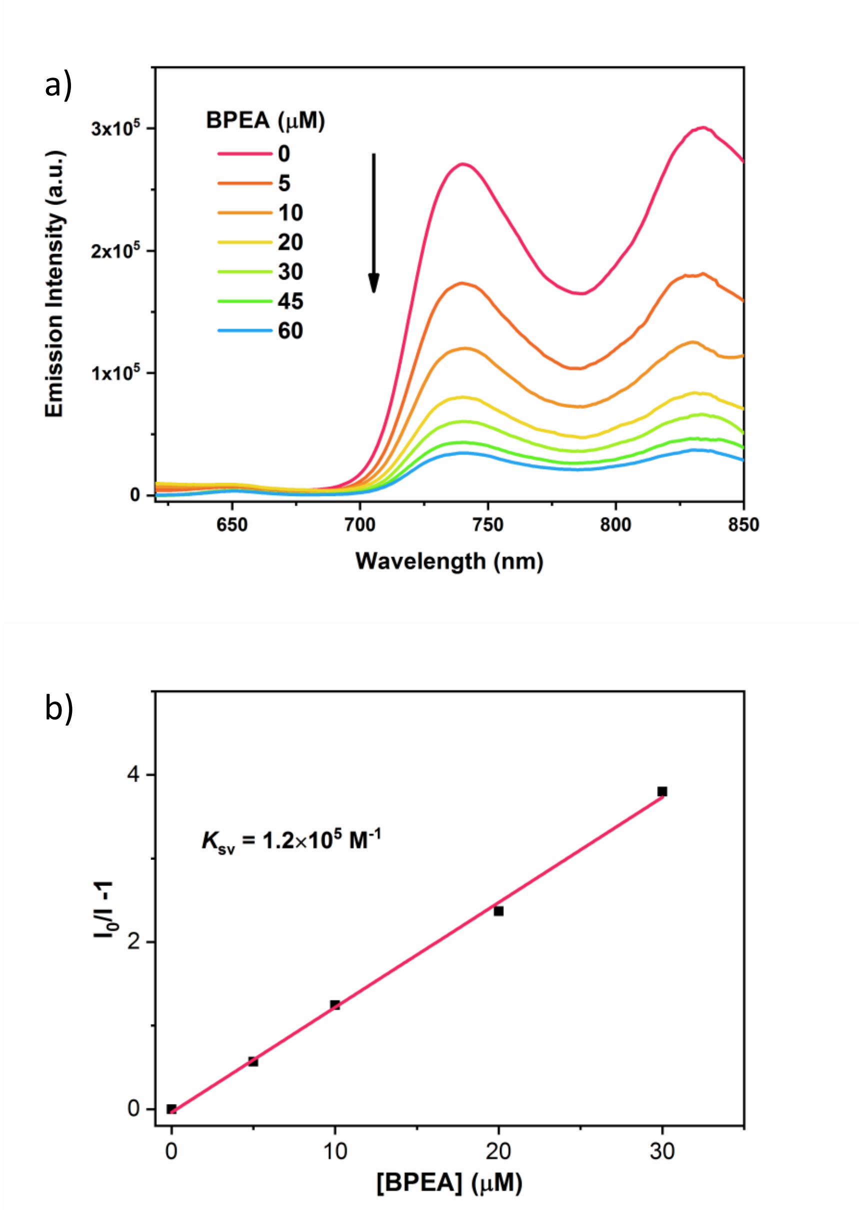


Fig. S22 a) The phosphorescence spectra of **Gd-1** with BPEA in different concentration in degassed toluene; b) the Stern–Volmer plot of **Gd-1** with BPEA in degassed toluene. ([**Gd-1**] = 0.5 μM, λ_{ex} = 561 nm)

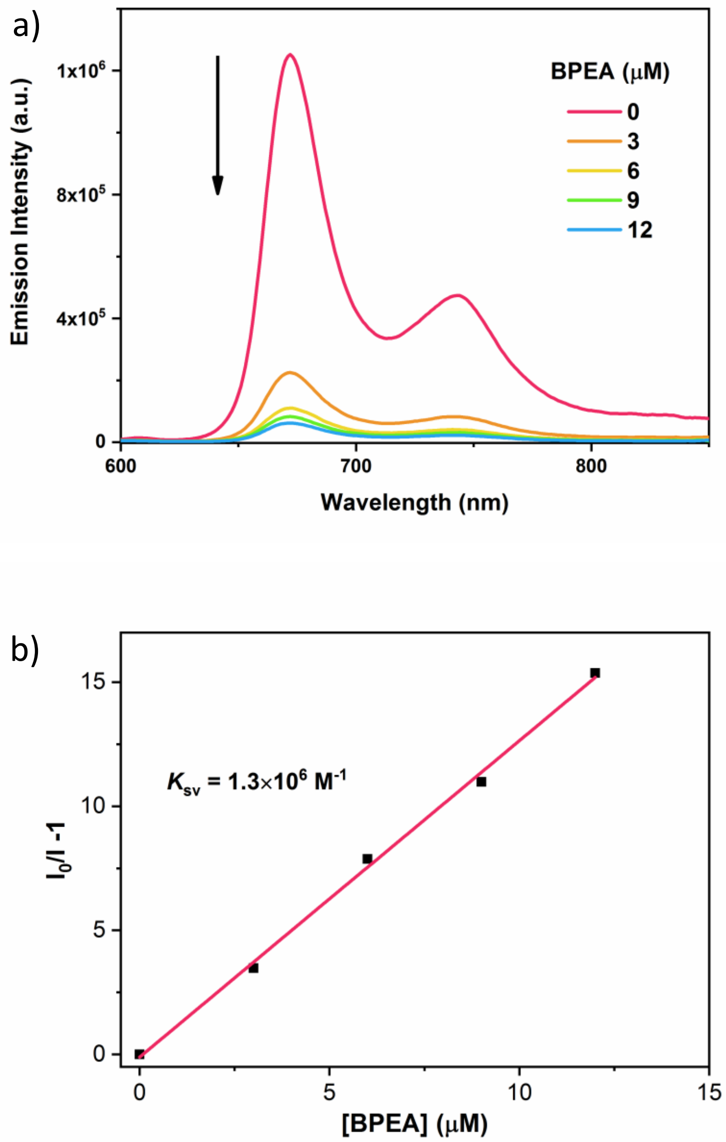


Fig. S23 a) The phosphorescence spectra of **Pd-1** with BPEA in different concentration in degassed toluene; b) the Stern–Volmer plot of **Pd-1** with BPEA in degassed toluene. ([**Pd-1**] = 0.5 μM, λ_{ex} = 561 nm)

