Unsymmetrically Substituted Donor–π–Acceptor-Type 5,15-Diazaporphyrin Sensitizers: Synthesis, Optical and Photovoltaic Properties


Introduction

Donor–π–acceptor (D–π–A)-type porphyrin derivatives have attracted considerable attention as functional dyes in the fields of dye-sensitized solar cells (DSSCs) and nonlinear optics (NLO) because they have intrinsically narrow HOMO–LUMO gaps and polarized excited states with a large charge-transfer (CT) character.[1–3] For example, DSSCs composed of TiO$_2$ and a D–π–A-type porphyrin, such as SM315,[1] exhibit high power conversion efficiencies (PCEs), whereas acetylene-linked D–π–A-type porphyrins, such as P1,[3a] show strong second-order NLO activity and have been used as dyes for second-harmonic generation imaging (Figure 1). In DSSCs, the D–π–A structure is indispensable for acceleration of charge injection from the excited state of the dye to the conduction band (CB) of TiO$_2$, as well as the first examples of unsymmetrical β-substituted donor–π–acceptor (D–π–A)-type 5,15-diazaporphyrin (DAP) sensitizers with both $p$-aminophenyl and $p$-carboxyphenyl groups at their peripheral 3-, 7-, 13-, and/or 17-positions have been synthesized for use in dye-sensitized solar cells (DSSCs). UV/Vis absorption and emission spectroscopy, electrochemical measurements, and DFT calculations revealed that these D–π–A dyes exhibit high light-harvesting properties over the whole visible range because of the intrinsic charge-transfer character of their electronic transitions. The cell performances of TiO$_2$-based DSSCs fabricated with the newly prepared DAP derivatives were evaluated under standard AM1.5 conditions. Among the four dyes examined, 13,17-bis($p$-carboxyphenyl)-3,7-bis($p$-(N,N-dimethylanino)phenyl)-DAP showed the highest power conversion efficiency (2.0%), which was 20 times larger than that obtained with 3-($p$-carboxyphenyl)-DAP. These results show that the DAP chromophore could be used as the electron-accepting π unit in various types of functional dyes.

Figure 1. Structures of porphyrins and diazaporphyrins discussed herein. $\lambda_{abs}$ = absorption maximum of the lowest-energy excitation, $\lambda_{em}$ = emission maximum.

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for suppression of charge recombination from the CB to the resulting dye radical cation.[14–16]

In general, D–π–A-type porphyrins contain donor and acceptor moieties at the meso- and/or β positions.[17–20] In addition, an acetylene spacer is often inserted between the porphyrin and D/A units, as in the structures of SM315 and P1, to extend π conjugation and improve the light-harvesting ability in the long-wavelength visible region. However, this type of molecular design usually requires multistep synthetic reactions and may restrict the development of easily accessible porphyrin-based dyes. In this context, the design of new chrophores that have a large CT character and good light-harvesting properties, but do not contain an additional acetylene unit, is intriguing.

In contrast to porphyrins, which have intrinsic D2h symmetry, 5,15-diazaporphyrin (DAP) has D6h symmetry and characteristic optical and electrochemical properties derived from 1) the nondegenerate HOMO–HOMO−1 and LUMO/LUMO +1, and 2) the low-lying LUMO of the π system.[4–5] Most importantly, DAP exhibits a more intense Q band than that of porphyrins owing to the symmetry-allowed HOMO–LUMO electronic transition.[4,5] We have recently established convenient methods for the synthesis and peripheral functionalization of 10,20-dimesityl-DAPs (mesityl = 2,4,6-trimethylphenyl), and revealed that introducing electron-rich substituents, such as aminophenyl, thienyl, or porphyrinyl groups, into one of the β positions of the DAP ring provides the entire π system with a large CT character.[5–7] For example, the absorption and emission bands of the zinc(II) complex of 3-[p-(N,N-diphenylamino)phenyl]-DAP (P3) were considerably redshifted compared with the corresponding bands of reference ZnDAP compound P2 (Figure 1). The large Stokes shift of P3, as well as its solvatochromic behavior in solution, strongly suggested that the DAP chromophore acted as the electron-accepting π unit when an electron-donating substituent was introduced into the β position of the DAP ring.

