Electronic Supplementary Information for

Enhancing triplet sensitization ability of donor-acceptor dyads via intramolecular triplet energy transfer

Shanshan Liu[a], Xiangyang Wang[a], Heyuan Liu[c,], Li Shen[a], Dezhi Zhao[a], and Xiyou Li[b,*]*

[a.] College of Science, China University of Petroleum (East China), Qingdao, Shandong, 266580, China.

[b.] School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, Shandong, 266580, China.

[c.] College of New Energy, China University of Petroleum (East China), Qingdao, Shandong, 266580, China.

E-mail: xiyouli@upc.edu.cn; liuheyuan123@upc.edu.cn

Caption of Content

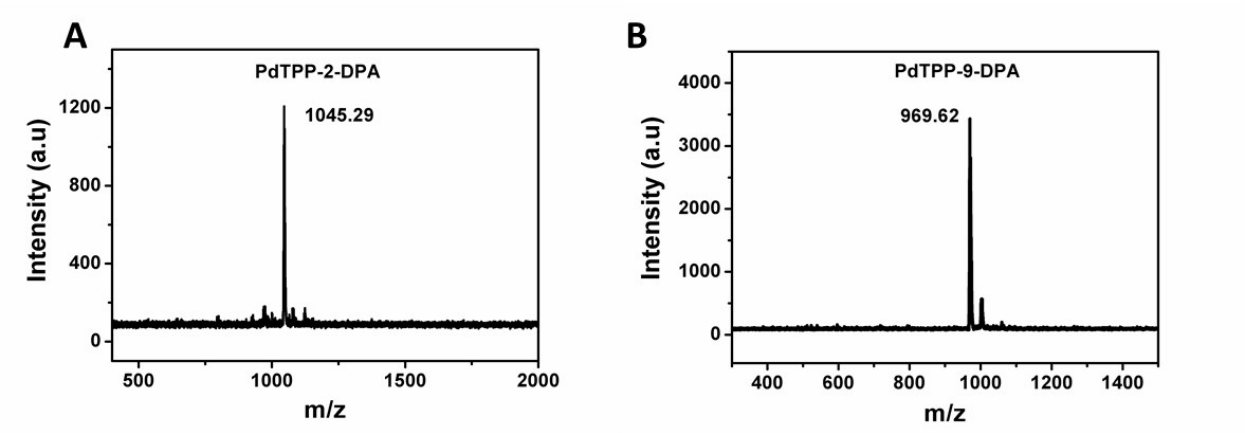

Fig. S1. Experimental isotopic pattern for the molecular ion of PdPor-2-DPA (A) and PdPor-9-DPA (B) shown in the MALDI-TOF mass spectra.

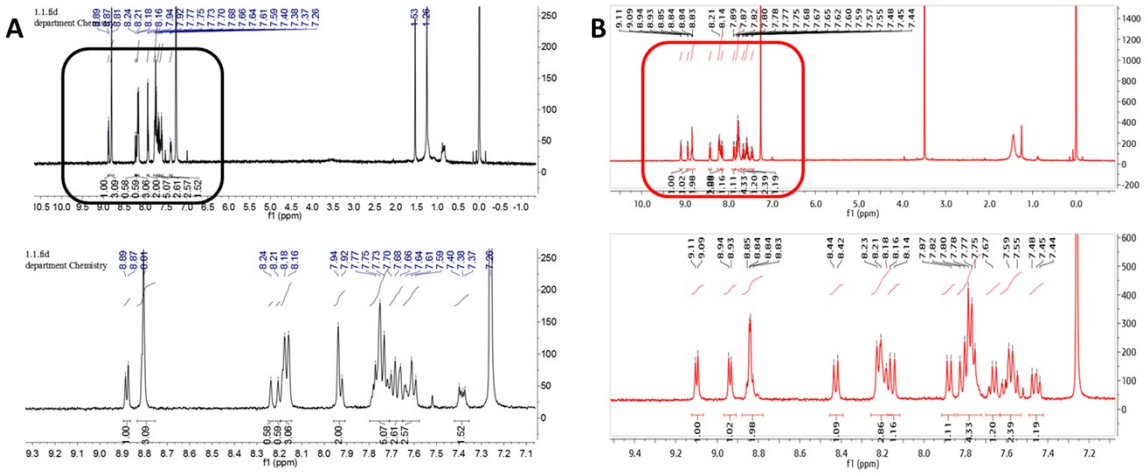

Fig. S2. ^{1}H NMR spectra of PdPor-2-DPA (A) and PdPor-9-DPA (B) in $CDCl_3$.