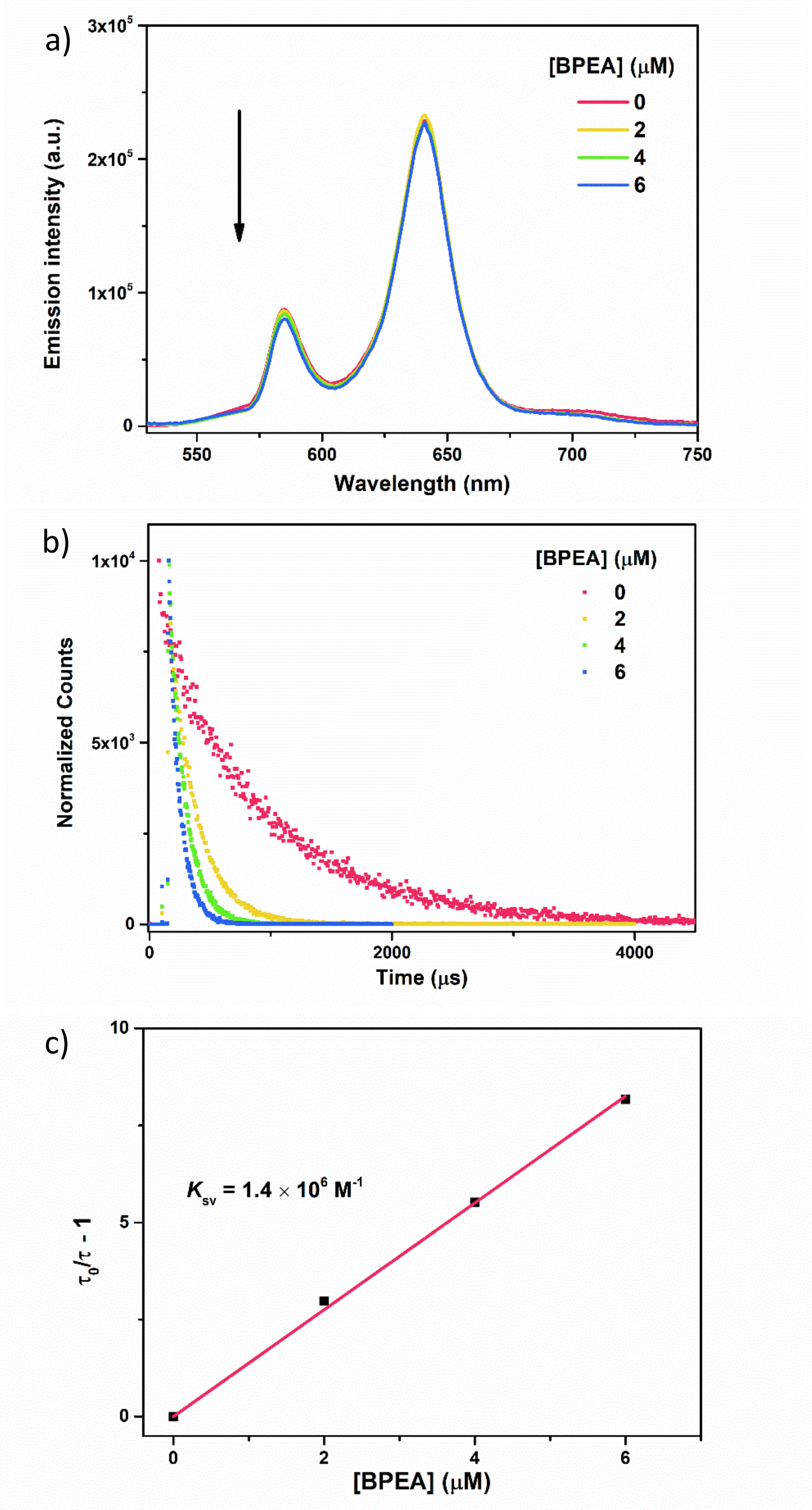


Fig. S24 a) The emission and b) decay (λ_{em} = 715 nm) spectra of **Zn-1** with BPEA in different concentration in degassed toluene; c) the Stern–Volmer plot of **Zn-1** with BPEA in degassed toluene (K_{sv} is determined according to $\tau_0/\tau = 1 + K_{SV}$[BPEA], due to the weak phosphorescence of **Zn-1**). ([**Zn-1**] = 0.5 μM, λ_{ex} = 561 nm)

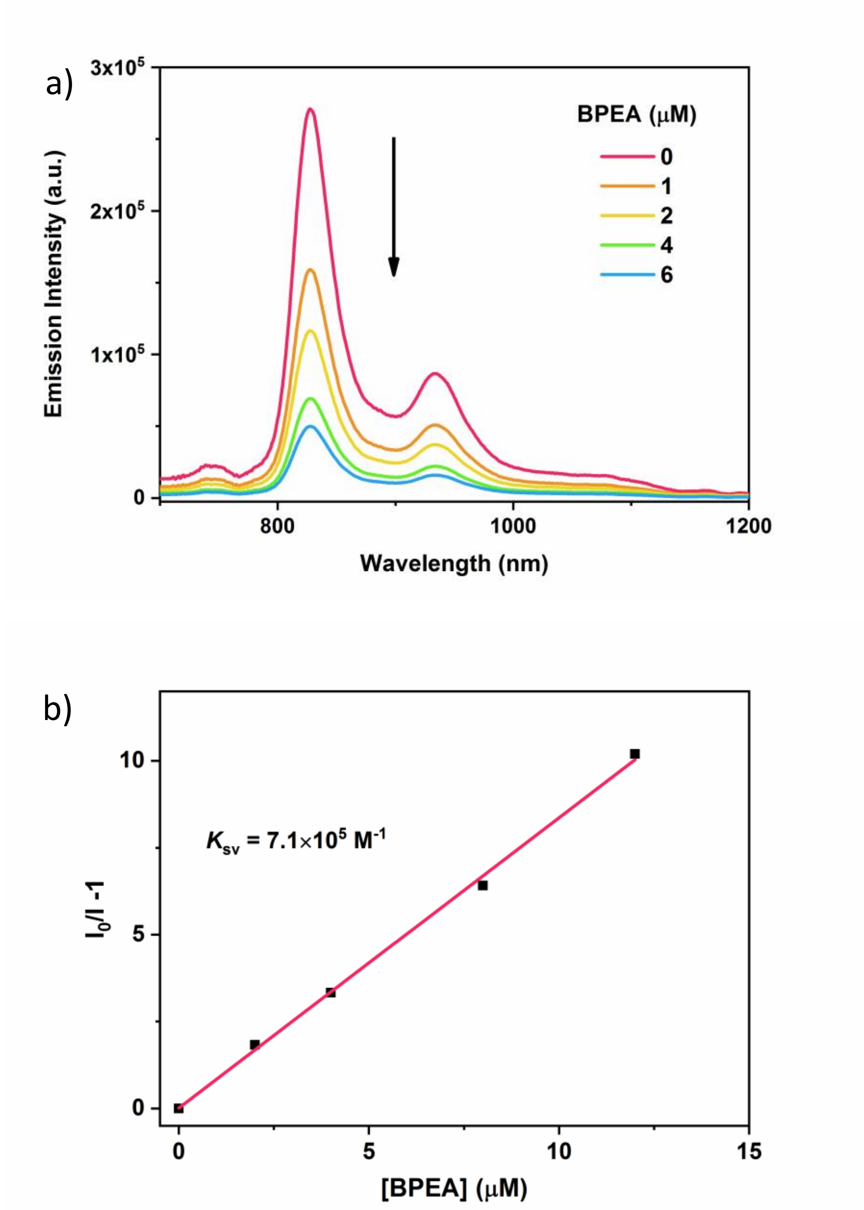
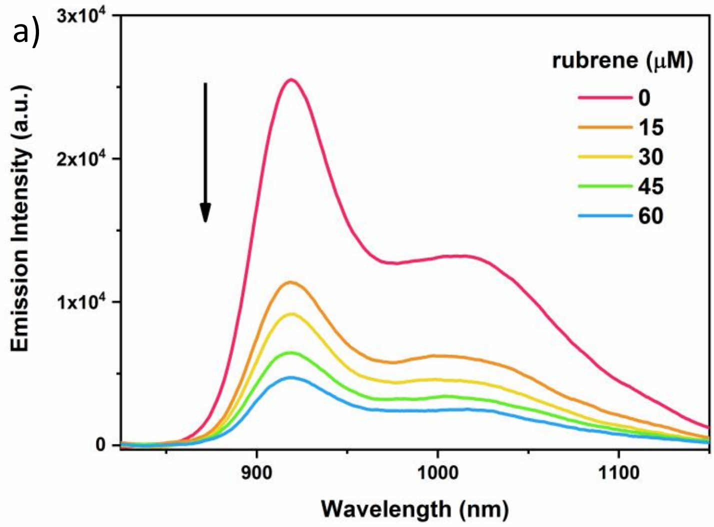


