Supporting Information for

Metallonaphthalocyanines as Triplet Sensitizers for Near-Infrared Photon Upconversion beyond 850 nm

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Materials.

All reagents and solvents for synthesis were used as received without further purification. 5,9,14,18,23,27,32,36-Octabutoxy-2,3-naphthalocyanine (**Nac**) was purchased from Aldrich and used as received.

TDI was synthesized according to the reported methods.[1] ^{1}H NMR (300 MHz, $CDCl_3$, TMS standard): δ (ppm) 1.20 (d, *J* = 6.8 Hz, 24H, CH_3), 2.78 (quintet, *J* = 6.8 Hz, 4H, $CHCH_3$), 7.36 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 7.50 (t, *J* = 7.7 Hz, 2H, Ar-*H*), 8.66 (d, *J* = 8.3 Hz, 4H, Ar-*H*), 8.75 (s, 4H, Ar-*H*), 8.77 (d, *J* = 8.3 Hz, 4H, Ar-*H*). Elemental analysis; calculated for $C_{58}H_{46}N_2O_4$: C 83.43, H 5.55, N 3.35, Found: C 82.98, H 5.36, N 3.23.

Characterizations.

^{1}H NMR (300 MHz) spectra were measured on a Bruker DRX-spectrometer using TMS as the internal standard. Elemental analysis was conducted at the Elemental Analysis Center, Kyushu University. Absorption spectra were recorded on a JASCO V-670 spectrophotometer. Fluorescence spectra were measured by using a PerkinElmer LS 55 fluorescence spectrometer. NIR phosphorescence spectra were measured using a Horiba FluoroLog-3 fluorescence spectrometer. Time-resolved photoluminescence lifetime measurements were carried out by using a time-correlated single photon counting lifetime spectroscopy system, HAMAMATSU Quantaurus-Tau C11567-01. Upconverted emission spectra were recorded on a Hamamatsu Photonics PMA-12 with the excitation source using an external, adjustable semiconductor laser (856 nm, 0-78 mW). The absolute quantum yield was measured in an integrating sphere using a Hamamatsu Photonics absolute quantum yield measurement system. Transient absorption spectra were measured using a UNISOKU TSP-2000 laser flash photolysis system.

Determination of TTA-UC quantum yield.

The upconverted luminescence quantum efficiency (Φ_{UC}) was determined relative to a standard, luminescence of **Nac** in 1,2-dichlorobenzene (Φ_{std} = 0.034), according to the following equation

$$\Phi_{UC} = \Phi_{std}\left(\frac{A_{std}}{A_{UC}}\right)\left(\frac{I_{UC}}{I_{std}}\right)\left(\frac{\eta_{UC}}{\eta_{std}}\right)^2 \qquad \text{(S1)}$$

where Φ, A, I and η represent the quantum yield, absorbance at 856 nm, integrated photoluminescence spectral profile, and a refractive index of the solvent The subscripts *UC* and *std* denote the parameters of the upconversion and standard systems. The quantum efficiency of **Nac** was determined relative to a standard, Nile Red in 1,2-dichlorobenzene (Φ = 0.86).

Determination of intersystem crossing (ISC) efficiency.

The ISC efficiency (Φ_{ISC}) of donors was determined by flush photolysis measurement according to the reported procedure.[2] We measured laser pulse intensity dependence of transient absorbance of **PtNac** and **PdNac** in toluene (20 μM). We used toluene as the solvent because we observed a decomposition of sensitizers in 1,2-DCB under high-power pulsed laser. We excited at 452 nm (**PtNac**) or 468 nm (**PdNac**) and observed transient absorbance at 680 nm. Fitting the plot of ΔA vs. E to an equation S2 allows calculation of Φ_{ISC} and ε_T^*.

$$\Delta A = \mathrm{a}\{1 - \exp(-bE)\} \qquad \text{(S2)}$$

$$\mathrm{a} = (\varepsilon_T^* - \varepsilon_0)c_0 l \qquad \text{(S3)}$$

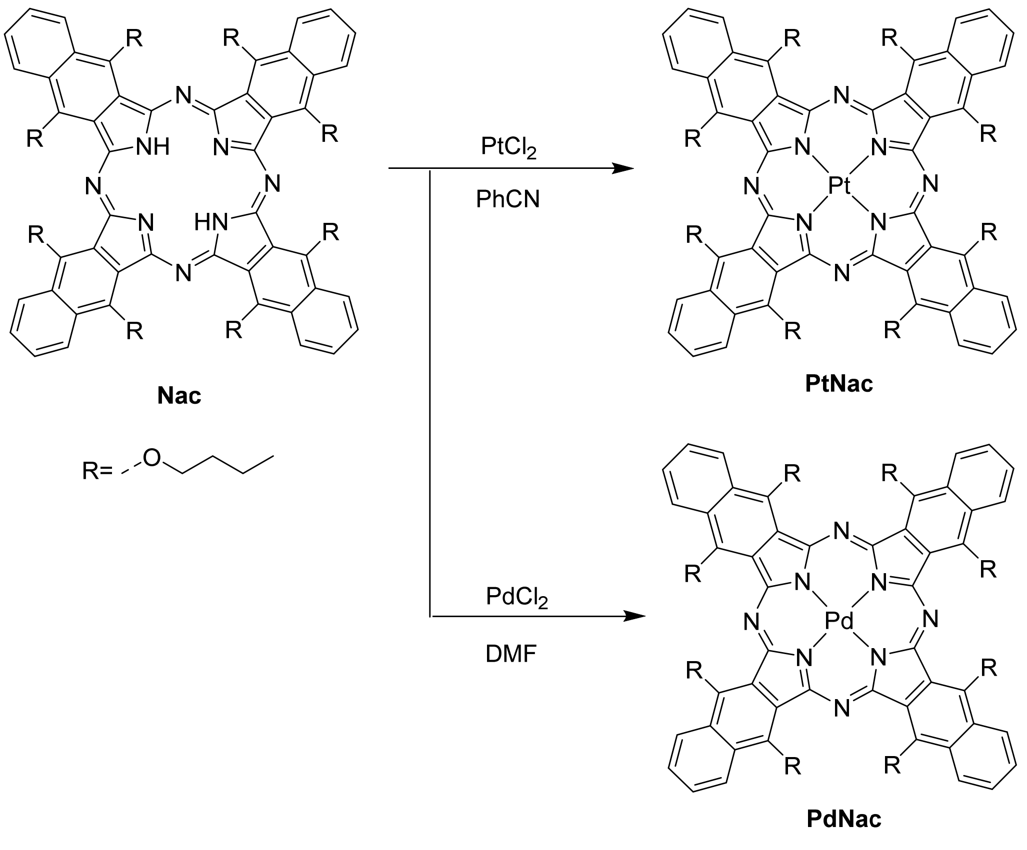
$$b = 2303\varepsilon^{0}_{exc}\Phi_{ISC} \qquad \text{(S4)}$$

where E is given in Einstein cm^{-2}, ε_T^* and ε_0 are the molar absorption coefficients of the triplet excited state and the ground state, respectively, at 680 nm, c_0 is the ground-state concentration before pulsed excitation, l is the optical path length in the direction of the monitoring beam, ε^{0}_{exc} is the molar absorption coefficient of the ground state at the excitation wavelength (Fig. S2).

Density functional theory (DFT) calculations.

We used DFT to optimize the lowest lying singlet (S_0) and triplet (T_1) geometries employing Becke's three parameter hybrid functional using the Lee, Yang, and Parr correlation functional (B3LYP) with a 6-311G** basis set.[3, 4] The S_0-S_1 energy gap was obtained as 1.89 eV using time-dependent DFT (TDDFT) with a 6-311++G** basis set, which shows a good agreement with the experimental absorption peak at 1.86 eV in 1,2-dichlorobenzene.

Synthetic Procedure of donors.