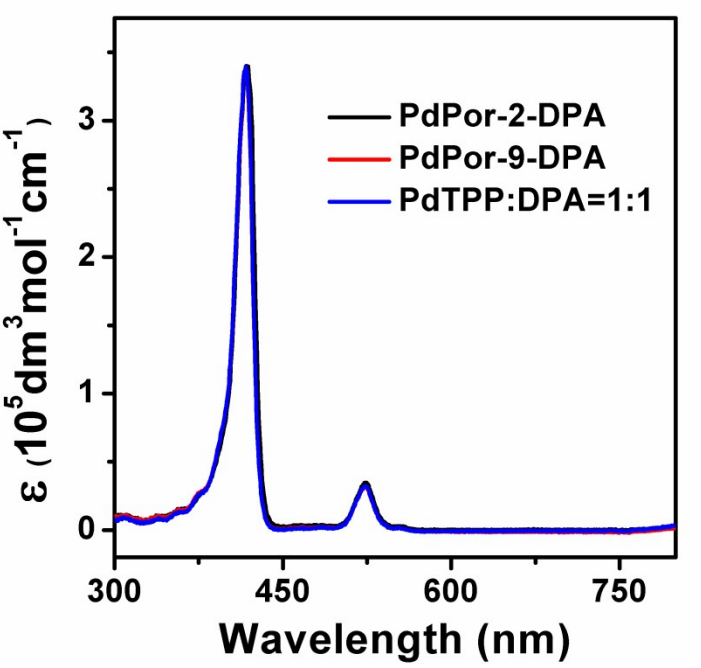

Fig. S3. Absorption spectra of PdPor-2-DPA, PdPor-9-DPA and mixed solution of PdTPP: DPA=1:1. PdPor-2-DPA and PdPor-9-DPA, c = 1.0×10^{-5}; in mixed solution, PdTPP and DPA, c = 1.0×10^{-5} in deaerated toluene.

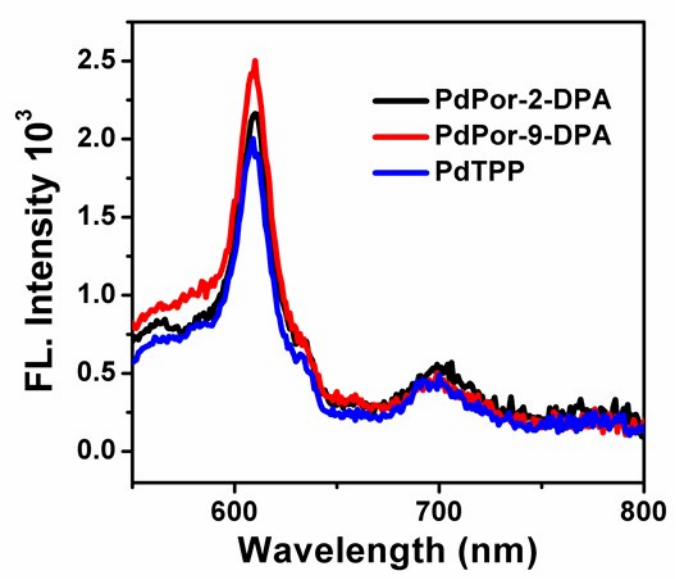

Fig. S4. Luminescence emission spectra of PdPor-2-DPA, PdPor-9-DPA and PdTPP.; λ_{ex} = 532 nm, c = 1.0×10^{-5} M in aerated Toluene, 293K.

