Supporting Information for

An experimental and theoretical study of
Dimethylaminostyril BODIPY - Perylenetetracarboxylic
derivatives dyads: synthesis, properties and DFT calculation.

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Experimental Section

Synthesis of compound 7

8-Phenyl-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (260 mg, 0.8 mmol), 4-dimethylaminobenzaldehyde (480 mg, 3.2 mmol), piperidine (0.68 ml), acetic acid (0.57 ml) and toluene (5 ml) were refluxed for 6 h in the presence of Dean-Stark apparatus. After the reaction reached completion, the solvent was removed in vacuum, after column chromatography by silica gel eluting with a gradient of dichloromethane-petroleum ether (v/v 3:7) to dichloromethane, compound 7 was obtained as a green solid (220 mg, 46.8%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (m, 6 H), 7.47 (m, 3 H), 7.37 – 7.30 (m, 2 H), 7.19 (d, $J = 16.2$ Hz, 2 H), 6.72 (d, $J = 8.7$ Hz, 4 H), 6.59 (s, 2 H), 3.03 (s, 12 H), 1.42 (s, 6 H).
Figure S1 The UV-vis spectra of compounds 2 (a), PBI-BODIPY (b), PTAC-BODIPY (c), and OMe-PTAC-BODIPY (d) in CH$_2$Cl$_2$ (1.0×10$^{-5}$ mol/L) at room temperature upon addition the solution of ceric ammonium nitrate in acetonitrile (1.0×10$^{-3}$ mol/L). The peaks located at 943 nm were assigned to the absorption of BODIPY cations.
Figure S2 Near infrared phosphorescence spectra of compounds 7 and three dyads in CH$_2$Cl$_2$ at room temperature (1.0×10$^{-5}$ mol/L), excited at 650 nm. The samples were detected after oxygen was removed by bubbling N$_2$ for 30min.
Figure S3. UV-Vis absorption spectra (a) and Fluorescence emission spectra (b) of compounds 2 (Br-BODIPY), 7 (H-BODIPY), and 3 (BODIPY boronic ester), in CH$_2$Cl$_2$ at room temperature (1.0×10$^{-5}$ mol/L). The fluorescence emission spectra was excitated at 650nm.
Figure S4 Differential pulse voltammograms (DPV) versus Ag/AgCl, Fc/Fc$^+$ was used as external standard, and 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NP$_6$) dissolved in CH$_2$Cl$_2$ was employed as the supporting electrolyte. Scan rate = 5 mV/s. LUMO levels estimated by the onset of reduction peaks and calculated according to $E_{\text{LUMO}} = -(4.8 + E_{\text{Ronset}})$ eV. LUMO levels estimated by the onset of reduction peaks and calculated according to $E_{\text{HOMO}} = - (4.8 + E_{\text{Oonset}})$ eV.
Figure S5 Cyclic voltammograms of dyads versus Ag/AgCl, Fc/Fc$^+$ was used as external standard, and 0.1 M tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) dissolved in CH$_2$Cl$_2$ was employed as the supporting electrolyte. Scan rate = 5 mV/s.
<table>
<thead>
<tr>
<th></th>
<th>OMePTAC-BODIPY</th>
<th>PTAC-BODIPY</th>
<th>PBI-BODIPY</th>
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</thead>
<tbody>
<tr>
<td>$\Delta G_{CS}$</td>
<td>-0.1 eV</td>
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<td>-0.69 eV</td>
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<td>$\Delta G_{CR}$</td>
<td>-1.53 eV</td>
<td>-1.47 eV</td>
<td>-0.94 eV</td>
</tr>
<tr>
<td>$E_{CS}$</td>
<td>1.53 eV</td>
<td>1.47 eV</td>
<td>0.94 eV</td>
</tr>
</tbody>
</table>

Table S1. The thermodynamic driving force for photoinduced electron transfer was calculated from the Weller equation, $E_{CS} = E(D^+/D) - E(A^-/A) + \Delta G_S$, where $E(D^+/D)$ is the oxidation potential of the donor, and $E(A^-/A)$ is the reduction potential of the acceptor, $\Delta G_S (-0.14eV)$ is the static Coulombic energy.

$$\Delta G_S = -\frac{e^2}{4\pi \varepsilon_S \varepsilon_0 R_{CC}} - \frac{e^2}{8\pi \varepsilon_0} \left( \frac{1}{R_D} + \frac{1}{R_A} \right) \left( \frac{1}{\varepsilon_{REF}} - \frac{1}{\varepsilon_S} \right)$$

$\varepsilon_{REF}$ is the static dielectric constant of the solvent used for the electrochemical studies, $\varepsilon_S$ is the static dielectric constant of the solvent in the absorption spectra.

For $\varepsilon_{REF} = \varepsilon_S$

$$\Delta G_S = -\frac{e^2}{4\pi \varepsilon_S \varepsilon_0 R_{CC}}$$

$R_{CC}$ = center-to-center separation distance between the electron donor and electron acceptor (Perylenetetracarboxylic derivatives), determined
by DFT optimization of the geometry.

Figure S6. Switching of the singlet oxygen (\(1^1O_2\)) photosensitizing ability. The decrease of the absorbance at 414 nm of DPBF as a function of irradiation time for PBI-BODIPY, PTAC-BODIPY, OMePTAC-BODIPY, Br-BODIPY, BODIPY and Methylene blue (\(\lambda_{ex} = 650\) nm, the irradiation power is 3mV). (The concentration of DPBF was \(4\times10^{-5}\) mol/L, and the concentration of dyes is \(1\times10^{-6}\) mol/L in DCM), the experiment was carried out in the dark. The slopes of fitting line were shown in the figure in the same color.
NMR

Compound 1:

Compound 2:
Compound 7:
Compound 3:
Compound 4:

Compound 5:
PBI–BODIPY:
PTAC –BODIPY:
OMe-PTAC –BODIPY: