Supplementary Information

Thermally-Activated Upconversion Based on Triplet Fusion for Deep Red Photoactivation of Ru(II) Complex

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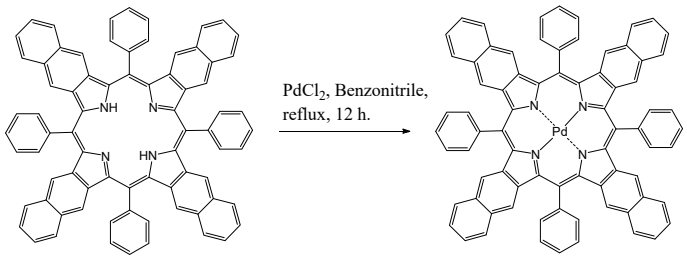
1. The Synthesis and Purification of PdTPTNP

The synthesis method refers to the previous literature[1, 2].



H_2TPTNP **PdTPTNP**

Scheme S1. Synthesis of Pd (II)-tetraphenyltetranaphthoporphyrin (PdTPTNP).

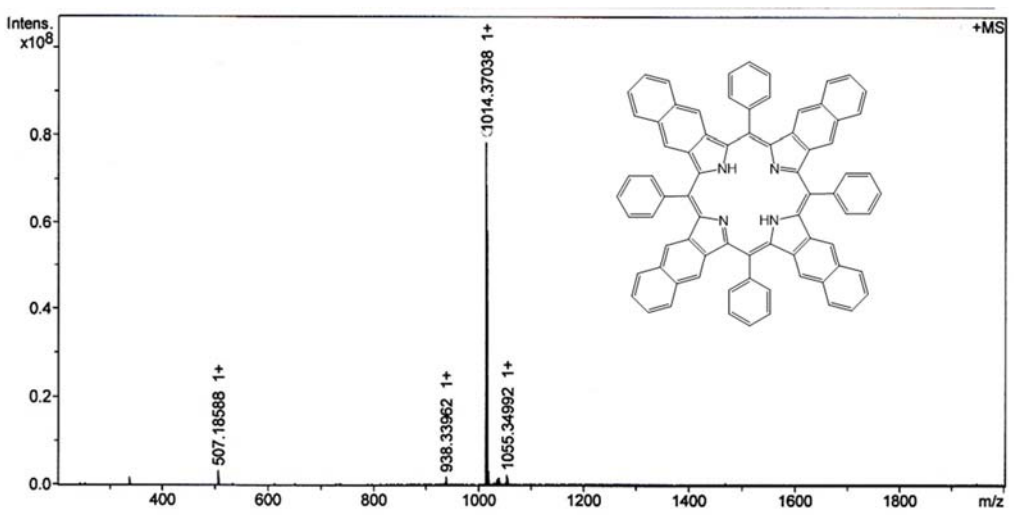


Fig. S1. Mass spectrum of H_2TPTNP.

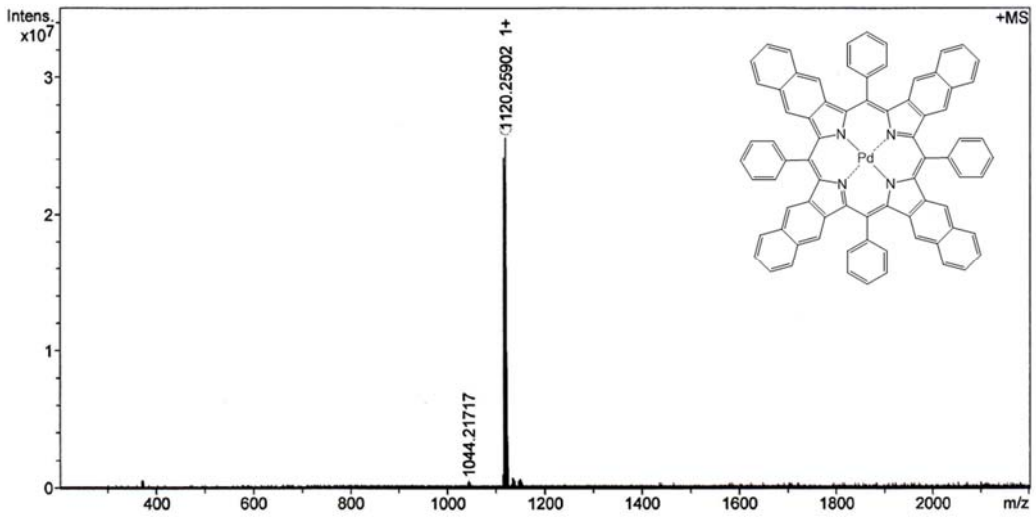


Fig. S2. Mass spectrum of PdTPTNP. MALDI-TOF: *m*/*z*: found 1119.25, calcd. for [M^+] $C_{100}H_{60}N_4O_8Pd$ 1120.25.

