

Invited Paper

## Porphyrin-Perylene Dyes for Dye-Sensitized Solar Cells

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Two novel porphyrin-perylene dyads **1** and **2** for DSSC applications have been synthesized. The absorption band of the perylene fills up the trough between the Soret and Q bands of the porphyrin, leading to an increase in the absorption efficiency of the dye. The highly conjugated acetylenic bridge mediates strong electronic coupling between the porphyrin and perylene units and results in the extension of  $\pi$ -conjugation of the porphyrin ring. The Soret and Q bands are broadened and red-shifted and the light-harvesting effect is thus improved. We propose that energy transfer occurs from the photoexcited perylene to porphyrin for dyad **1** whereas energy transfer proceeds from the excited porphyrin to perylene for dyad **2**. Our studies show that multichromophoric dyes used for DSSC can be designed in a rational manner with predictable photophysical behavior and efficient light-harvesting properties, but the efficiency of the energy transfer process in a consecutive model needs to be controlled for a significant improvement of the cell performance using perylene-porphyrin sensitizers.

**Keywords:** DSSC; Energy transfer; Perylene; Porphyrin; Photovoltaics.

### INTRODUCTION

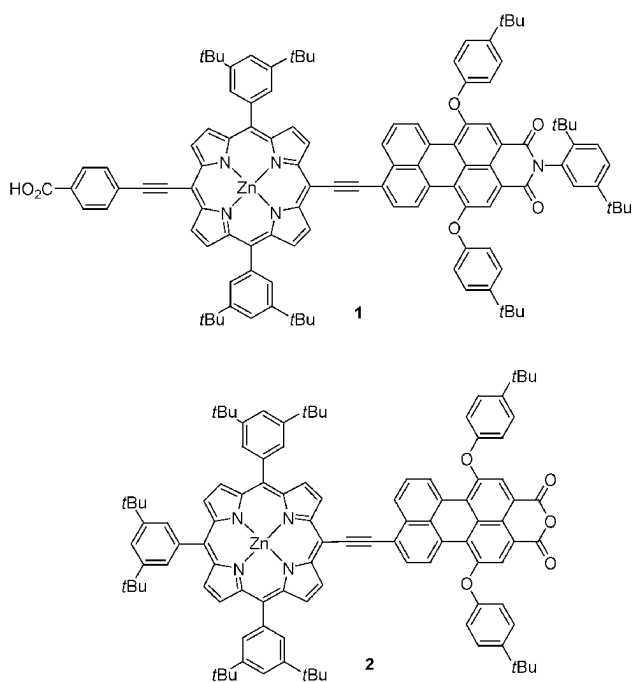
There have been increasing interests in the research and development of renewable energy technologies as the energy demand is growing worldwide. The renewable sources may come from hydroelectric resource, ocean currents, wind power, geothermal energy, and solar energy.<sup>1</sup> Among these options, solar energy represents a most attractive choice to meet our energy demand in the future because the energy produced from the sun is environmental friendly and infinite. However, the high cost of current silicon-based photovoltaic panels has limited their wide application and replacement of the traditional fossil fuel.<sup>2</sup> Recently, dye-sensitized solar cells (DSSC) have emerged as an alternative to conventional solar cells due to their low cost and simple preparation processes.<sup>3</sup> To date, the most efficient DSSC are based on the ruthenium complexes of polypyridines absorbed on nanocrystalline TiO<sub>2</sub> surface and the maximum energy conversion efficiencies were over 11%.<sup>4</sup> Although the performance of ruthenium complexes shows the best efficiency so far, there are some challenging issues such as the rareness, low absorption coefficients, and environmental concerns on the ruthenium dye based

DSSC. The weaknesses of ruthenium dyes have prompted scientists to develop organic dyes for use in DSSC because they show many advantages as photosensitizers for DSSC.<sup>2,3</sup> First, they exhibit much higher absorption coefficient than the ruthenium complexes. Second, a variety of molecular structures can be easily modified and their optical, photophysical, and electrochemical properties can be tuned. Third, the production cost is low and the resources are more abundant relative to metal complexes. Therefore, many efficient organic dyes have been designed and synthesized.<sup>2,3</sup>

Porphyrins are one of the most studied macrocycles because of their importance in biological systems.<sup>5</sup> For example, porphyrins have been widely employed as light-harvesting antenna because their structural similarity to chlorins and bacteriochlorins which are naturally occurring pigments in plants and bacterial photosynthetic systems, respectively.<sup>6</sup> Therefore, numerous porphyrins and related derivatives have been investigated as photosensitizers in DSSC.<sup>7</sup> The use of porphyrins in DSSC has two major advantages: (i) facile modification on four *meso* and eight  $\beta$  sites to fine-tune the electrochemical and photophysical

properties and (ii) a strong Soret band in the range 400-450 nm and moderate Q bands in the range 550-650 nm. To be an efficient dye, it is necessary to absorb intensely across the whole visible spectrum and even the near-IR region. However, the absorption gap between the Soret and Q bands decreases the light-harvesting efficiency. One approach to circumvent this problem is to introduce an appropriate auxiliary pigment that can fill up the absorption gap in the 450-550 nm region. Similar to porphyrin derivatives, perylene imides and bisimides are a class of heterocycles that have been widely investigated in industry. Recently, their applications in light harvesting,<sup>8</sup> photovoltaics,<sup>9</sup> studies of photoinduced charge and energy transfer processes,<sup>10</sup> electronics, and optoelectronics as n-type materials<sup>11</sup> have been developed. They also exhibit chemical and thermal stability and show numerous unique photophysical, optical, and electrochemical properties that attract scientific interests in many different areas. In general, perylene imides show strong absorption band in the trough region between the Soret and Q bands of porphyrins. Therefore, they are ideal auxiliary pigments in combination with porphyrins to improve light-harvesting efficiency. In this paper, we present the synthesis, characterization, absorption and fluorescence properties of two porphyrin-perylene dyads **1** and **2** (Chart 1) for use in DSSC.

**Chart 1** Structures of dyads **1** and **2**



## EXPERIMENTAL

All reagents and solvents were obtained from commercial sources and were used without further purification unless otherwise noted. Column chromatography was performed on silica gel (Merck, 70-230 Mesh ASTM). <sup>1</sup>H NMR spectra (Varian spectrometer) at 400 MHz, UV-visible spectra (Varian Cary 50), UV-visible-NIR spectra (Shimadzu UV-3600), emission spectra (Aminco-Bowman Series 2 or a JASCO FP-6000 spectrofluorometer), MALDI-TOF-MS and FAB-MS mass spectra (Bruker APEX II spectrometer and a JMS-SX/SX102A Tandem Mass spectrometer, respectively, operating in the positive ion detection mode) were recorded on the indicated instruments.

**Dyad 5:** A mixture of porphyrin **3** (29 mg, 0.03 mmol), and perylene **4** (32 mg, 0.036 mmol) in dry THF (15 mL) and NEt<sub>3</sub> (3 mL) was degassed with dinitrogen for 10 min, and then Pd<sub>2</sub>(dba)<sub>3</sub> (6.6 mg, 7.5 mmol) and AsPh<sub>3</sub> (18 mg, 0.06 mmol) were added to the mixture. The solution was refluxed for 14 h under dinitrogen. The solvent was removed in vacuo. The residue was purified on a column chromatograph (silica gel) using hexane/CH<sub>2</sub>Cl<sub>2</sub> = 4/1 as eluent. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/methanol gave **5** (20.6 mg, 39%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.84 (d, *J* = 4.4 Hz, 2H), 9.70 (d, *J* = 4.8 Hz, 2H), 9.57-9.53 (m, 2H), 9.23 (d, *J* = 8.0 Hz, 1H), 8.97 (d, *J* = 4.4 Hz, 2H), 8.90 (d, *J* = 4.4 Hz, 2H), 8.37-8.35 (m, 3H), 8.02 (d, *J* = 1.6 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.81 (s, 2H), 7.57-7.53 (m, 2H), 7.47-7.42 (m, 5H), 7.18-7.14 (m, 4H), 6.98 (d, *J* = 2.0 Hz, 1H), 1.55 (s, 36H), 1.43-1.42 (m, 21H), 1.35-1.34 (m, 18H), 1.30 (s, 9H), 1.28 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 164.19, 153.95, 153.26, 152.30, 151.87, 150.54, 150.24, 149.94, 148.47, 147.30, 143.75, 141.65, 132.98, 132.71, 131.74, 130.88, 130.27, 129.54, 128.72, 128.43, 128.22, 127.50, 127.19, 126.10, 124.47, 124.25, 124.05, 121.85, 120.84, 118.75, 118.62, 110.20, 101.99, 101.38, 97.49, 94.99, 35.51, 34.99, 34.40, 34.17, 31.74, 31.44, 31.16, 19.09, 11.91; UV-vis (THF): λ<sub>max</sub>/nm (ε, 10<sup>3</sup>M<sup>-1</sup>cm<sup>-1</sup>) = 443 (169), 543 (60), 684 (102); FAB-MS: *m/z* calcd for C<sub>117</sub>H<sub>125</sub>N<sub>5</sub>O<sub>4</sub>SiZn: 1757; found 1759 ([M+2H]<sup>+</sup>).

**Dyad 1:** To a solution of **5** (35 mg, 0.02 mmol) was added TBAF (0.04 mL of 1.0 M solution in THF, 0.04 mmol) in THF (10 mL). The solution was stirred under N<sub>2</sub> for 30 min, and then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed under reduced pressure to give the crude deprotected intermediate, which was then added to a mixture of 4-iodobenzoic acid (22.3 mg, 0.09 mmol) in dry

THF (9 mL) and NEt<sub>3</sub> (2 mL). The solution was degassed with dinitrogen for 10 min; then Pd<sub>2</sub>(dba)<sub>3</sub> (4 mg, 4.5 mol) and AsPh<sub>3</sub> (11 mg, 0.036 mmol) were added to the mixture. The mixture was refluxed for 8 h under dinitrogen. The solvent was removed in vacuo, and the residue was purified on a column chromatograph (silica gel) using CH<sub>2</sub>Cl<sub>2</sub>/methanol = 9/1 as eluent. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/methanol gave **1** (13.6 mg, 44%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.84 (d, *J* = 4.0 Hz, 2H), 9.73 (d, *J* = 4.0 Hz, 2H), 9.55-9.52 (m, 2H), 9.21 (d, *J* = 8.4 Hz, 1H), 8.95 (d, *J* = 8.4 Hz, 4H), 8.36-8.34 (m, 3H), 8.29 (d, *J* = 8.0 Hz, 2H), 8.08-8.05 (m, 6H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 2H), 7.80-7.57 (m, 2H), 7.44-7.42 (m, 5H), 7.17-7.13 (m, 4H), 6.98 (s, 1H), 1.57 (s, 36H), 1.35-1.34 (m, 18H), 1.30 (s, 9H), 1.28 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 164.18, 153.95, 153.97, 153.26, 151.94, 151.90, 150.55, 150.44, 149.96, 148.59, 147.33, 143.78, 141.58, 137.50, 133.69, 133.04, 132.96, 132.67, 131.74, 131.37, 131.15, 131.05, 130.47, 130.38, 130.13, 129.85, 129.70, 129.32, 129.04, 128.72, 128.40, 128.22, 127.90, 127.52, 127.18, 126.97, 126.88, 126.10, 124.60, 124.38, 124.07, 121.88, 120.86, 118.74, 118.62, 101.88, 100.54, 100.33, 96.46, 95.20, 35.51, 35.00, 34.40, 34.16, 31.74, 31.43, 31.16, 29.63; UV-vis (THF): λ<sub>max</sub>/nm (ε, 10<sup>3</sup>M<sup>-1</sup>cm<sup>-1</sup>) = 448 (116), 544 (35), 693 (61); FAB-MS: *m/z* calcd for C<sub>115</sub>H<sub>109</sub>N<sub>5</sub>O<sub>6</sub>Zn:1720; found 1721 ([M+H]<sup>+</sup>).

Dyad **7**: A mixture of porphyrin **6** (28 mg, 0.03 mmol), and perylene **4** (39 mg, 0.045 mmol) in dry THF (12 mL) and NEt<sub>3</sub> (3 mL) was degassed with dinitrogen for 10 min, and then Pd<sub>2</sub>(dba)<sub>3</sub> (6.6 mg, 7.5 μmol) and AsPh<sub>3</sub> (18 mg, 0.06 mmol) were added to the mixture. The solution was refluxed for 13 h under dinitrogen. The solvent was removed in vacuo. The residue was purified on a column chromatograph (silica gel) using hexane/CH<sub>2</sub>Cl<sub>2</sub> = 4/1 as eluent. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/methanol gave **5** (17.8 mg, 42%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.90 (d, *J* = 4.4 Hz, 2H), 9.58-9.55 (m, 2H), 9.29 (d, *J* = 8.0 Hz, 1H), 9.04 (d, *J* = 4.8 Hz, 2H), 8.54 (s, 4H), 8.38-8.37 (m, 3H), 8.06 (s, 2H), 8.03 (s, 2H), 7.90 (t, *J* = 8.4 Hz, 2H), 7.80 (s, 2H), 7.77 (s, 1H), 7.47-7.43 (m, 5H), 7.19-7.15 (m, 4H), 6.99 (s, 1H), 1.55 (s, 36H), 1.52 (s, 18H), 1.36 (s, 18H), 1.32 (s, 9H), 1.30 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 164.22, 153.88, 153.31, 152.30, 150.80, 149.99, 149.85, 148.36, 148.25, 147.25, 143.76, 142.02, 133.68, 132.68, 132.18, 131.67, 130.83, 130.03, 129.70, 129.46, 128.73, 128.52, 128.18, 127.50, 127.19, 126.13, 124.83, 124.62, 124.14, 123.44, 121.79, 120.64, 118.75, 118.62, 102.53,

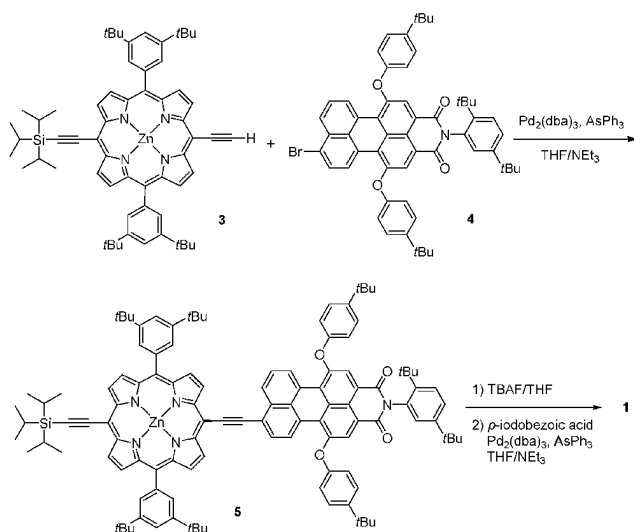
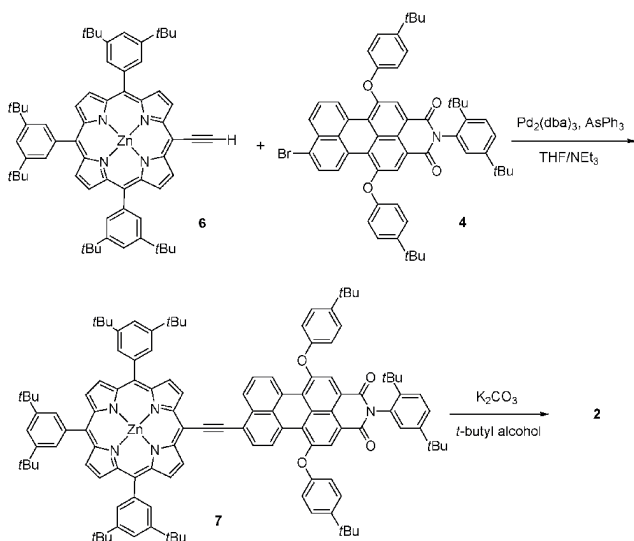
97.84, 94.41, 35.51, 34.99, 34.42, 34.18, 31.75, 31.45, 31.18, 29.66; UV-vis (THF): λ<sub>max</sub>/nm (ε, 10<sup>3</sup>M<sup>-1</sup>cm<sup>-1</sup>) = 436 (172), 543 (51), 666 (73); FAB-MS: *m/z* calcd for C<sub>120</sub>H<sub>125</sub>N<sub>5</sub>O<sub>4</sub>Zn: 1765; found 1766 ([M+H]<sup>+</sup>).