Fig. S25 a) The phosphorescence spectra of **Lu-2** with BPEA in different concentration in degassed toluene; b) the Stern–Volmer plot of **Lu-2** with BPEA in degassed toluene. ([**Lu-2**] = 0.5 μM, λ_{ex} = 561 nm)



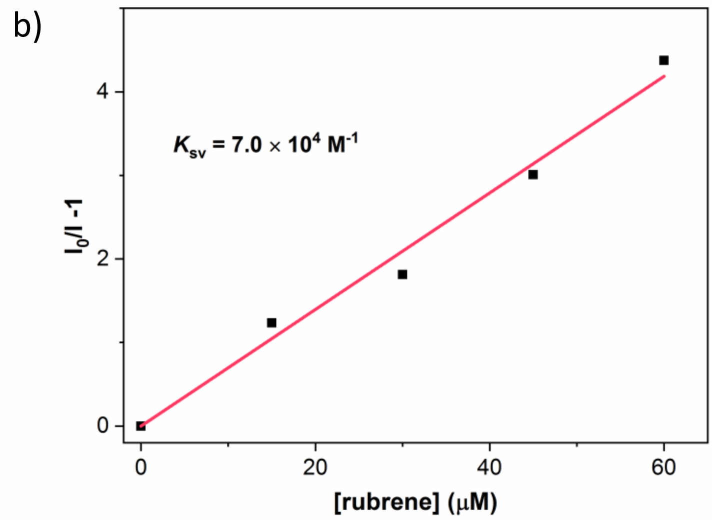


Fig. S26 a) The phosphorescence spectra of **Lu-3** with rubrene in different concentration in degassed toluene; b) the Stern–Volmer plot of **Lu-3** with rubrene in degassed toluene. ([**Lu-3**] = 0.5 μM, λ_{ex} = 639 nm)

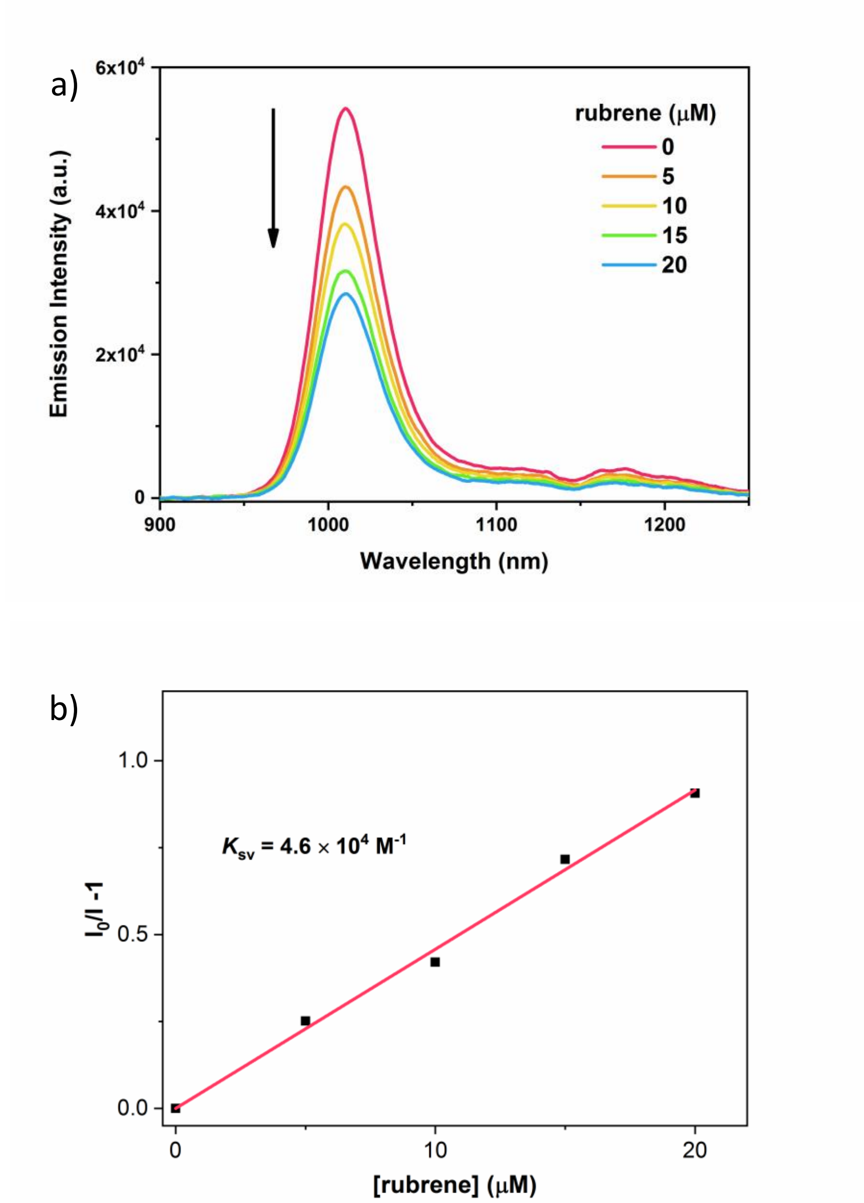


Fig. S27 a) The phosphorescence spectra of **Lu-4** with rubrene in different concentration in degassed toluene; b) the Stern–Volmer plot of **Lu-4** with rubrene in degassed toluene. ([**Lu-4**] = 0.5 μM, λ_{ex} = 659 nm)