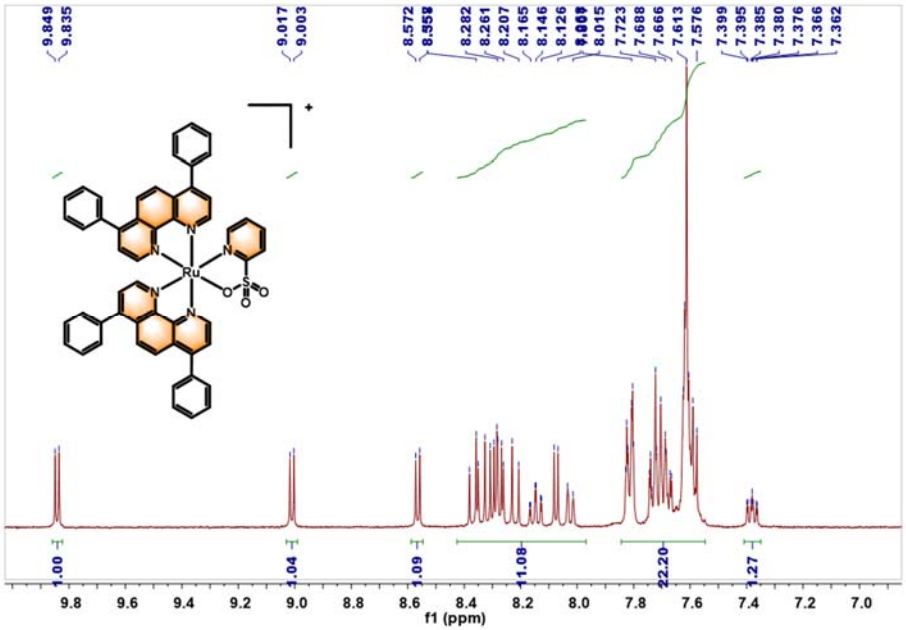


Fig. S3. ^{1}H NMR of $[Ru(dip)_2(Py\text{-}SO_3)](NO_3)$

^{1}H-NMR (400 MHz, $(CD_3)_2CO$ δ 9.85 (d, *J* = 5.6 Hz, 1H), 9.01(d, *J* = 5.6 Hz, 1H), 8.57(d, *J* = 6.0 Hz, 1H), 8.38–8.02(m, 11H), 7.83–7.58(m, 22H), 7.42–7.35(m, 1H).