Dyad **2**: A mixture of porphyrin **7** (44 mg, 0.025 mmol) and KOH (0.5 M, 1 mL) in *t*-BuOH (2 mL) was refluxed for 2 h. After the solution was cooled to 25 °C, AcOH (3.7 mL) were added and the solution was stirred for 5 min. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was collected and the solvent was removed in vacuo. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/methanol gave **2** (17.2 mg, 42%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.84 (d, *J* = 4.0 Hz, 2H), 9.51 (d, *J* = 8.0 Hz, 2H), 9.51 (d, *J* = 8.0 Hz, 1H), 9.02 (d, *J* = 4.4 Hz, 2H), 8.82 (s, 4H), 8.35 (d, *J* = 8.0 Hz, 1H), 8.17 (s, 2H), 8.05-8.01 (m, 6H), 7.92 (t, *J* = 7.2 Hz, 1H), 7.79-7.75 (m, 3H), 7.47-7.43 (m, 5H), 7.10 (t, *J* = 8.0 Hz, 4H), 1.54 (s, 36H), 1.50 (s, 18H), 1.35 (s, 18H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 159.81, 159.77, 153.68, 153.16, 152.32, 150.90, 150.09, 149.67, 148.44, 148.30, 147.64, 142.17, 142.06, 133.58, 133.20, 132.28, 131.69, 131.27, 130.81, 129.90, 129.71, 129.51, 129.12, 128.09, 128.01, 127.65, 127.50, 127.32, 126.89, 125.74, 125.23, 124.88, 124.42, 123.53, 120.70, 118.72, 118.61, 116.64, 116.45, 103.36, 97.56, 94.38, 35.01, 34.98, 34.43, 31.76, 31.73, 31.41, 29.66; UV-vis (THF): λ<sub>max</sub>/nm (ε, 10<sup>3</sup>M<sup>-1</sup>cm<sup>-1</sup>) = 437 (157), 542 (38), 668 (56); FAB-MS: *m/z* calcd for C<sub>106</sub>H<sub>104</sub>N<sub>4</sub>O<sub>5</sub>Zn: 1578; found 1580 ([M+2H]<sup>+</sup>).

## RESULTS AND DISCUSSION

Perylene imides normally behave as electron acceptors. However, introduction of electron-donating phenoxy groups to the bay positions of the perylene ring would decrease the electron-accepting capability of the perylene. Lindsey et al. have synthesized perylene-porphyrin arrays, in which the perylene units are substituted with phenoxy groups.<sup>12,13</sup> It was found that excitation of the perylene results in emission predominantly from the porphyrin with a small amount of emission from the perylene because the perylene-to-porphyrin energy transfer is energetically downhill. The design of compound **1** is based on the same idea. It is expected that light absorption by the perylene would be followed by energy transfer to the porphyrin, pumping the porphyrin to its excited state and leading to electron transfer to TiO<sub>2</sub> for compound **1**-based DSSC.<sup>14</sup>

For compound **2**, the anhydride of the perylene would be converted to the corresponding dicarboxylate when absorbed on the surface of TiO<sub>2</sub>. In such a case, the perylene

**Scheme I** Synthetic route for dyad **1****Scheme II** Synthetic route for dyad **2**

unit is an electron acceptor and excitation of porphyrin should result in energy or electron transfer from the porphyrin to the perylene. It is well known that elongation of the  $\pi$ -system of a porphyrin results in broadening of the absorption bands. Therefore, in compounds **1** and **2** the porphyrin and perylene moieties are connected by a conjugated acetylene linker, which can efficiently mediate the electronic coupling between these two units to cover a broad absorption spectrum. The major factor in decreasing the efficiency of sensitized photocurrent generation is the formation of dye aggregates on the semiconductor sur-

face.<sup>15</sup> The *tert*-butyl groups on the porphyrin and perylene serve to increase the solubility of the dyads.

The acetylene bridge would mediate strong electronic interactions between the perylene and porphyrin macrocycle. Such interactions can be investigated by the UV-Vis absorption spectra, for examples, the peak broadening, peak shifts, and changes in the oscillator strength of absorptions.<sup>17,18</sup> The absorption spectra of the porphyrin-peryene dyes **1**, **2**, and two reference components **6** and **4** are shown in Fig. 1.