In 2013, we reported the first example of a DAP-based DSSC, in which P4 was used as a sensitizer (Figure 1).[8] Unfortunately, the PCE of this P4-based DSSC was very low (0.08%), not only because of the small driving force for electron injection from the excited state of P4 to the CB of TiO2, but also owing to the insufficient light-harvesting ability in the long-wavelength visible region. To use DAP derivatives as sensitizers for DSSCs, it is therefore necessary to raise the energy levels of their excited states and further narrow the HOMO–LUMO gaps of their π systems. We envisioned that these prerequisites could be simply achieved by introducing strongly electron-donating p-aminophenyl groups into the β positions of the DAP ring. Herein, we report the first examples of D–π–A-type DAP dyes, in which two or four of the β positions were substituted with p-aminophenyl (p-R1NC6H4; R = Ph, Me) and p-carboxyphenyl groups as the donor and anchor units, respectively.[9] These dyes were prepared by sequential bromination and cross-coupling reactions, and their structure–property relationships were studied by UV/Vis absorption and emission spectroscopy, electrochemical measurements, and DFT calculations. Furthermore, DSSCs based on the new DAP dyes were fabricated and their cell performances were evaluated under standard AM1.5 conditions.

Results and Discussion

The syntheses of the β-functionalized DAPs are illustrated in Schemes 1 and 2. Reference DAP dye 2, which contains no electron-donating group, was obtained by alkaline hydrolysis of ester 1.[6a] Reaction of 1 with NBS in CH2Cl2 at reflux afforded three regioisomers of β-bromo-DAP 3. The Rf value of one regioisomer (Rf = 0.22; CH2Cl2/AcOEt = 100/1) was different from the Rf values of the others (each, Rf = 0.40; CH2Cl2/AcOEt = 100/1). On the basis of their Rf values, the more polar regioisomer (Rf = 0.22) was assigned to 3-syn, and the less polar, inseparable regioisomers (Rf = 0.40) were assigned to 3-anti. Suzuki–Miyaura cross-coupling of 3-anti with p-(N,N-diphenylamino)-phenylboronic acid in the presence of K2CO3 and catalytic amounts of Pd(OAc)2 and CyJohnPhos in 1,4-dioxane–water at 80 °C afforded 4 as a mixture of two regioisomers. Alkaline hydrolysis of esters 4 gave corresponding carboxylic acids 5. The UV/Vis absorption spectrum of the mixture of regioisomers of

4 in CH₂Cl₂ showed a Q band at \( \lambda_{\text{abs}} = 619 \) nm, which was red-shifted compared with that of 1 (\( \lambda_{\text{max}} = 596 \) nm).

Next, we synthesized 3,7,13,17-tetraaryl-DAPs 11–14 (Scheme 2). Reaction of 7, which was available in one step from 6 and NBS, with NaN₃ and Pb(acac)₂ in n-propanol at reflux afforded two regioisomers of dibromo-DAPs as their lead(II) complexes. Deometallation of the crude lead(II) complexes, followed by insertion of zinc(II) ions into the resulting free bases, gave 3,7-dibromo-DAP 8-syn and 3,13-dibromo-DAP 8-anti in 6% and 16% yield, respectively, based on the amount of starting material 7. These regioisomers had different \( R_f \) values and were successfully separated from each other by column chromatography on silica gel. Suzuki–Miyaura cross-coupling of 8-syn with \( p \)-ethoxycarbonylphenylboronic acid gave 3,7-diaryl-DAP 9. The syn stereochemistry of 9 was confirmed by preliminary X-ray crystallographic results, although the quality of the diffraction data was not at a publishable level. Bromination of 9 with NBS proceeded regioselectively to yield 10, which underwent Suzuki–Miyaura cross-coupling with \( p-(N,N\text{-diphenylamino})- \) and \( p-(N,N\text{-dimethylamino}) \) phenylboronic acids to give 11 and 12, respectively. Alkaline hydrolysis of the ester groups of 11 and 12 afforded the corresponding carboxylic acids 13 and 14, respectively.