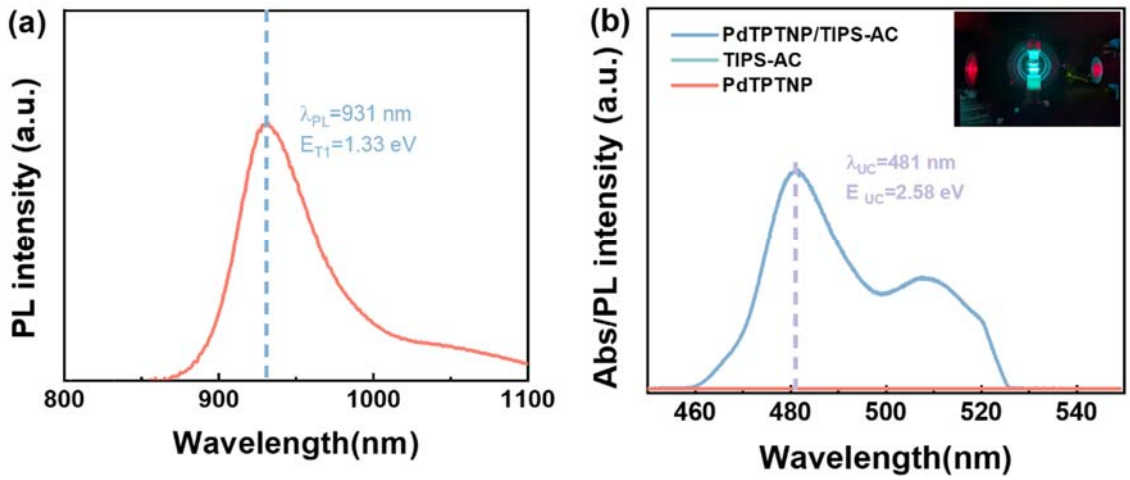


Fig. S4 (a) Phosphorescence spectrum of PdTPTNP (10^{-5} M) in air-free toluene (λ_{ex}=730 nm). (b) UC emission spectra of PdTPTNP (6 μM)/TIPS-Ac (5 mM), TIPS-Ac (5 mM) and PdTPTNP (6 μM) in air-free toluene (λ_{ex}=730 nm).

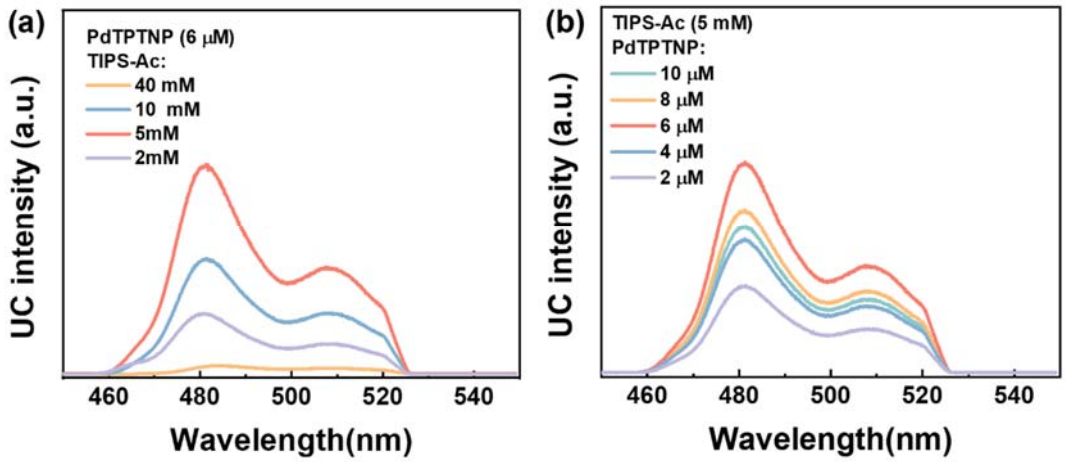


Fig. S5 TTA Upconversion spectra of (a) PdTPTNP (6 μM)/TIPS-Ac with varying concentrations of TIPS-Ac and (b) PdTPTNP/TIPS-Ac (5 mM) with varying concentrations of PdTPTNP in deaerated toluene (λ_{ex} = 730 nm, incident power density is 342 mW/cm^2).

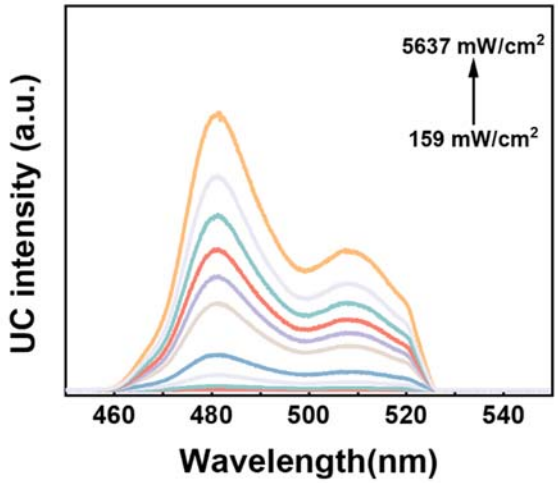


Fig. S6 UC emission spectra of PdTPTNP (6 μM)/TIPS-Ac (5 mM) in deaerated toluene with various excitation intensity from 159 mW/cm^2 to 5637 mW/cm^2 (λ_{ex}=730 nm).