Synthesis of **PtNac**.[5]

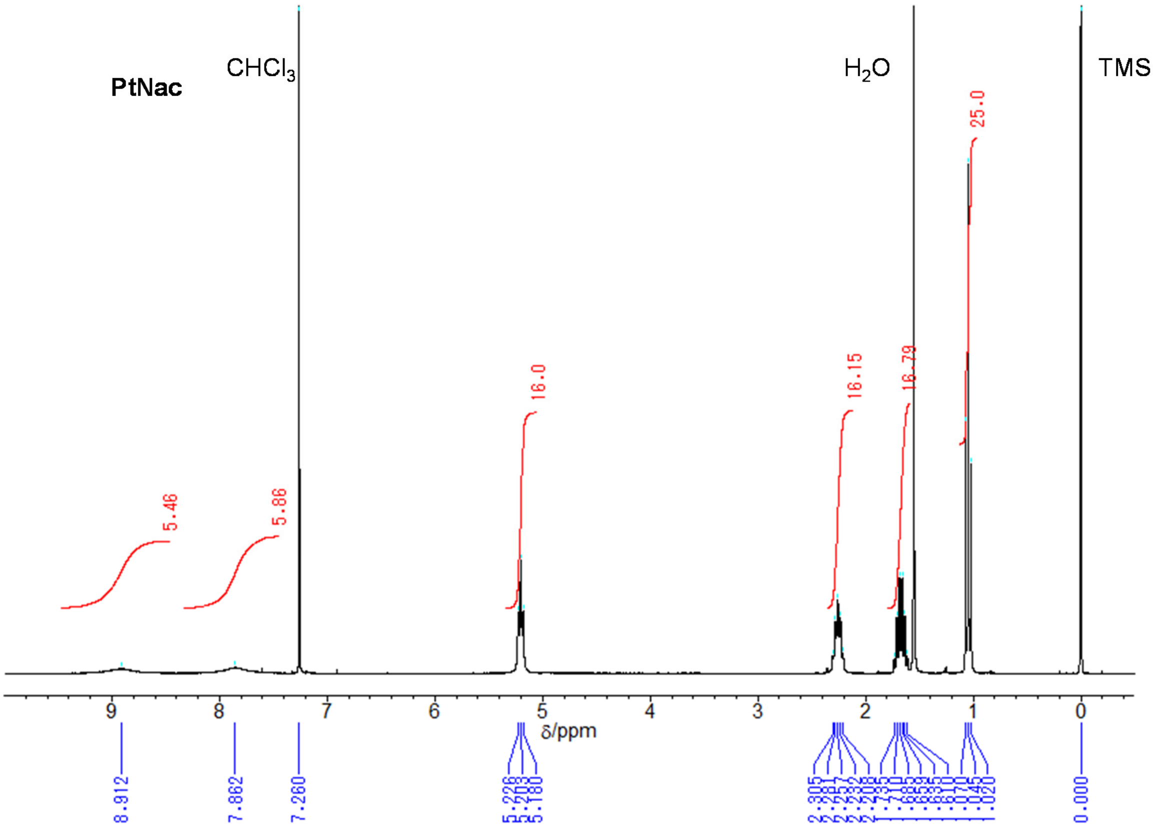
Under Ar, **Nac** (39 mg, 0.03 mmol) and $PtCl_2$ (72 mg, 0.27 mmol) in benzonitrile (2 mL, bubbled with Ar) were heated at 150 °C for 16 h with tracing disappearance of original absorption bands. The resulting mixture was cooled to the room temperature and then evaporated under vacuum (40 °C). The residue was chromatographed (Al_2O_3, toluene) and washed with methanol and hexane to obtain **PtNac** as a dark green solid (6 mg, 0.004 mmol, 13%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS standard): δ (ppm) 1.05 (t, J = 7.4 Hz, 24H, CH_3), 1.67 (sextet, J = 7.5 Hz, 16H,

CH_2CH_3), 2.26 (quintet, *J* = 7.2 Hz, 16H, $CH_2CH_2CH_3$), 5.20 (t, *J* = 6.9 Hz, 16 H, OCH_2), 7.86 (br, Ar*H*), 8.91 (br, Ar*H*). Elemental analysis; calculated for $C_{80}H_{88}N_8O_8Pt$: C 64.72, H 5.97, N 7.55, Found: C 64.63, H 6.00, N 7.50.