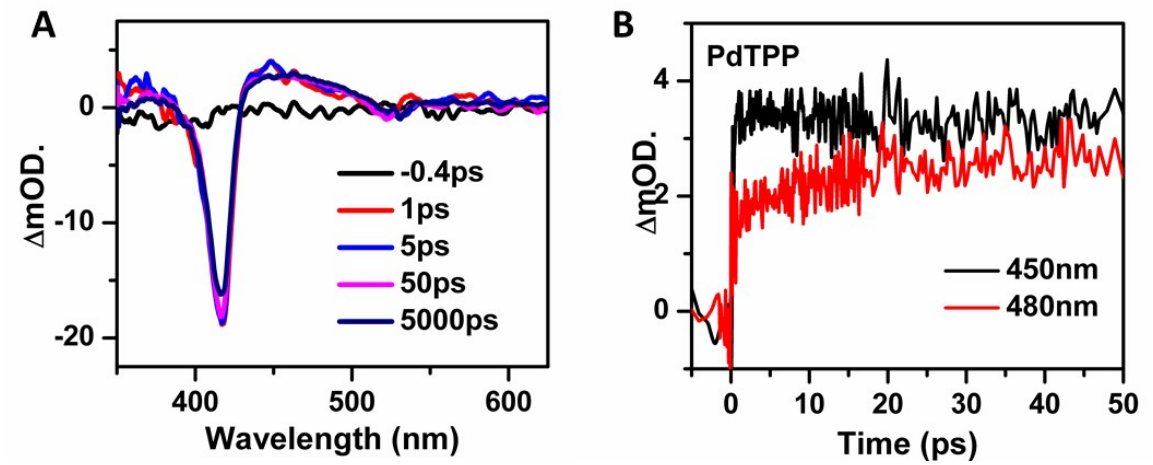

Fig. S5. *fs*-TA spectra (A) and single-wavelength dynamics probed at 450 and 480 nm (B) of PdTPP. λ_{ex} = 532 nm, c = 2.0×10^{-5} M in deaerated toluene, 293K.

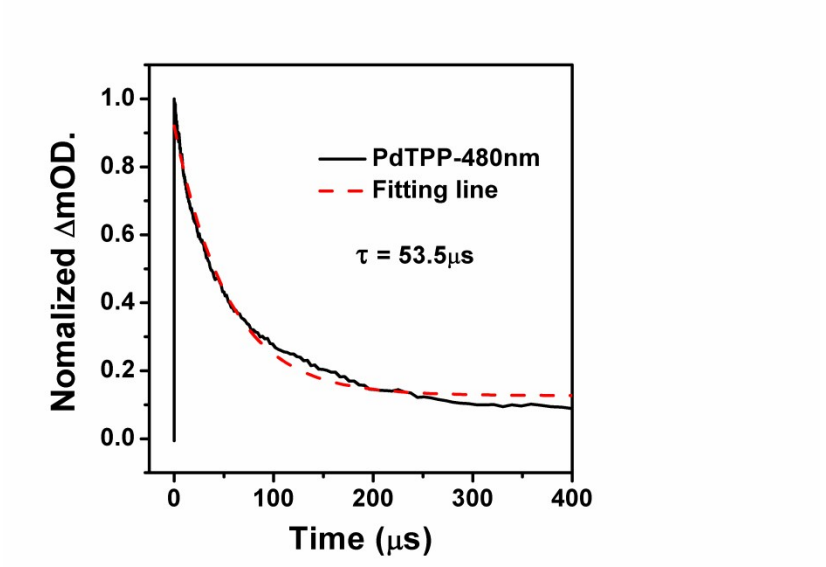

Fig. S6. Single-wavelength dynamics of PdTPP probed at 480 nm from nanosecond TA spectra. λ_{ex} = 532 nm, c = 2.0×10^{-5} M in deaerated toluene, 293 K.