Porphyrin **6** shows a Soret band at 427 nm and Q bands at 560 and 602 nm, whereas perylene **4** exhibits a moderate absorption at 512 nm with a shoulder at 482 nm. The absorption spectra of dyad **2** are very different from the sum of their respective components **4** and **6**. The absorption gaps between the Soret and Q bands are filled up by absorption of the perylene unit. As expected, attachment of the perylene to the porphyrin via the carbon-carbon triple bond gives significant perturbation of the ground state properties of the perylene and the porphyrin. The absorption band caused by the perylene unit is broadened and red-shifted to 542 nm. Both the Soret and Q bands of **2** show a significant red shift, indicating a decreased energy gap between the HOMO and the LUMO as a consequence of extension of  $\pi$ -conjugation.<sup>17,19</sup> Furthermore, compound **2** exhibits broadening of the Soret band, suggesting the strong electronic coupling between the porphyrin and the perylene. The peak broadening and red shifts are even more pronounced for compound **1** because the  $\pi$ -conjugation is more expanded in the molecule. It is noteworthy that dyads **1** and **2** exhibit significantly intensified Q bands due to the

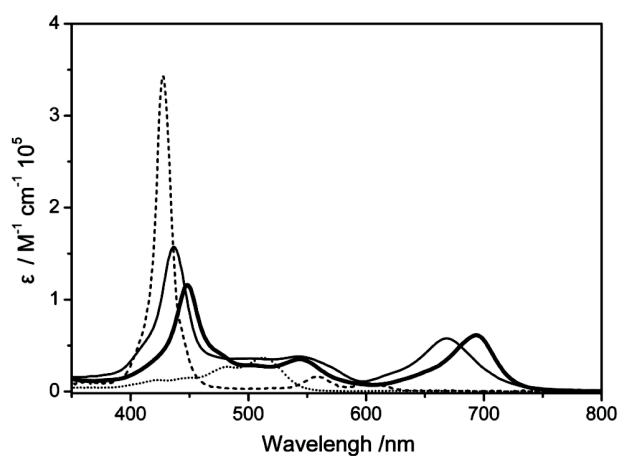


Fig. 1. Absorption spectra of **1** (bold), **2** (plain), **4** (dot), and **6** (dash) in THF.

energy splitting between the  $a_{1u}$  and  $a_{2u}$  orbitals, or the  $E_g$  orbitals.<sup>17,20</sup>

The emission spectra for dyads **1**, **2**, and the component subunits **4** and **6** in  $\text{CH}_2\text{Cl}_2$  at room temperature are shown in Fig. 2. The fluorescence for perylene **4** consists of a main feature at 540 nm and a shoulder at 580 nm. The emission for porphyrin **6** is dominated by the Q(0,0) and Q(0,1) bands at 616 and 668 nm. The emission properties of **4** and **6** are typical for perylene and porphyrin chromophores, respectively. Dyad **1** in  $\text{CH}_2\text{Cl}_2$  exhibits essentially no emission from the perylene unit even when this component is primarily pumped at 554 nm, indicative of essentially quantitative energy transfer from the perylene to the porphyrin unit. In the case of dyad **2**, the emission occurs primarily from the perylene even when the porphyrin unit is excited at 436 nm. Only slight emission is observed from the porphyrin unit as can be seen from the minor intensity in the range 700–800 nm. The result is diagnostic of efficient energy transfer from the excited porphyrin to the perylene element in dyad **2**. On the basis of the emission measurements, the models for the possible energy transfer and electron transfer processes of dyads **1**- and **2**-based DSSC are depicted in Fig. 3.