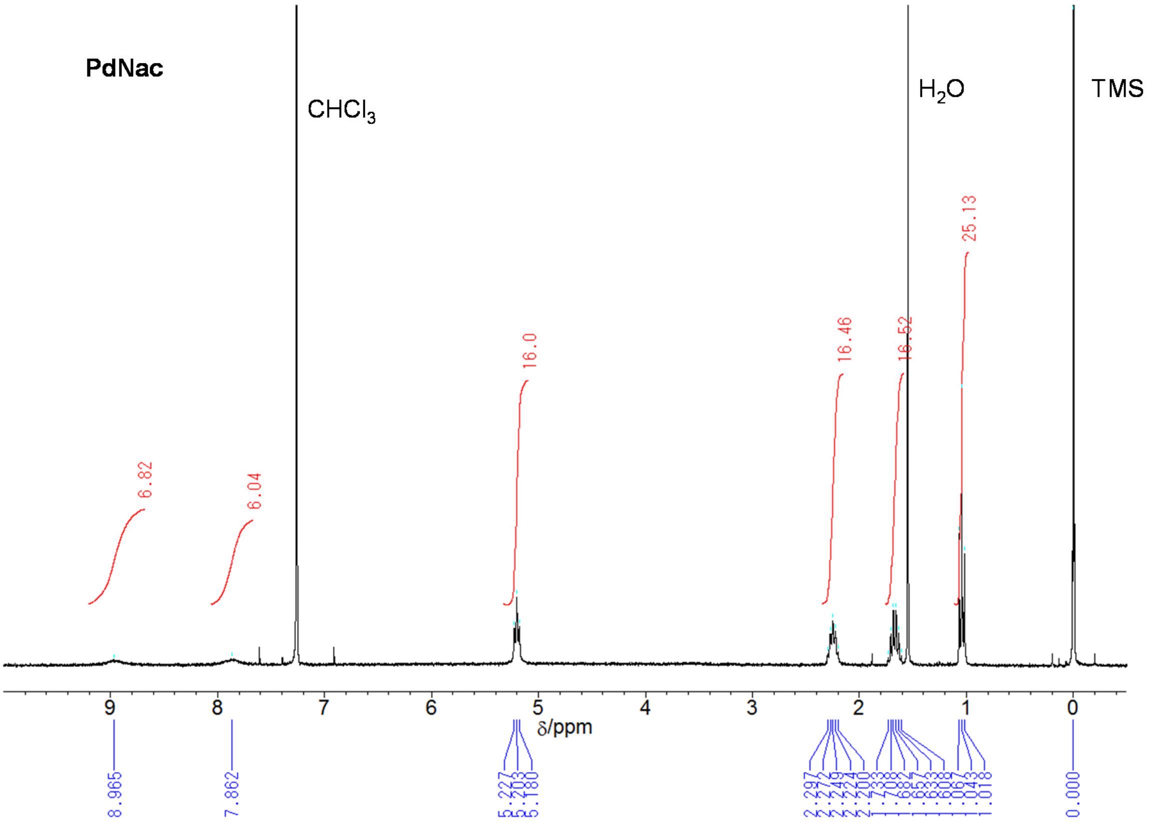
Synthesis of **PdNac**.[5, 6]

Under Ar, **Nac** (39 mg, 0.03 mmol) and $PdCl_2$ (48 mg, 0.27 mmol) in DMF (19 mL, bubbled with Ar) were refluxed for 6 h with tracing disappearance of original absorption bands. The resulting mixture was cooled to the room temperature and then evaporated to dryness with a rotary evaporator (45 °C). The residue was chromatographed (Al_2O_3, toluene) and washed with methanol and hexane to obtain **PdNac** as a dark brown solid (22 mg, 0.016 mmol, 53%).

