Electronic Supplementary Information for

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

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**Caption of Content**

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

**Fig. S2.** $^1$H NMR spectra of PdPor-2-DPA and PdPor-9-DPA in CDCl$_3$.

**Fig. S3.** Absorption spectra of PdPor-2-DPA, PdPor-9-DPA and mixed solution of PdTTP: DPA=1:1.

**Fig. S4.** Luminescence emission spectra of PdPor-2-DPA, PdPor-9-DPA and PdTTP.

**Fig. S5.** fs-TA spectra and single-wavelength dynamics of PdTTP.

**Fig. S6.** Single-wavelength dynamics of PdTTP probed at 480 nm from nanosecond TA spectra.

**Fig. S7-9.** Comparison of TA spectra and single-wavelength dynamics of PdPor-2-DPA(S7), PdPor-9-DPA(S8) PdTTP (S9) between the raw data and the fitting data obtained from the global analysis.

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

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

**Table S1.** The orientation angle of the phthalocyanine ring determined from polarized UV–vis absorbance of the QLS films of compounds 1-2.
**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, $c = 1.0 \times 10^{-5}$; in mixed solution, PdTPP and DPA, $c = 1.0 \times 10^{-5}$ in deaerated toluene.

Fig. S4. Luminescence emission spectra of PdPor-2-DPA, PdPor-9-DPA and PdTPP.; $\lambda_{ex} = 532$ nm, $c = 1.0 \times 10^{-5}$ M in aerated Toluene, 293K.
**Fig. S5.** fs-TA spectra (A) and single-wavelength dynamics probed at 450 and 480 nm (B) of PdTPP. $\lambda_{ex} = 532$ nm, $c = 2.0 \times 10^{-5}$ M in deaerated toluene, 293K.

**Fig. S6.** Single-wavelength dynamics of PdTPP probed at 480 nm from nanosecond TA spectra. $\lambda_{ex} = 532$ nm, $c = 2.0 \times 10^{-5}$ 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 $S_1$($\text{PdPor}^*-\text{DPA}$)$\rightarrow T_1$($\text{PdPor}^*-\text{DPA}$) 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 (S₁(PdPor*-DPA) → T₁(PdPor*-DPA) → T₁(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 $S_1(PdPor^*) \rightarrow T_1(PdPor^*)$ 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.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Φ (%)</th>
<th>$\tau^a$ (μs)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdTPP-2-DPA</td>
<td>0.26 ± 0.03</td>
<td>108.98 ± 0.1 (91.33%)</td>
<td>1.027</td>
</tr>
<tr>
<td></td>
<td></td>
<td>147.57 ± 0.1 (8.67%)</td>
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<tr>
<td>PdTPP-9-DPA</td>
<td>0.23 ± 0.03</td>
<td>79.96 ± 0.1 (77.94%)</td>
<td>1.019</td>
</tr>
<tr>
<td></td>
<td></td>
<td>119.23 ± 0.1 (22.06%)</td>
<td></td>
</tr>
<tr>
<td>PdTPP</td>
<td>0.41 ± 0.05</td>
<td>77.04 ± 0.1 (72.00%)</td>
<td>1.123</td>
</tr>
<tr>
<td></td>
<td></td>
<td>215.33 ± 0.1 (28.00%)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Phosphorescence lifetimes were monitored at 697 nm (c = 1.0 × 10⁻⁵ M).