Dyads **1** and **2** were sensitized onto  $\text{TiO}_2$  nanoparticle films to serve as working electrodes of DSSC devices for photovoltaic characterization.<sup>16,21,22</sup> We found that compound **1** bonded to  $\text{TiO}_2$  quite well but compound **2** was hardly adsorbed on the  $\text{TiO}_2$  films due to the poor interaction between the anhydride group and the surface of  $\text{TiO}_2$

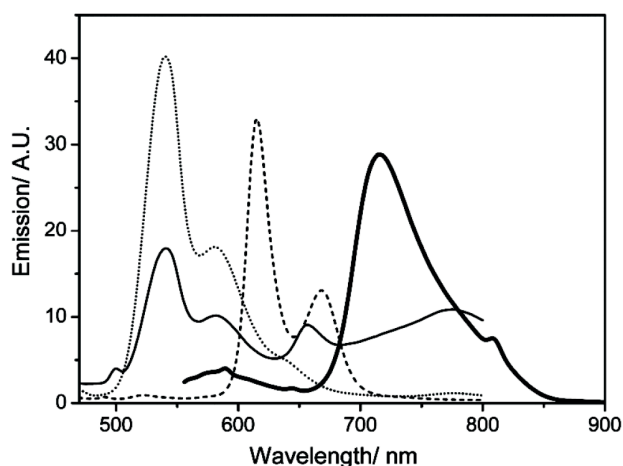


Fig. 2. Fluorescence spectra of **1** (bold), **2** (plain), **4** (dot), and **6** (dash) in THF. Excitation wavelengths: 554, 436, 415, 430 nm for **1**, **2**, **4**, and **6**, respectively.

Table 1. Absorption and emission for compounds **1**, **2**, **4** and **6** in THF

Compounds	Absorption /nm	Emission /nm
<b>1</b>	448, 544, 693	716
<b>2</b>	437, 542, 668	541, 582, 657, 775
<b>4</b>	482, 512	540, 580
<b>6</b>	427, 560, 602	616, 668

film. Fig. 4 shows the current-voltage characteristics of the devices made from immersion of  $\text{TiO}_2$  films into two different solutions of **1** and **2** (EtOH and THF). It shows that compound **2** has very poor cell performance due to its poor dye-loading amounts on  $\text{TiO}_2$  films. On the other hand, the device of compound **1** performs much better than that of compound **2**. For the device of **1** made with two different immersion conditions, the photovoltaic parameters are:  $J_{SC} / \text{mA cm}^{-2} = 0.349$ ,  $V_{OC} / \text{V} = 0.439$ ,  $FF = 0.44$ ,  $\eta = 0.07\%$

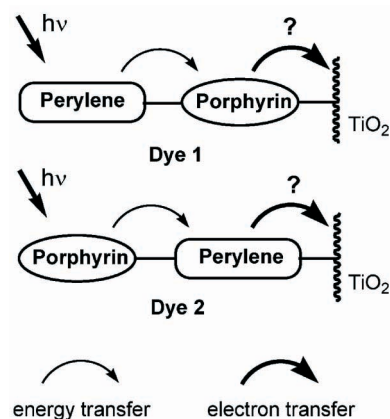


Fig. 3. Proposed models for energy transfer and electron transfer in **1**- and **2**-based DSSC.

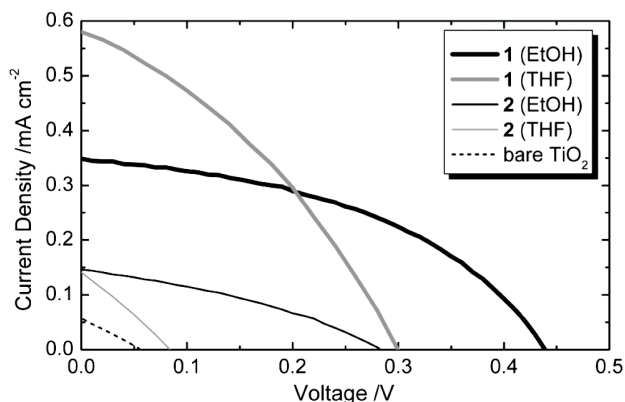


Fig. 4. Current-voltage characteristics of **1**- and **2**-based DSSC devices under two different dye soaking conditions.



(EtOH);  $J_{SC}/\text{mA cm}^{-2} = 0.580$ ,  $V_{OC}/V = 0.300$ ,  $FF = 0.35$ ,  $\eta = 0.06\%$  (THF). Apparently, the perylene-porphyrin based DSSC did not exhibit any promising feature for photovoltaic application. One possibility for the poor performance of compound **1** might be due to the quenching of the excitation energy in perylene so that the proposed consecutive energy/electron transfer process (Fig. 3) does not occur. Work is in progress to understand the dynamics of the proposed models illustrated in Fig. 3.

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