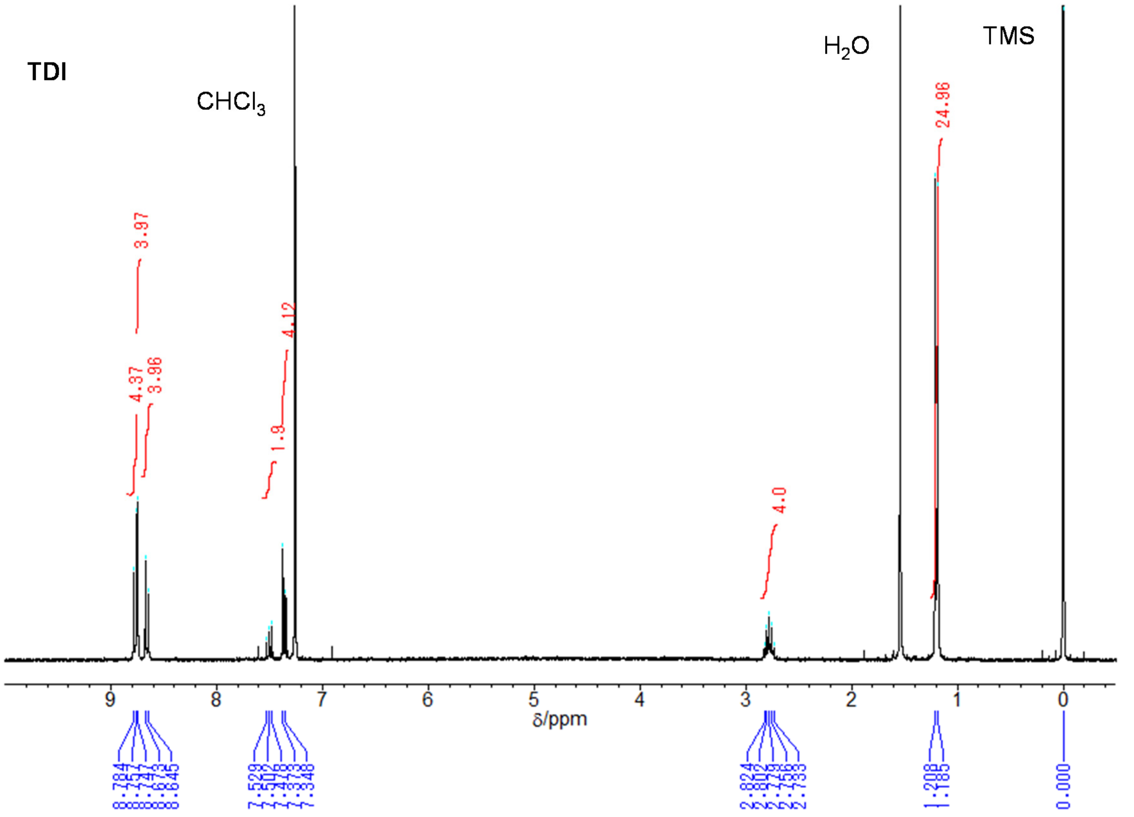
^1H NMR (300 MHz, $CDCl_3$, TMS standard): δ (ppm) 1.04 (t, *J* = 7.4 Hz, 24H, CH_3), 1.67 (sextet, *J* = 7.5 Hz, 16H, CH_2CH_3), 2.25 (quintet, *J* = 7.3 Hz, 16H, $CH_2CH_2CH_3$), 5.20 (t, *J* = 7.0 Hz, 16 H, OCH_2), 7.86 (br, Ar*H*), 8.96 (br, Ar*H*). Elemental analysis; calculated for $C_{80}H_{88}N_8O_8Pd$: C 68.83, H 6.35, N 8.03, Found: C 68.43, H 6.10, N 7.90.



^1H NMR spectrum (300 MHz, $CDCl_3$) of **PtNac**.



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **PdNac**.



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **TDI**.