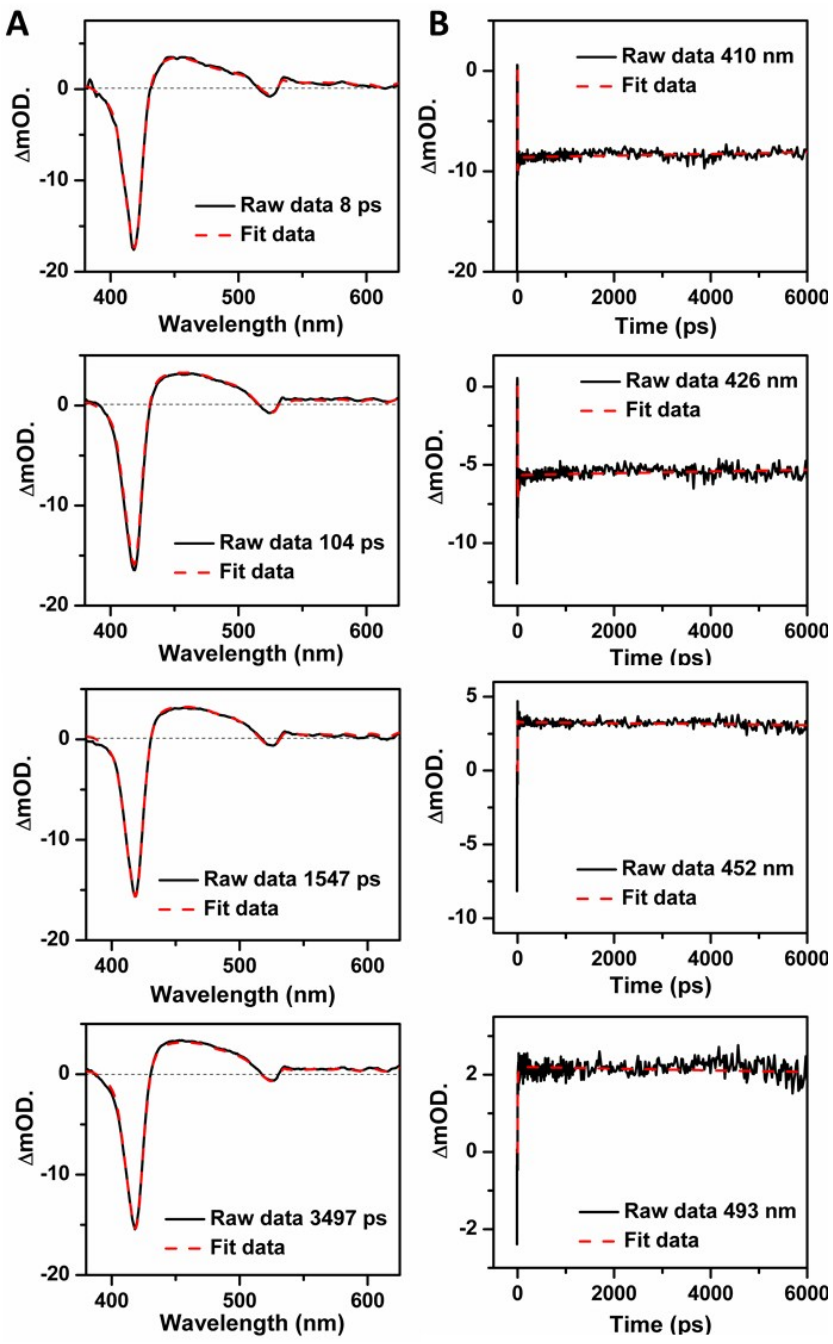

Fig. S7. Comparison of TA spectra(A) and single-wavelength dynamics(B) of PdPor-2-DPA between the raw data and the fitting data in S_1(PdPor*-DPA)→T_1(PdPor*-DPA) model obtained from the global analysis.