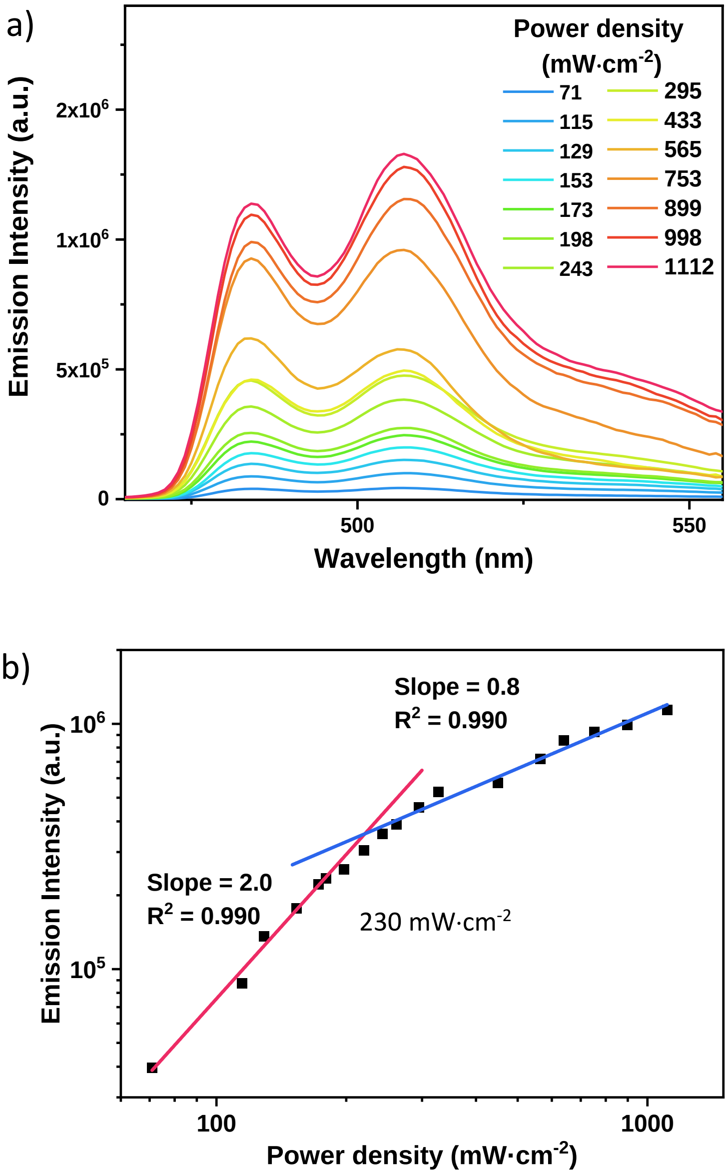
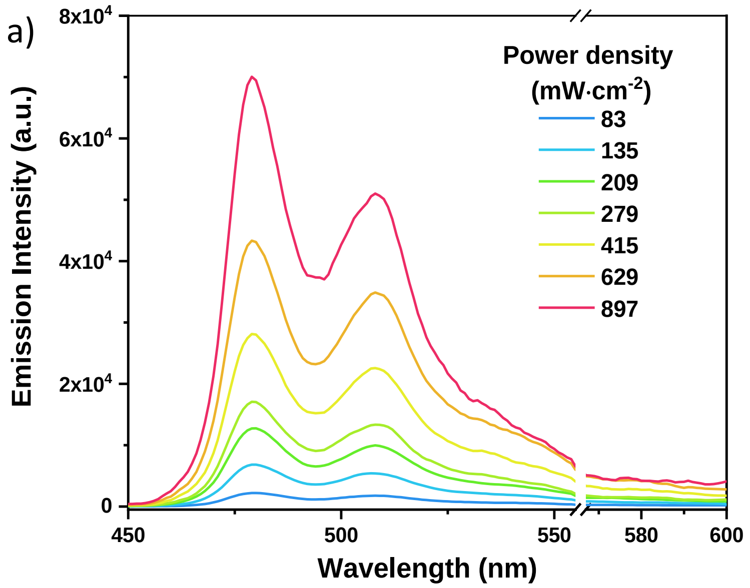


Fig. S28 a) Upconverted fluorescence spectra of **Gd-1**/BPEA at different excitation power; b) the double logarithmic plots of upconversion intensity at 480 nm measured as a function of power density of a 561 nm incident laser for **Gd-1**/BPEA in degassed toluene (the threshold excitation power density = 230 mW·cm^{-2}). ([**Gd-1**] = 0.5 μM, [BPEA] = 60 μM, λ_{ex} = 561 nm)



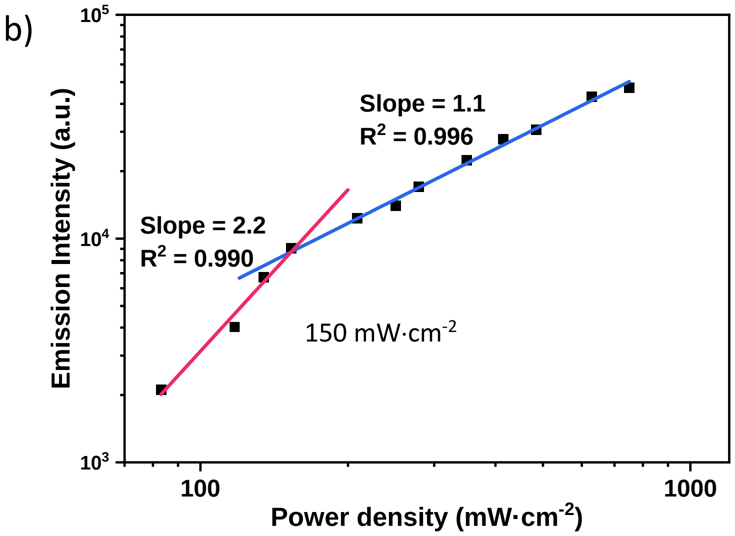


Fig. S29 a) Upconverted fluorescence spectra of **Pd-1**/BPEA at different excitation power; b) the double logarithmic plots of upconversion intensity at 480 nm measured as a function of power density of a 561 nm incident laser for **Pd-1**/BPEA in degassed toluene (the threshold excitation power density = 150 mW·cm^{-2}). ([**Pd-1**] = 0.5 μM, [BPEA] = 60 μM, λ_{ex} = 561 nm)