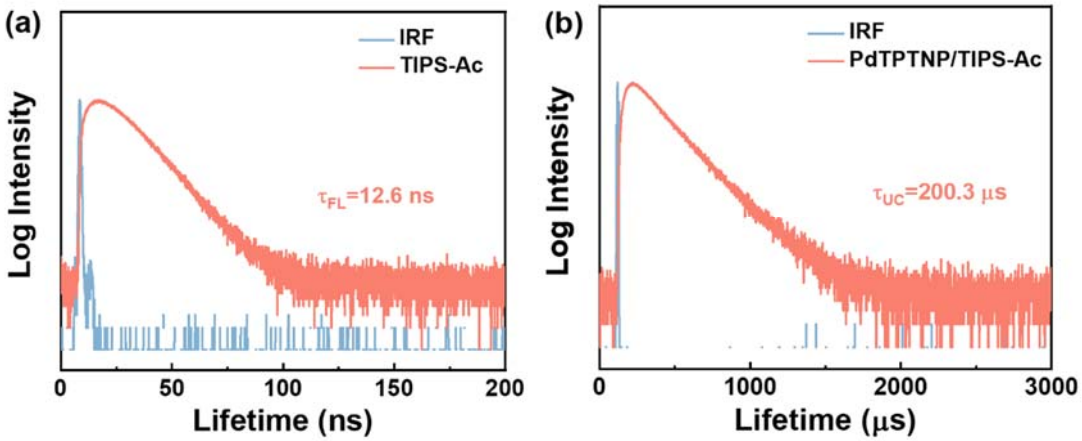


Fig. S7 Decay kinetics of (a) photoluminescence of TIPS-Ac (5 mM) in deaerated toluene (λ_{ex}=405 nm) and (b) delayed fluorescence of PdTPTNP (6 μM)/TIPS-Ac (5 mM) in deaerated toluene (λ_{ex}=730 nm).

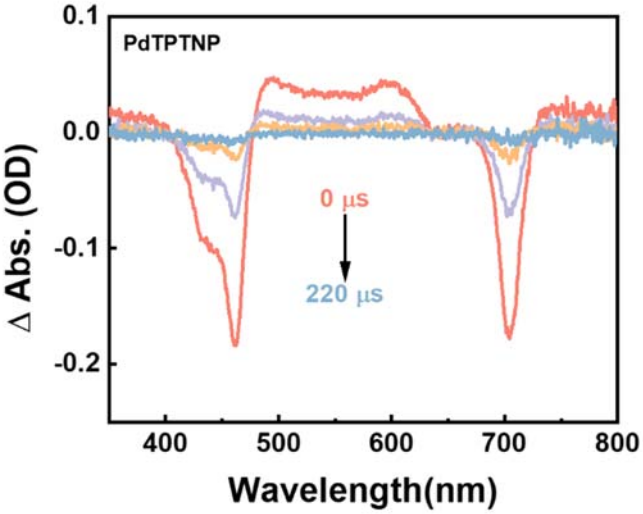


Fig. S8 TA spectra at different delayed time of PdTPTNP (6 μM in deoxygenated toluene) excited by 700 nm pulse laser.

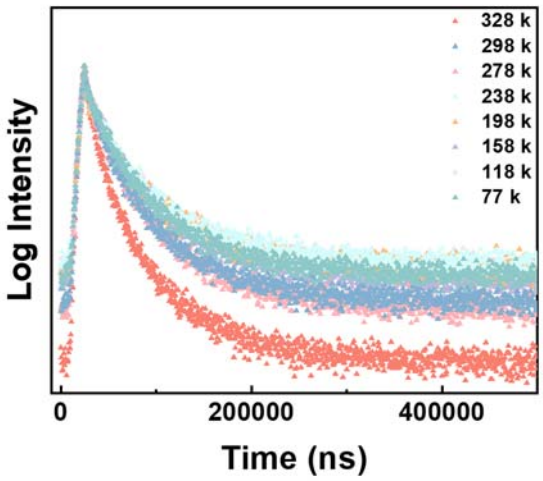


Fig. S9 Phosphorescence decay at 945 nm from PdTPTNP/TIPS-Ac (1/5000) at different temperature.

Table S1. Fitted lifetime at 945 nm and Φ_{TET} of PdTPTNP (6 mM)/TIPS-Ac with different TIPS-Ac concentrations (λ_{ex}=730 nm).