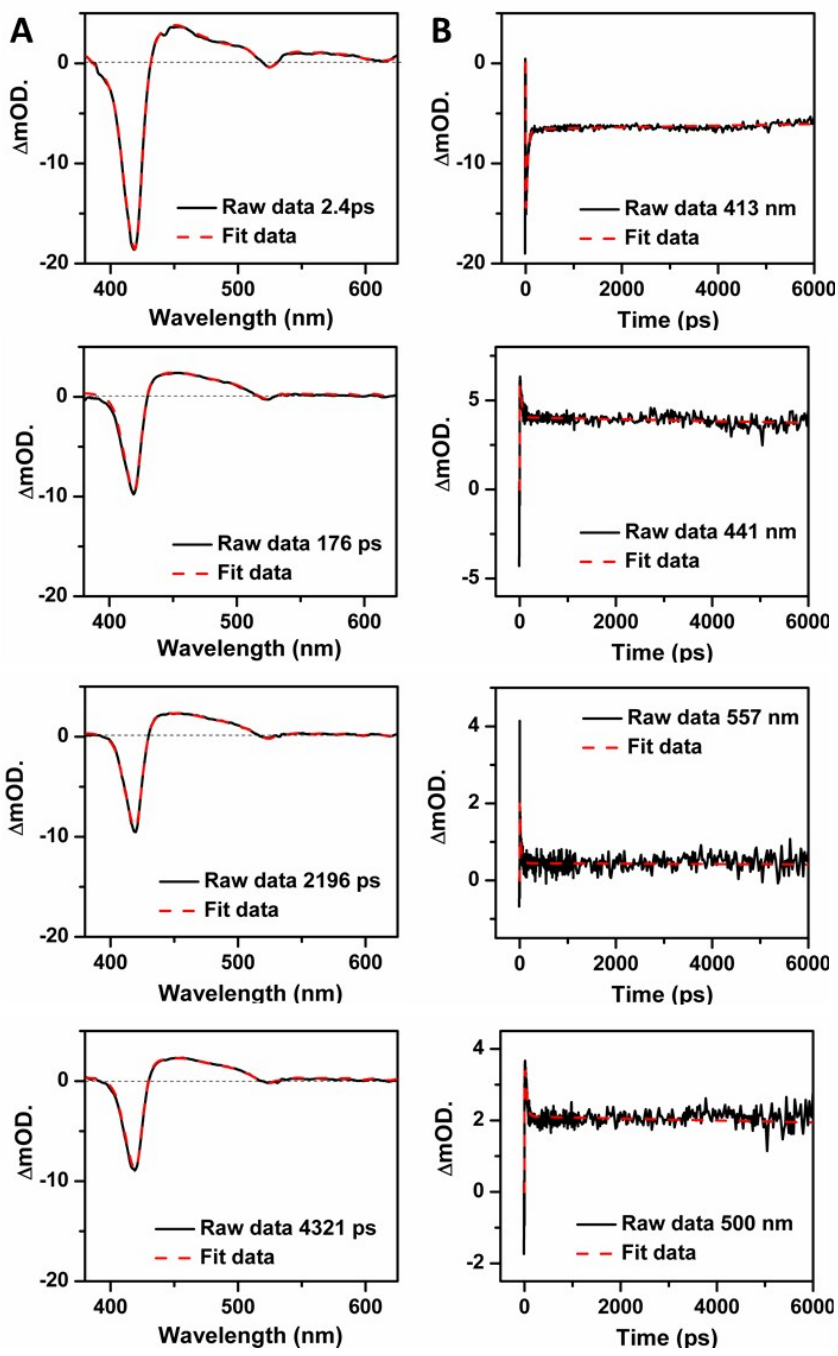

Fig. S8. Comparison of TA spectra (A) and single-wavelength dynamics (B) of PdPor-9-DPA between the raw data and the fitting data in (S_1(PdPor*-DPA)→T_1(PdPor*-DPA)→T_1(PdPor*-DPA*) model obtained from the global analysis.