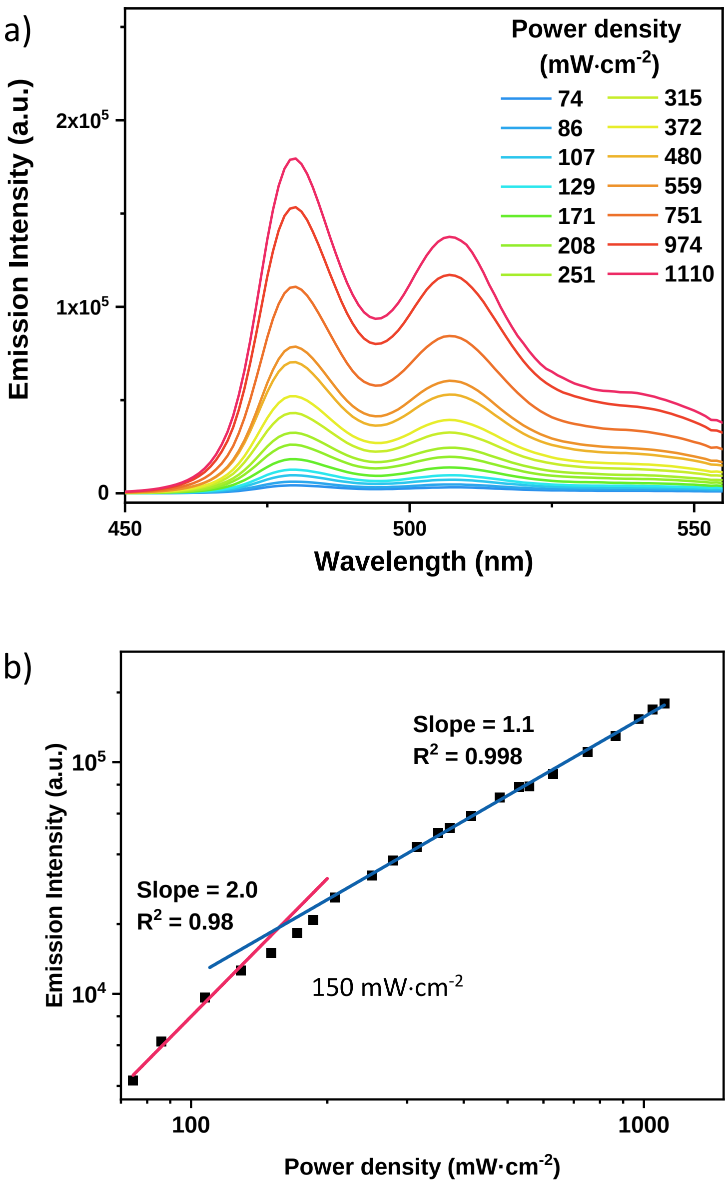


Fig. S30 a) Upconverted fluorescence spectra of **Zn-1**/BPEA at different excitation power; b) the double logarithmic plots of upconversion intensity at 480 nm measured as a function of power density of a 561 nm incident laser for **Zn-1**/BPEA in degassed toluene (the threshold excitation power density = 150 mW·cm^{-2}). ([**Zn-1**] = 0.5 μM, [BPEA] = 60 μM, λ_{ex} = 561 nm)

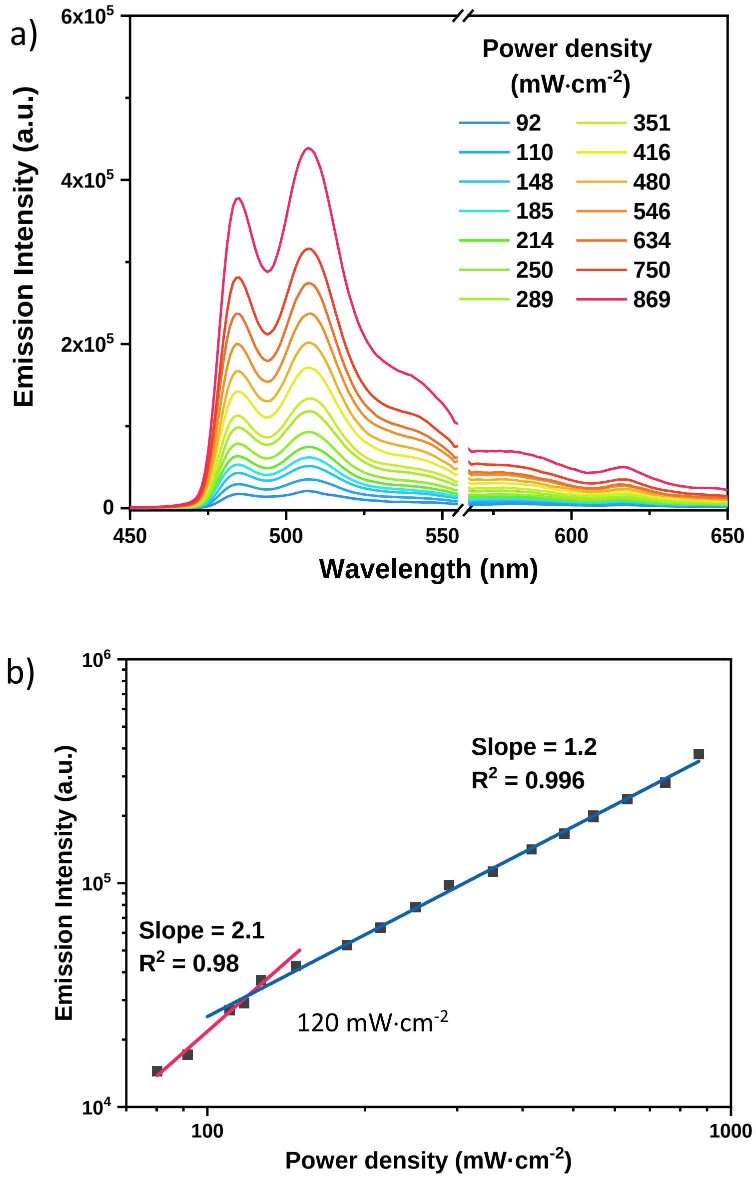


Fig. S31 a) Upconverted fluorescence spectra of **Lu-2**/BPEA at different excitation power; b) the double logarithmic plots of upconversion intensity at 480 nm measured as a function of power density of a 561 nm incident laser for **Lu-2**/BPEA in degassed toluene (the threshold excitation power density = 120 mW·cm^{-2}). ([**Lu-2**] = 0.5 μM, [BPEA] = 60 μM, λ_{ex} = 561 nm)

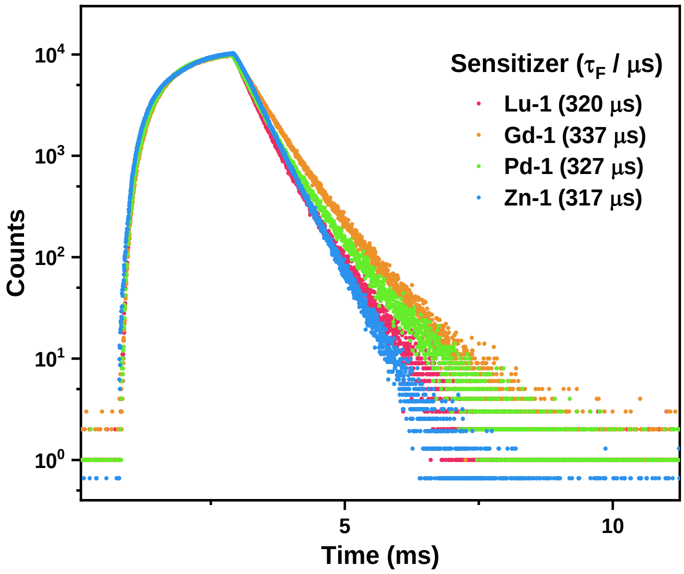


Fig. S32 Decay spectra of the delayed fluorescence boserved in TTA upconversion systems with **Lu-2** and **M-1** (M = Gd, Pd, Zn) as sensitizers and BPEA as acceptor in degassed toluene. (Excited by a 561 nm laser, λ_{em} = 480 nm)

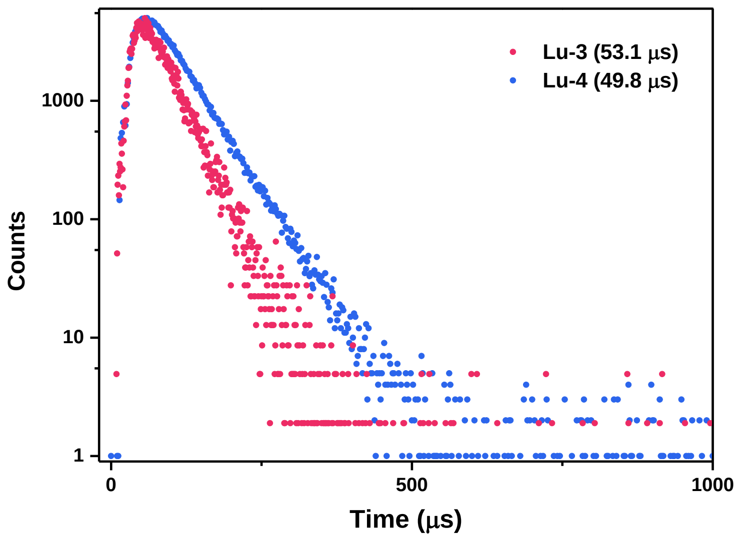


Fig. S33 Decay spectra of the delayed fluorescence boserved in TTA upconversion systems with **Lu-3** and **Lu-4** as sensitizers and rubrene as acceptor in degassed toluene. (Excited by 639 and 659 nm lasers for **Lu-3**/rubrene and **Lu-4**/rubrene systems respectively, λ_{em} = 561 nm)

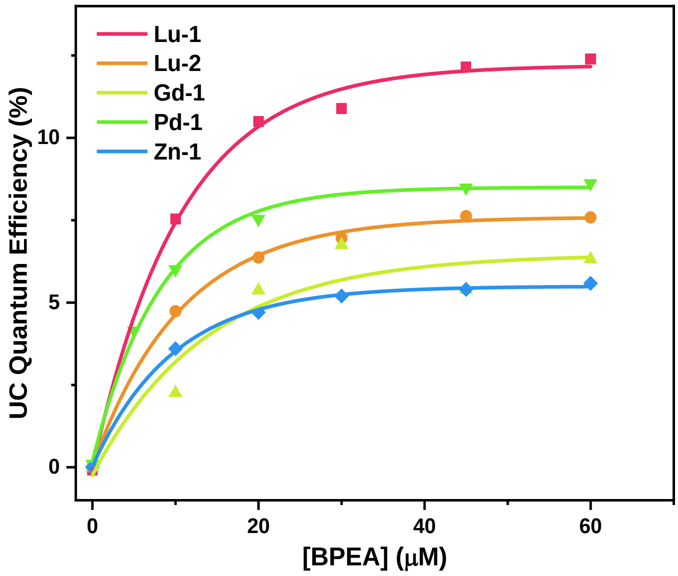


Fig. S34 Upconversion efficiencies (Φ_{UC}) as a function of BPEA concentration with the sensitizer at fixed concentration (0.5 μM) in degassed toluene.(λ_{ex} = 561 nm, 480 mW·cm^{-2})

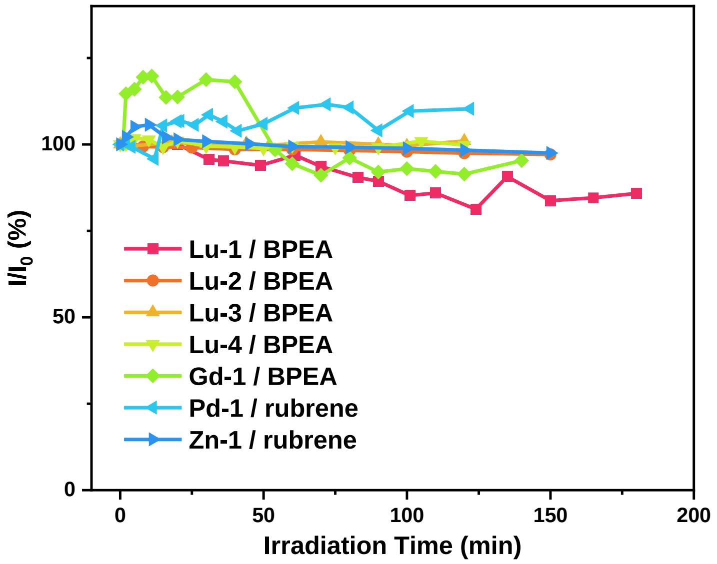


Fig. S35 Stability of the TTA upconversion emission of different upconversion systems upon continuous irradiation with excitation power density of 480 mW·cm^{-2} in degassed toluene. (Systems with **Lu-3** and **Lu-4** as sensitizers were excited at 639 and 659 nm respectively, while others at 561 nm) a)

b)