TIPS-Ac/mM	τ_1/μs	B_1/%	τ_2/μs	B_2/%	τ_{ave}/μs	Φ_{TET}/%
0	53.9	100	—	—	53.9	—
2	24.9	56.07	41.9	43.93	30.3	43.8
4	16.6	89.17	53.7	10.83	17.9	66.8
8	10.9	90.04	43.0	9.96	11.7	78.3
16	6.7	91.17	14.3	8.83	7.3	86.5
33	2.7	89.37	6.3	10.63	2.8	94.8

Table S2. Phosphorescence lifetime at 945 nm of PdTPTNP/TIPS-Ac (1/5000) at different temperature.

Temperature/K	τ_1/μs	B_1/%	τ_2/μs	B_2/%	τ_{ave}/μs
77	25.09	18.28	74.25	81.73	65.27
118	17.88	11.53	71.79	88.47	65.57
158	20.65	10.98	72.97	89.02	67.23
198	11.80	6.96	66.39	93.04	65.38
238	21.28	14.29	73.97	85.71	66.44
278	25.42	21.55	73.50	78.45	63.14
298	21.85	19.64	70.51	80.36	60.96
328	17.42	24.35	64.89	75.65	53.33

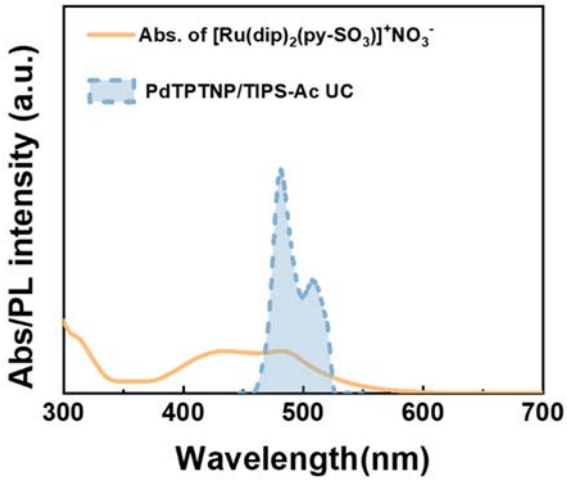


Fig. S10 Absorption spectrum of Ru1 (30 μM in ACN) and UC emission spectrum of PdTPTNP (6 μM)/TIPS-Ac (5 mM) in deaerated toluene (λ_{ex}=730 nm).

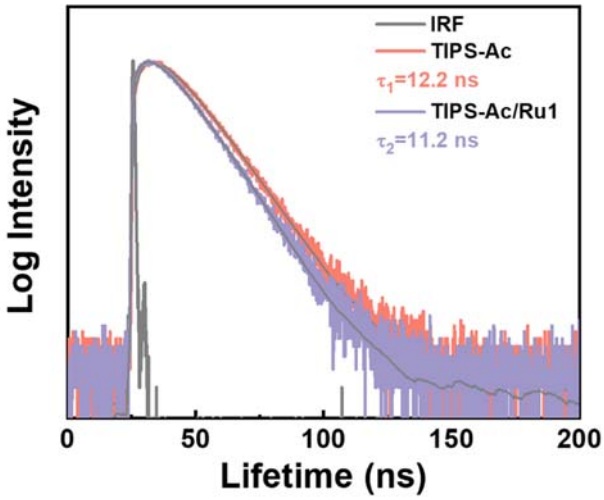


Fig. S11. Lifetime of TIPS-Ac (70 μM) at 480 nm before and after adding Ru1 (30 μM) excited by 405 nm.