Supporting figures and table:

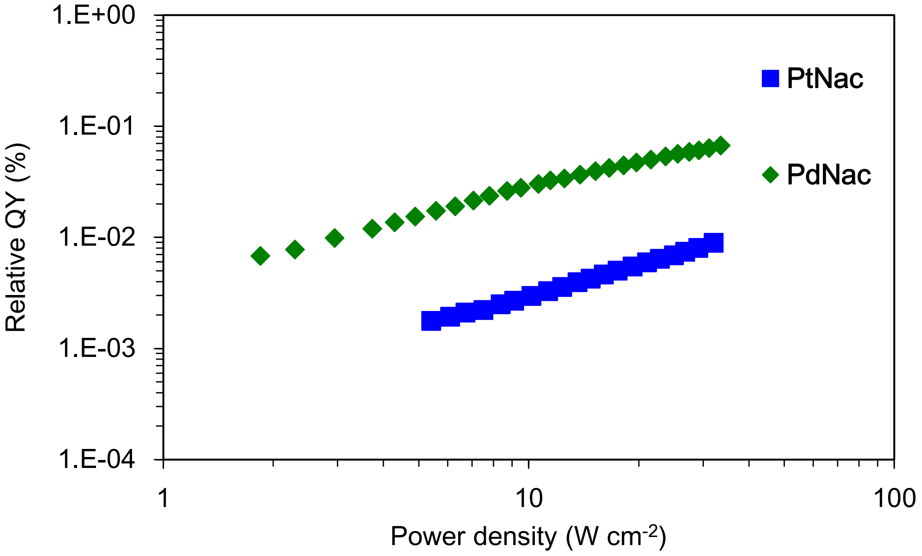


Figure S1. Double logarithmic plots of the relative UC quantum yield of the **PtNac-TDI** and **PdNac/TDI** pairs in deaerated 1,2-DCB as a function of excitation power density of 856 nm laser ([**Pt**/**PdNac**] = 0.05 mM, [**TDI**] = 0.6 mM, 810 nm short pass filter).

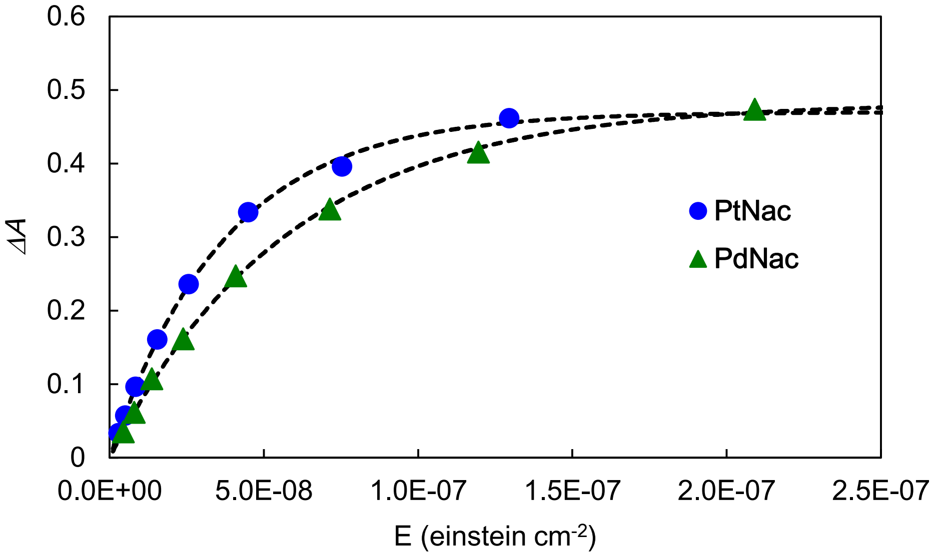


Figure S2. Laser pulse intensity dependence of the transient absorbance of donor solution in deaerated toluene obtained 0.05 μs (**PtNac**, 20 μM) and 0.2 μs (**PdNac**, 20 μM) after the laser pulse. Dotted lines represent least-squares fitting results using the equation S2.