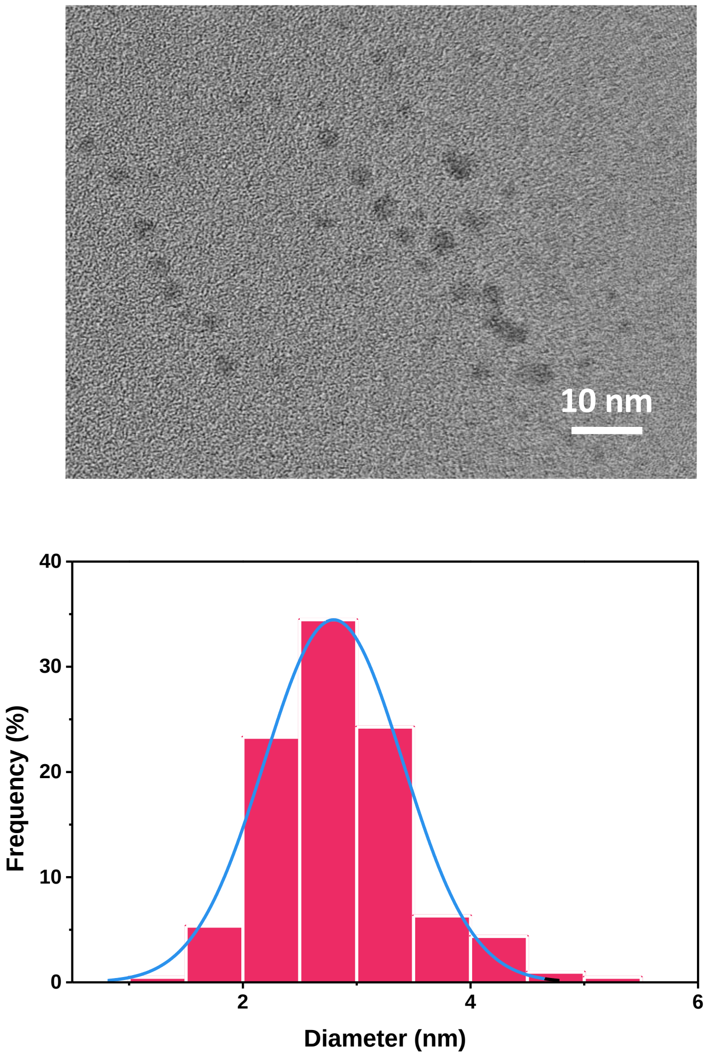


Fig. S36 (a) Transmission electron microscopy (TEM) image and (b) size distribution of UC-NMs loaded with **Lu-2**/BPEA at room temperature.

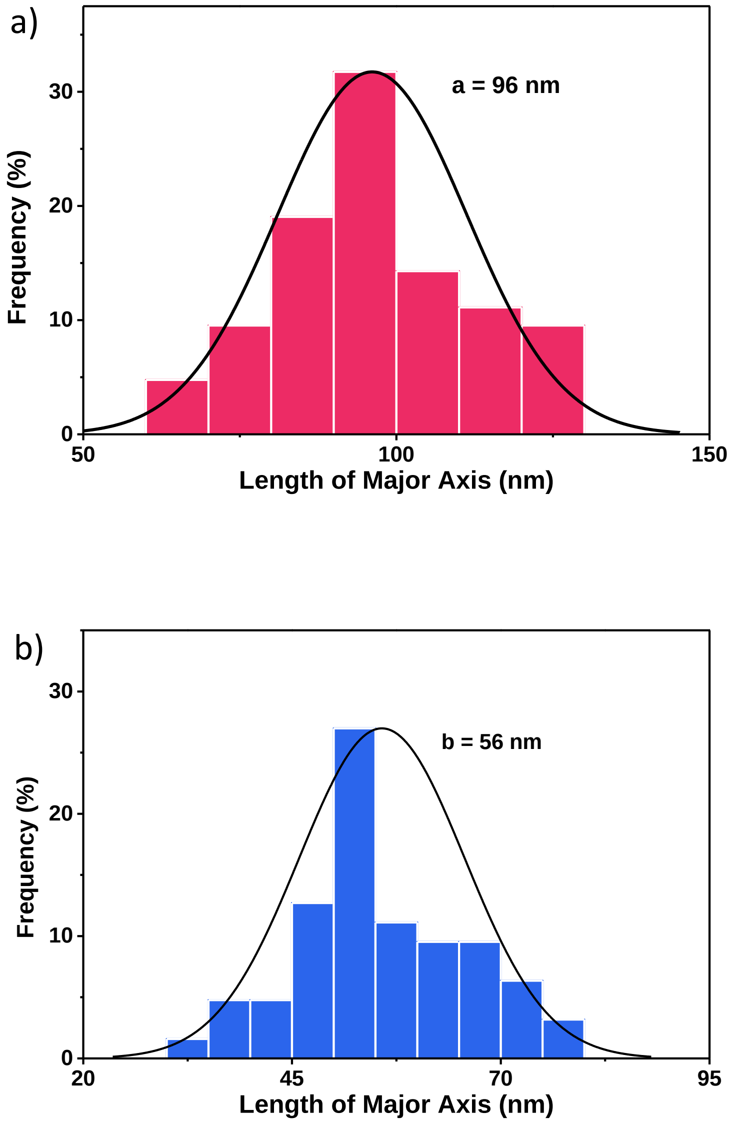


Fig. S37 (a) Major and (b) minor axis lengths distributions of UC-MSNs loaded with **Lu-1**/BPEA at room temperature measured by TEM.

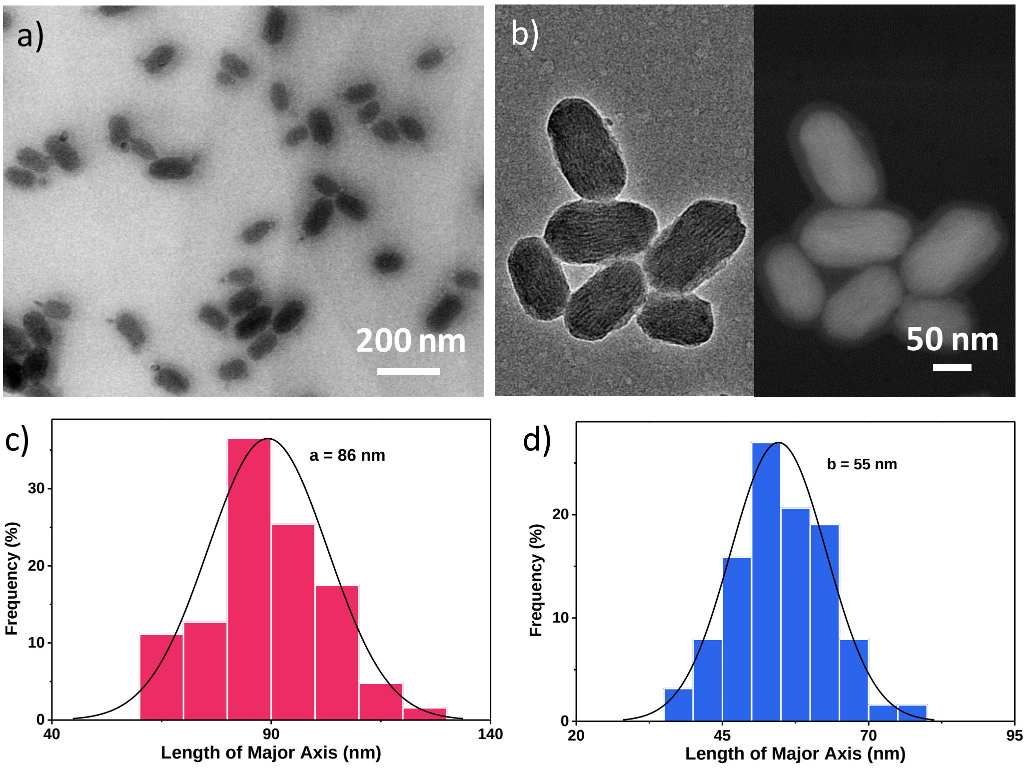


Fig. S38 (a) Transmission electron microscopy (TEM) image at 25kx magnification, (b) pore channel structure in bright field (left) and dark field (right) TEM image at 60kx magnification, (c) Major axis lengths distribution and (d) minor axis lengths distribution of UC-MSNs loaded with **Lu-2**/BPEA at room temperature.

