

## *Supporting information*

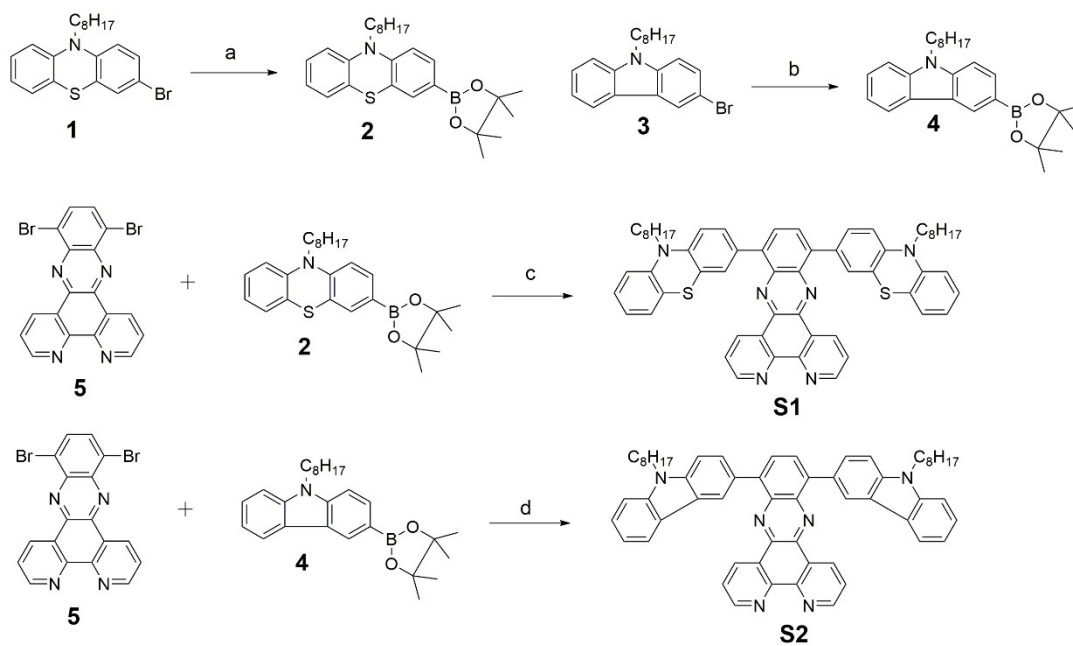
### New 2D- $\pi$ -2A organic dyes with bipyridine anchoring group for DSSCs

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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<sub>2</sub>, KOAc, DMF, 80 °C; b) bis(pinacolato)diboron, Pd(dppf)Cl<sub>2</sub>, KOAc, DMF, 80 °C; c) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, THF, 90 °C; d) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>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<sub>2</sub> (0.30 g) under dinitrogen. The mixture was heated under 80°C for overnight. The reaction mixture was cooled to room temperature and H<sub>2</sub>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<sub>4</sub>, 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%).  $\delta_{\text{H}}$  <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500Hz)  $\delta_{\text{H}}$  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.  $\delta_{\text{H}}$  <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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<sub>2</sub>CO<sub>3</sub> (0.63 g, 4.54 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.08 g) were dissolved in THF (50 mL) and H<sub>2</sub>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<sub>4</sub>, and evaporated in vacuo. The residue was purified by silica gel column chromatography (DCM/MeOH=50/1) to give S1 (0.73 g, 72%).  $\delta_{\text{H}}$  <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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,

6H).  $\delta_{\text{C}}$   $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) 152.43, 145.02, 140.16, 139.64, 138.23, 133.96, 132.23, 130.06, 129.87, 129.80, 127.64, 127.56, 127.36, 124.60, 124.20, 122.59, 115.50, 114.79, 47.64, 31.82, 29.36, 29.30, 27.11, 22.63, 14.15.

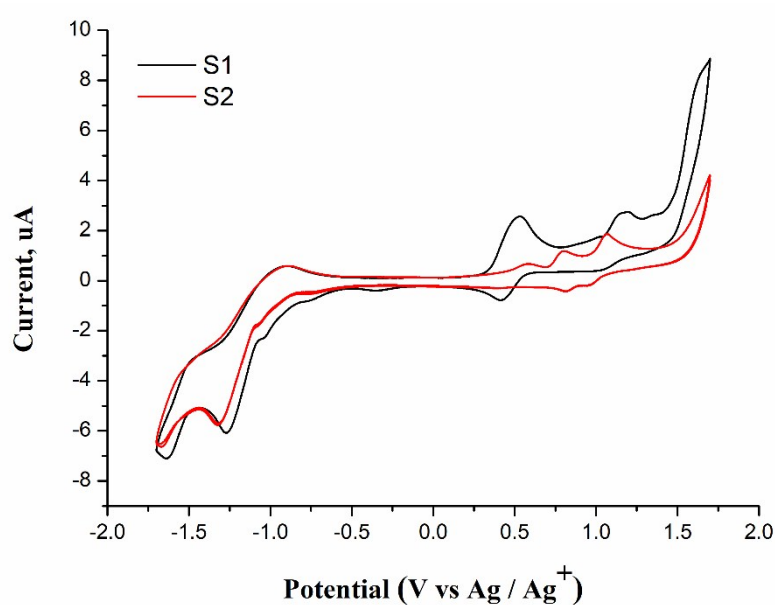
### **Synthesis of compound S2**

The preparation method was the same as that of S1.  $\delta_{\text{H}}$   $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 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).  $\delta_{\text{C}}$   $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 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, 22.67, 14.14.