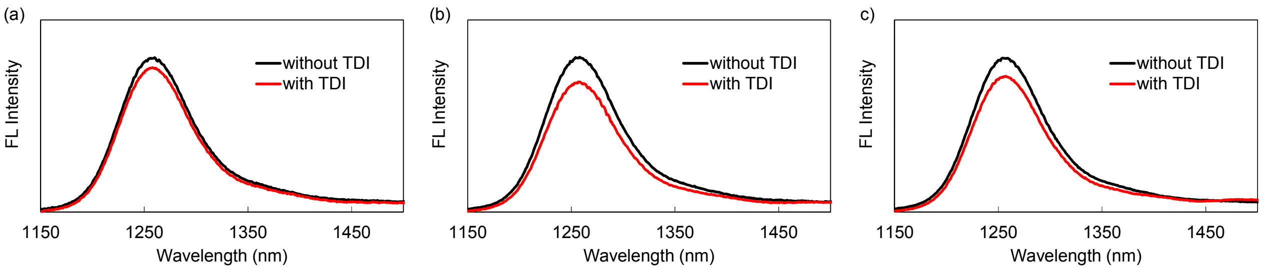


Figure S3. Phosphorescence spectra of **PtNac** in deaerated 1,2-DCB with and without **TDI** using different **PtNac** concentrations of (a) 0.1 mM, (b) 0.05 mM, and (c) 0.02 mM ([**TDI**] = 0.6 mM).

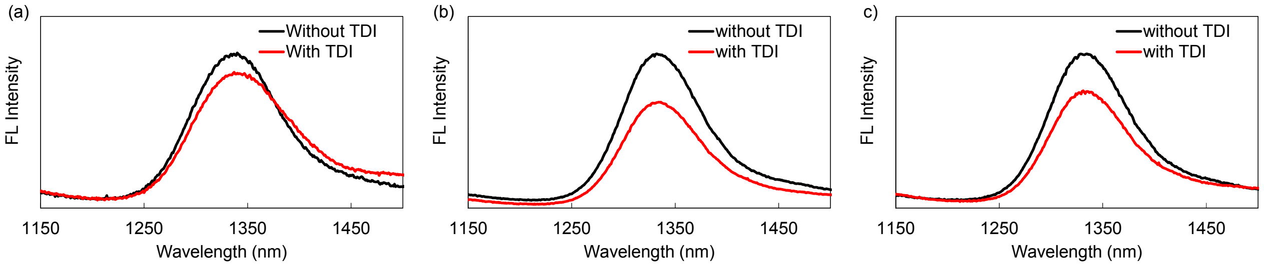


Figure S4. Phosphorescence spectra of **PdNac** in deaerated 1,2-DCB with and without **TDI** using different **PtNac** concentrations of (a) 0.1 mM, (b) 0.05 mM, and (c) 0.02 mM ([**TDI**] = 0.6 mM).

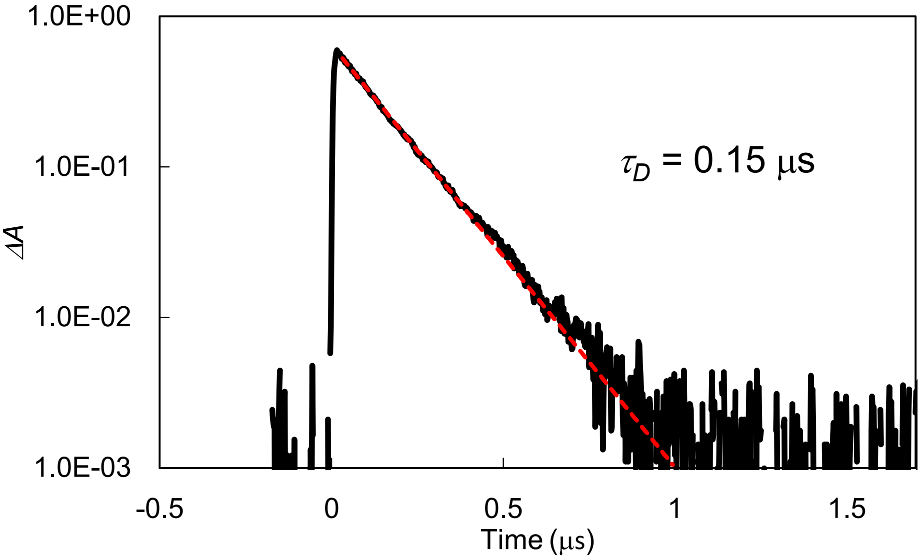


Figure S5. Time-resolved single wavelength absorption kinetics of **PtNac** (20 μM) in deaerated toluene monitored at 680 nm (λ_{ex} = 462 nm). The red dotted lines represent exponential function fitting result.

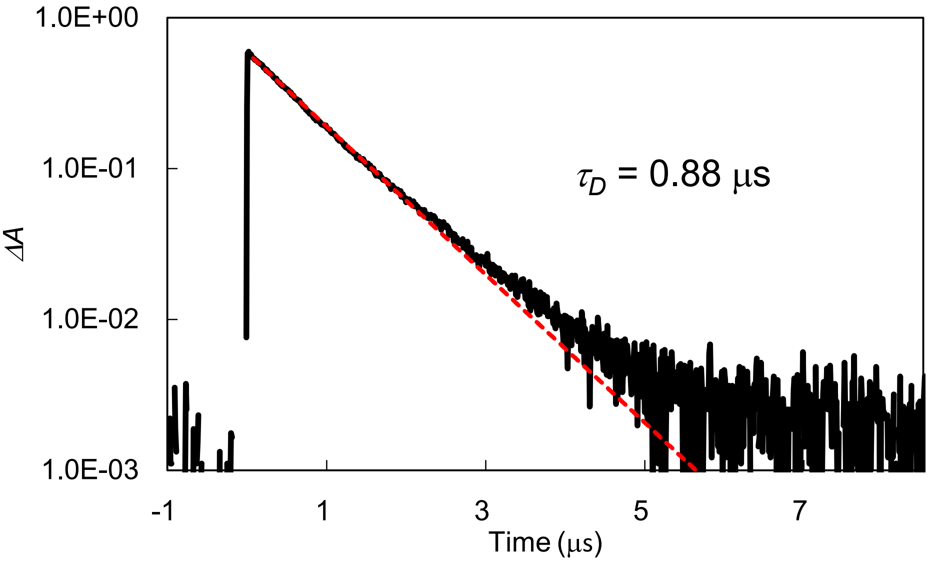


Figure S6. Time-resolved single wavelength absorption kinetics of **PdNac** (20 μM) in deaerated toluene monitored at 680 nm (λ_{ex} = 468 nm). The red dotted lines represent exponential function fitting result.

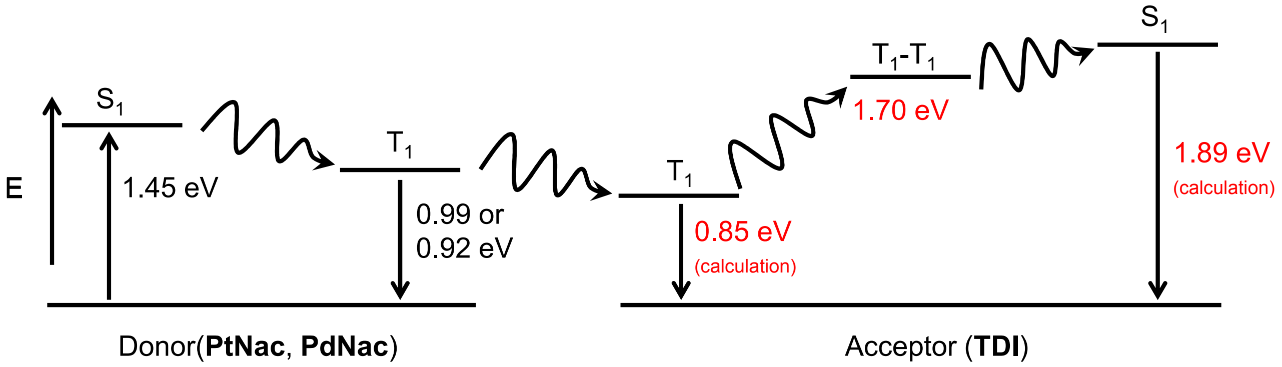


Figure S7. Qualitative energy level diagram of the sensitized triplet-triplet annihilation process. The T_1 energy level of acceptor **TDI** was obtained by DFT calculations.

Supporting references:

1 F. Nolde, J. Qu, C. Kohl, N. G. Pschirer, E. Reuther and K. Müllen, *Chem. Eur. J.*, 2005, **11**, 3959-3967.

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