Supporting information

New 2D-π-2A organic dyes with bipyridine anchoring group for DSSCs

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Synthesis of the dyes

Scheme S1 synthesis procedure of S1 and S2. Reagents and conditions: a) bis(pinacolato)diboron, Pd(dppf)Cl$_2$, KOAc, DMF, 80°C; b) bis(pinacolato)diboron, Pd(dppf)Cl$_2$, KOAc, DMF, 80°C; c) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, H$_2$O, THF, 90°C; d) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, H$_2$O, THF, 90°C.
**Synthesis of compound 2**

A mixture of compound 1 (3.00 g, 7.68 mmol), bis(pinacolato)diboron (2.93 g, 11.53 mmol) and KOAc (2.26 g, 23.05 mmol) in DMF (50 mL) was added Pd(dppf)Cl$_2$ (0.30 g) under dinitrogen. The mixture was heated under 80°C for overnight. The reaction mixture was cooled to room temperature and H$_2$O (150 mL) was added, the mixture was extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over MgSO$_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound 2 (2.51 g, 75%).

δ$_{\text{H}}$ $^1$H NMR (CDCl$_3$, 500Hz)  δ$_{\text{H}}$ 7.62-7.65 (m, 2H), 7.14-7.18 (m, 2H), 6.92 (t, $J$ = 7.5 Hz, 1H), 6.87 (d, $J$ = 8.0 Hz, 2H), 3.88 (t, $J$ = 7.0 Hz, 2H), 1.80-1.86 (m, 2H), 1.42-1.49 (m, 2H), 1.30-1.40 (m, 20H), 0.93 (t, $J$ = 6.5 Hz, 3H).

**Synthesis of compound 4**

The preparation method was the same as that of compound 2. δ$_{\text{H}}$ $^1$H NMR (CDCl$_3$, 400 MHz) 8.60 (s, 1H), 8.12-8.14 (d, $J$ = 7.6 Hz, 1H), 7.91-7.93 (d, $J$ = 7.6 Hz, 1H), 7.43-7.47 (m, 1H), 7.38-7.40 (d, $J$ = 8.4 Hz, 2H), 7.21-7.25 (m, 1H), 4.27-4.30 (t, $J$ = 7.2 Hz, 2H), 1.83-1.87 (m, 2H), 1.40 (s, 12H), 1.25-1.34 (m, 10H), 0.84-0.87 (t, $J$ = 6.8 Hz, 3H).

**Synthesis of compound S1**

Under nitrogen, compound 5 (0.50 g, 1.14 mmol), compound 2 (1.24 g, 2.84 mmol), K$_2$CO$_3$ (0.63 g, 4.54 mmol) and Pd(PPh$_3$)$_4$ (0.08 g) were dissolved in THF (50 mL) and H$_2$O (10 mL). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and extracted by DCM (3×50 mL). The combined organic layers were washed with brine, dried over MgSO$_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (DCM/MeOH=50/1) to give S1 (0.73 g, 72%). δ$_{\text{H}}$ $^1$H NMR (CDCl$_3$, 400 MHz) 9.16-9.18 (m, 4H), 7.88 (s, 2H), 7.68 (s, 2H), 7.63-7.65 (d, $J$ = 8.0 Hz, 4H), 7.20-7.23 (m, 4H), 7.03-7.05 (d, $J$ = 8.4 Hz, 2H), 6.94-6.99 (m, 4H), 3.95-3.98 (t, $J$ = 7.2 Hz, 4H), 1.90-1.97 (m, 4H), 1.49-1.54 (m, 4H), 1.24-1.43 (m, 16H), 0.86-0.89 (t, $J$ = 6.8 Hz,
Synthesis of compound S2

The preparation method was the same as that of S1. δ_H 1H NMR (CDCl₃, 400 MHz)
9.37-9.39 (m, 2H), 9.20-9.21 (m, 2H), 8.78-8.79 (s, 2H), 8.17-8.22 (m, 4H), 8.09-8.11
(m, 2H), 7.61-7.66 (m, 4H), 7.51-7.56 (m, 4H), 7.28-7.30 (m, 4H), 4.43-4.46 (t, J =
7.2 Hz, 4H), 1.97-2.04 (m, 4H), 1.49-1.53 (m, 4H), 1.40-1.43 (m, 4H), 1.24-1.32 (m,
12H), 0.85-0.89 (t, J = 6.8 Hz, 6H). δ_C 13C NMR (CDCl₃, 100 MHz) 152.15, 148.28,
140.92, 140.19, 139.83, 139.69, 134.00, 130.75, 129.04, 127.96, 125.39, 124.14,
123.27, 122.88, 120.32, 119.11, 108.95, 108.22, 43.36, 31.87, 29.49, 29.29, 27.47,
Table S1 Optical and electrochemical properties of dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}$/nm ($\varepsilon \times 10^4$ M$^{-1}$ cm$^{-1}$)</th>
<th>$b_{\text{OX}}$/V (NHE)</th>
<th>$c_{0-0}$/eV</th>
<th>$d_{\text{OX}}$/V (NHE)</th>
<th>Loading amounts (10$^{-7}$ mol cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>493 (1.54)</td>
<td>0.96</td>
<td>1.90</td>
<td>-0.94</td>
<td>3.45</td>
</tr>
<tr>
<td>S2</td>
<td>473 (1.65)</td>
<td>1.02</td>
<td>2.06</td>
<td>-1.04</td>
<td>1.18</td>
</tr>
</tbody>
</table>

$^a$Absorption maximum in DCM solution ($1 \times 10^{-5}$ M), $^b$the ground state oxidation potentials, $^c_{0-0}$ was estimated from the absorption spectra, $^d_{\text{OX}}$ was calculated by the formula: $E'_{\text{OX}} = E_{\text{OX}} - E_{0-0}$.

Fig. S1 Cyclic voltammogram of S1 and S2 in DCM, 0.1 M TBAPF$_6$, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag$^+$ as reference electrode, scan rate: 100 mV s$^{-1}$, calibrated with ferrocene/ferrocenium (Fc/Fc$^+$) as an external reference.
Fig. S2 FTIR spectra of dye powders and dyes adsorbed on TiO$_2$ nanoparticles.