**Table S1** Optical and electrochemical properties of dyes

Dye	<sup>a</sup> $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	<sup>b</sup> $E_{\text{OX}}/\text{V}$ (NHE)	<sup>c</sup> $E_{0-0}/\text{eV}$	<sup>d</sup> $E^*_{\text{OX}}/\text{V}$ (NHE)	Loading amounts ( $10^{-7} \text{ mol cm}^{-2}$ )
S1	493 (1.54)	0.96	1.90	-0.94	3.45
S2	473 (1.65)	1.02	2.06	-1.04	1.18

<sup>a</sup>Absorption maximum in DCM solution ( $1 \times 10^{-5} \text{ M}$ ), <sup>b</sup>the ground state oxidation potentials, <sup>c</sup> $E_{0-0}$  was estimated from the absorption spectra, <sup>d</sup> $E^*_{\text{OX}}$  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<sub>6</sub>, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag<sup>+</sup> as reference electrode, scan rate: 100 mV s<sup>-1</sup>, calibrated with ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as an external reference.

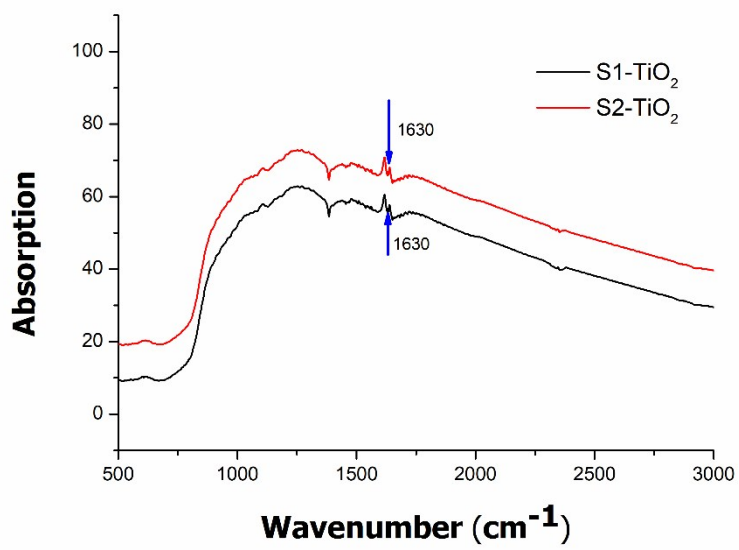
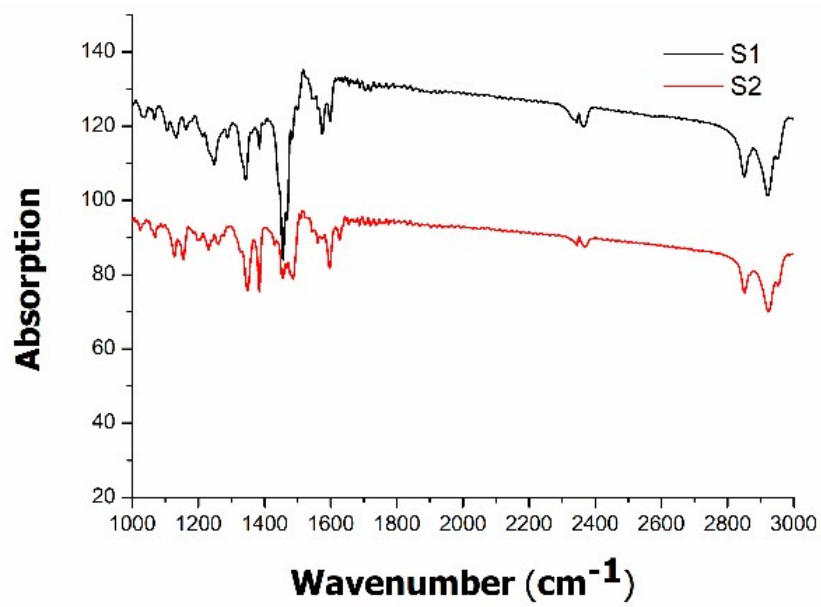


Fig. S2 FTIR spectra of dye powders and dyes adsorbed on TiO<sub>2</sub> nanoparticles.