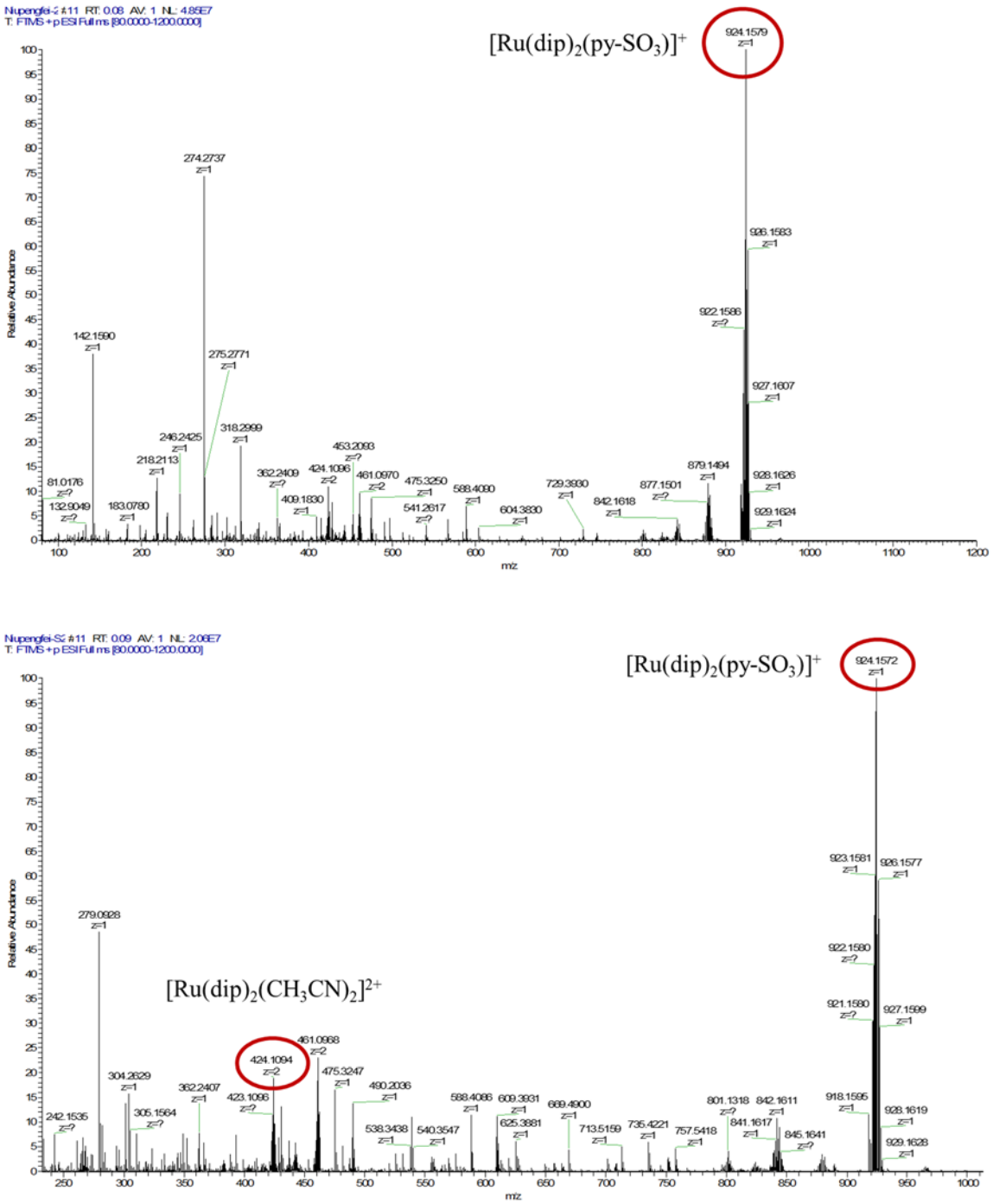


Fig. S12. HR ESI-MS spectra of UC-$[Ru(dip)_2(py\text{-}SO_3)]^+NO_3^-$ before (top) and after 700 nm light irradiation (bottom) in mixed solvent (THF:ACN=4:6). m/z=924.1572 for $[Ru(dip)_2(py\text{-}SO_3)]^+$ and m/z=424.1090 for $[Ru(dip)_2(CH_3CN)_2]^{2+}$.

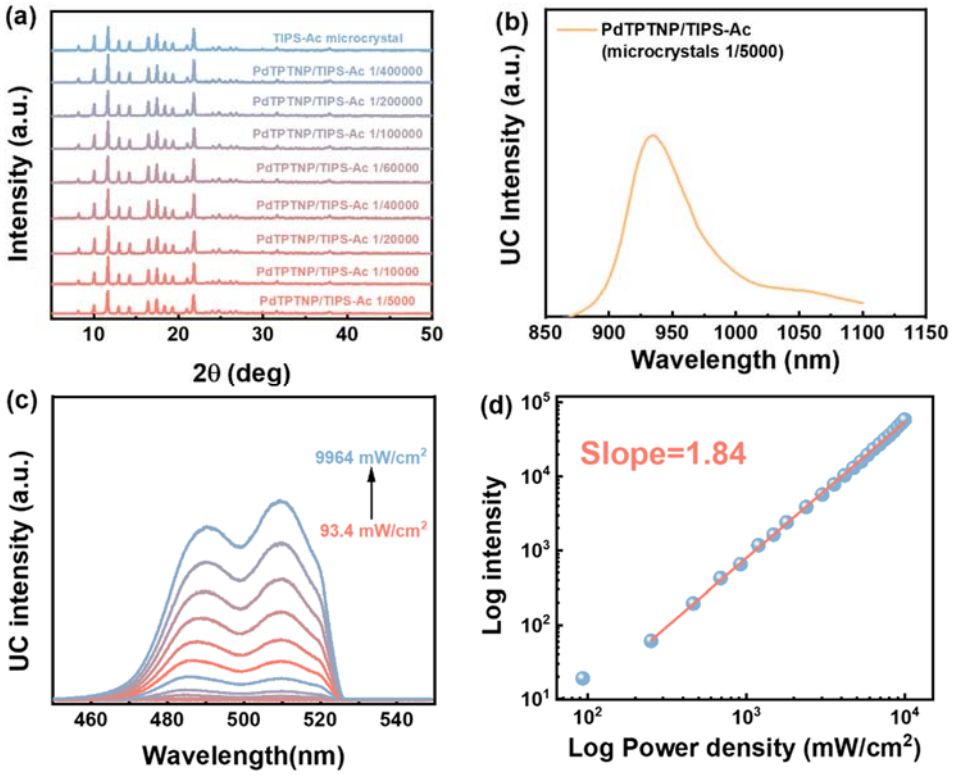


Fig. S13 (a) XRD patterns of PdTPTNP/TIPS-Ac nanocrystals and TIPS-Ac crystals without doping. XRD spectra were measured with a Bruker D8 Focus X-ray diffractometer equipped with CuKα1 radiation (1.54050 Å). (b) Phosphorescence spectrum of PdTPTNP/TIPS-Ac microcrystals at a ratio of 1/5000 (λ_{ex} = 730 nm). The phosphorescence characteristic of PdTPTNP/TIPS-Ac microcrystals at a ratio of 1/5000 is identical to that of PdTPTNP in solution, indicating no obvious aggregation of PdTPTNP. (c) Dependence of UC emission spectra and UC emission intensity at 480 nm on the various incident power densities (λ_{ex}=730 nm). (d) Dependence of UC emission intensity at 480 nm on the various incident power densities.

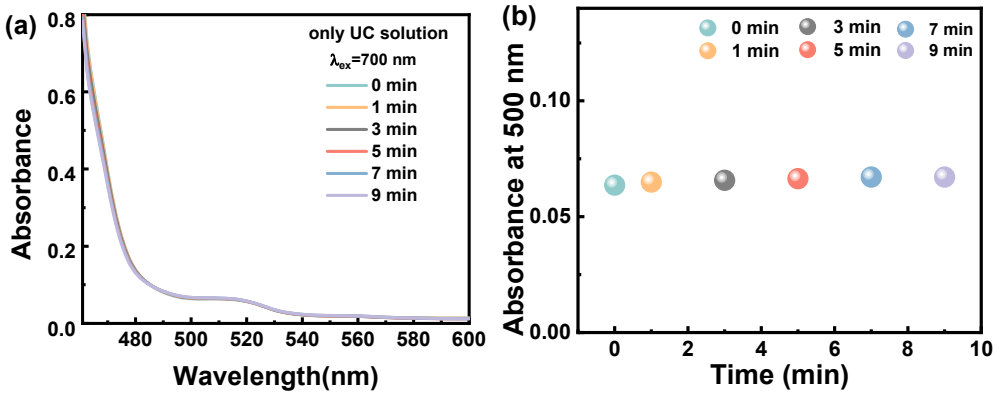


Fig. S14 (a) Time-course UV/vis absorption spectra of upconversion solution PdTPTNP (6 μM)/TIPS-Ac (5 mM) under 700 nm LED irradiation in in THF/ACN (4/6 v/v, 271 mW/cm²). (b)

Corresponding absorbance changes at 500 nm of PdTPTNP (6 μM)/TIPS-Ac (5 mM) under irradiation.

References

1. M. D. Perez, C. Borek, S. R. Forrest and M. E. Thompson, *Journal of the American Chemical Society*, 2009, **131**, 9281-9286.
2. B. S. Filatov M A, Ilieva I Z, et al., *The Journal of Organic Chemistry*, 2012, **77**, 11119-11131.