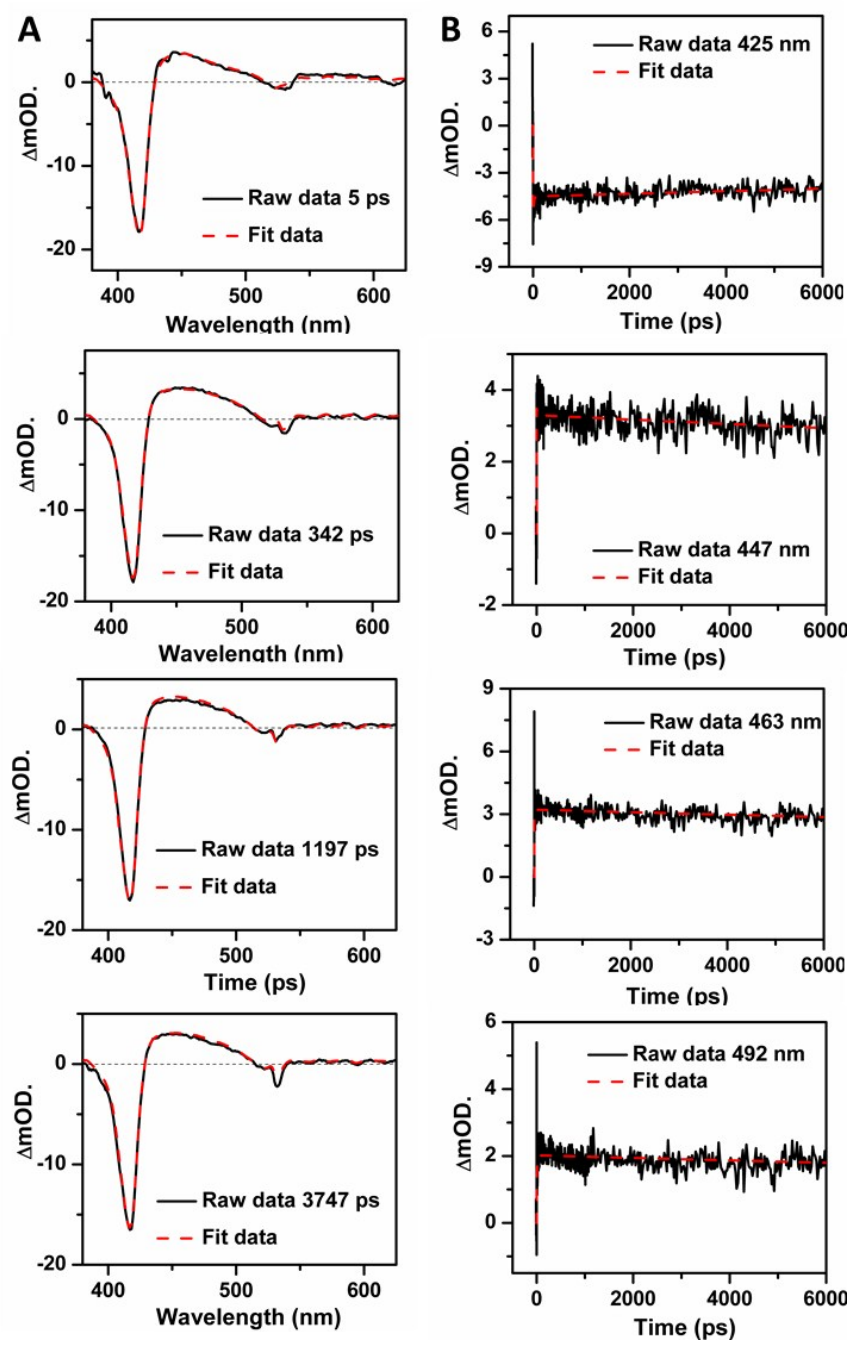

Fig. S9. Comparison of TA spectra(A) and single-wavelength dynamics(B) of PdTPP between the raw data and the fitting data in S_1(PdPor*)→T_1(PdPor*) model obtained from the global analysis.