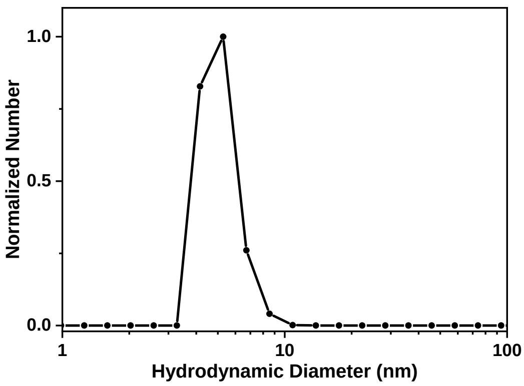


Fig. S39 Dynamic light scattering (DLS) of **Lu-2**/BPEA loaded UC-NM.

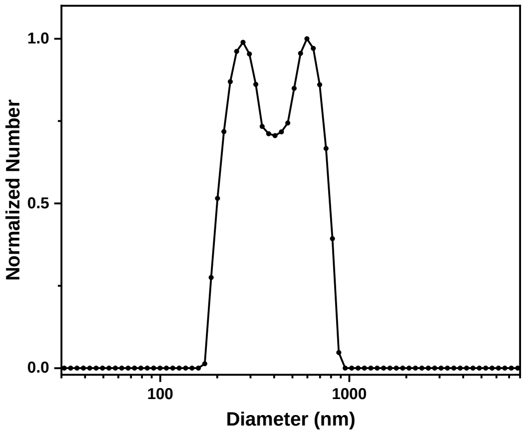


Fig. S40 Dynamic light scattering (DLS) of **Lu-2**/BPEA loaded UC-MSN. (274±4 and 585±8 nm)

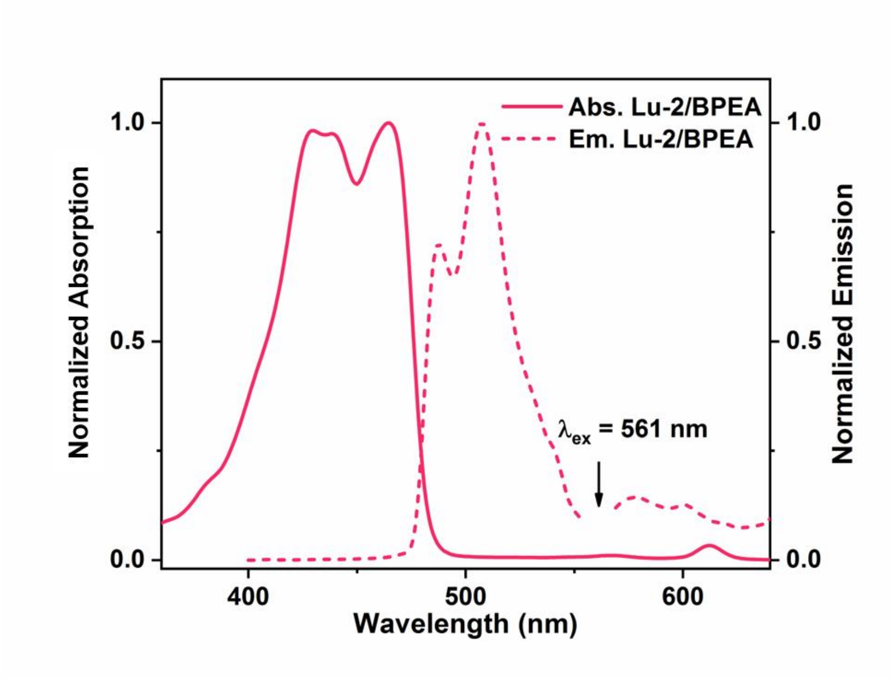


Fig. S41 Normalized absorption (solid) and emission (dash) spectra (λ_{ex} = 561 nm, 480 mW·cm^{-2}) of UC-NMs loaded with **Lu-2**/BPEA pair in water under ambient atmosphere.

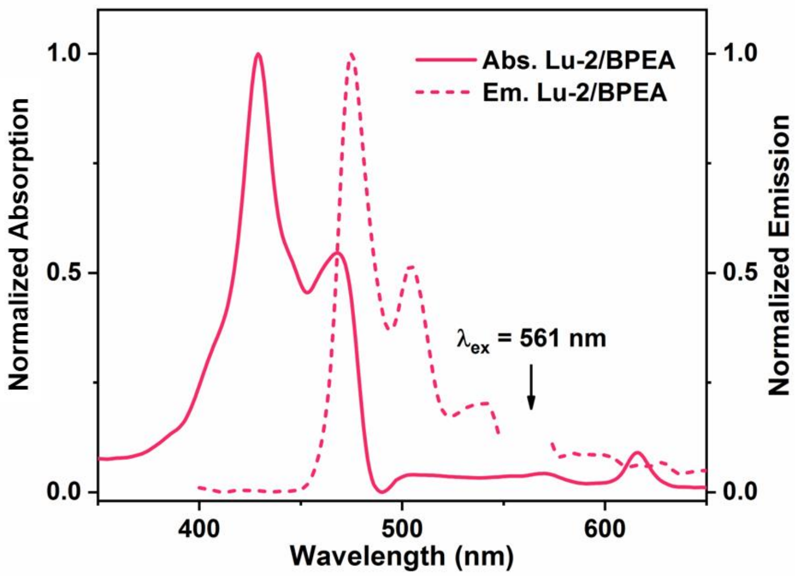


Fig. S42 Normalized absorption (solid) and emission (dash) spectra (λ_{ex} = 561 nm, 480 mW·cm^{-2}) of UC-MSNs loaded with **Lu-2**/BPEA pair in water under ambient atmosphere.

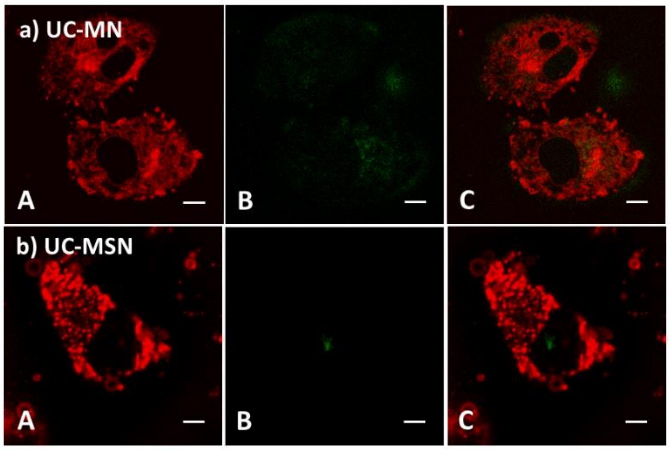


Fig. S43 Confocal fluorescence image of living HeLa cell with BPEA only (no sensitizer) by 455 - 525 nm channel under laser excitation at (A) 405 nm (red, prompt fluorescence); (B) 543 nm (green, upconverted fluorescence); and (C) merged images of (A) and (B). Row a, b: image of (a) NMs (incubated for 15 min) and (b) MSNs (incubated for 4 h). (Scale bar presents 20 μm)