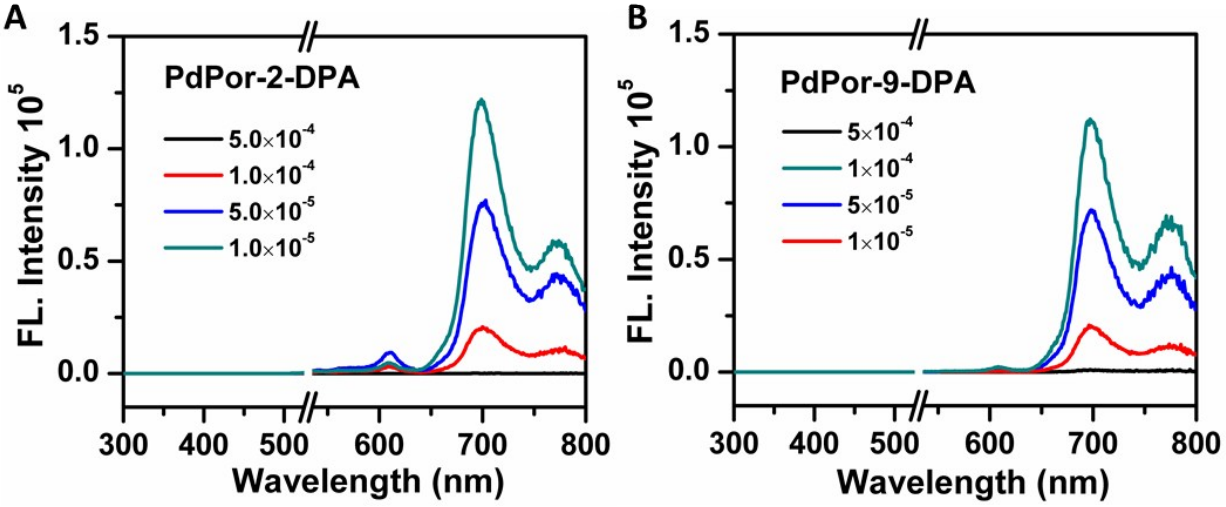

Fig. S10. Dependence of luminescence spectra on the concentration of PdPor-2-DPA (A) or PdPor-9-DPA (B) in deaerated toluene with 532 nm laser excitation (25 mW).

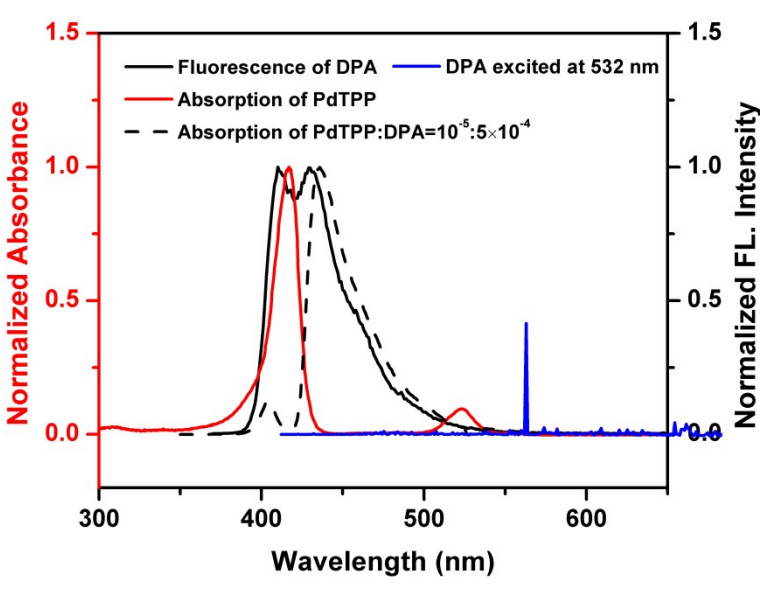

Fig. S11. Absorption spectrum of PdTPP; fluorescence emission spectrum of DPA; upconversion emission spectrum of PdTPP and DPA, in deaerated toluene.

Table S1. Phosphorescence quantum yields and lifetimes of these compounds at 293 K.

Compounds	Φ (%)	τ^a (μs)	χ^2
PdTPP-2-DPA	0.26±0.03	108.98±0.1 (91.33%) 147.57±0.1 (8.67%)	1.027
PdTPP-9-DPA	0.23±0.03	79.96±0.1 (77.94%) 119.23 ±0.1 (22.06%)	1.019
PdTPP	0.41±0.05	77.04±0.1 (72.00%) 215.33±0.1 (28.00%)	1.123

[a]Phosphorescence lifetimes were monitored at 697 nm ($c = 1.0 \times 10^{-5}$ M).

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