The UV/Vis absorption and fluorescence spectra of 1, 4, 11, and 12 in CH₂Cl₂ are shown in Figure 2 and Figure S1 in the Supporting Information. The spectra of the D–π–A-type DAPs 4, 11, and 12 contained broad Q bands with absorption maxima (\( \lambda_{\text{abs}} \)) at 619, 654, and 670 nm, respectively, and broad emission bands with emission maxima (\( \lambda_{\text{em}} \)) at 772, 783, and 805 nm, respectively. Introduction of aminophenyl groups at the periphery considerably improved the light-harvesting ability of the DAP π systems in the long-wavelength region (\( \Delta \lambda_{\text{abs}} = 23 \) (4 vs. 1), 44 (11 vs. 9), and 60 nm (12 vs. 9); Figure S2 in the Supporting Information). From the intersections of the absorption and fluorescence spectra, the optical HOMO–LUMO gaps (\( \Delta E_{\text{H–L}} \)) of 4, 11, and 12 were determined to be 1.85, 1.76, and 1.69 eV, respectively. Furthermore, the large Stokes shifts observed for 4, 11, and 12, as well as their solvatochromic behavior in solutions of toluene, THF, CH₃CN, CHCl₃, CH₂Cl₂, and DMF, suggest that the \( \beta \)-aminophenyl groups have a critical impact on the CT character of the entire π system (Table S1 and Figure S3 in the Supporting Information). Lippert–Mataga plots for these D–π–A dyes have large slopes (\( \Delta \varepsilon \alpha \beta = 6.4 \times 10^{-3} \) (4), 5.9 \times 10⁻³ (11), and 4.7 \times 10⁻³ cm⁻¹ (12)), which implies that their HOMO–LUMO electronic transitions provide intrinsically high CT character in the excited states. The spectral features of carboxylic acids 5, 13, and 14 (Figure S4 in the Supporting Information) were almost identical to those of the corresponding esters. Notably, D–π–A-type 3,7,13,17-tetraaryl-DAPs 11–14 were able to absorb almost all visible light. The \( \lambda_{\text{abs}} \) values of 4, 11, and 12 were considerably larger than those of D–π–A-type porphyrin analogues, such as HKK-4 and ZnPH2 (Figure 3).
To obtain further insight into the origin of the CT character and the structures of 13 and 14, we conducted DFT and time-dependent (TD) DFT calculations on model compounds 13-m and 14-m, in which the meso-mesityl groups were replaced by phenyl groups (Figure 4 and Table S2 in the Supporting Information). In each model, the β-aryl groups lean towards the DAP π plane to a large extent, and the torsion angles at the inter-ring bonds (27.6°–30.3° for 13-m, 25.4°–30.2° for 14-m) are close to those observed in the X-ray crystal structure of 3,7,13,17-tetraphenyl-DAP (16.2°–34.6°).[5a] The inter-ring bond lengths between the β-aryl groups and the DAP ring (1.464–1.467 Å for 13-m, 1.461–1.467 Å for 14-m) are appreciably shorter than those between the meso-phenyl groups and the DAP ring (1.499 Å); this reflects the reduced single-bond character of the Cβ@Caryl bonds. It is therefore likely that the β-aryl and DAP rings in 13-m and 14-m are effectively π conjugated. As shown in Figure 4, the HOMO and HOMO−1 are largely localized on the aminophenyl groups, whereas the LUMO, LUMO +1, HOMO−2, and HOMO−3 are distributed over the DAP ring. Two low-energy excitations (<2 eV) calculated for each model by using the TD-DFT method are dominated by the HOMO–LUMO and HOMO−1–LUMO transitions. The substantial CT character of these two excitations, from the two aminophenyl groups (donor) to the DAP ring (acceptor), generates polarized excited states. This explains the definite solvatochromism observed for structurally related D–π–A dyes 11 and 12. In addition to the low-energy CT excitations, several intense excitations (oscillator strength > 0.1) that originate from DAP-based π–π* transitions are involved in the visible region. The theoretical results for 13-m and 14-m qualitatively support the observed spectra of 13 and 14, which contain broad absorption bands with several absorption maxima (Figure S4 in the Supporting Information).

To evaluate the extent of the electronic effects of the β-aryl substituents on the redox properties of the DAP π system, we measured the redox potentials of 4, 9, 11, and 12 in THF with
Bu₄NPF₆ as the electrolyte (Table 1 and Figure S5 in the Supporting Information). The first oxidation potential (Eox⁺ vs. Fc/Fc⁻) of 4 (+0.50 V) was less positive than that of 1 (+0.76 V) and comparable to that of P3 (+0.49 V). Additionally, the Eox⁺ values of 11 (+0.53 V) and 12 (+0.27 V) were less positive than that of 9 (+0.77 V). These data indicate that the introduction of p-amino phenyl groups onto the β positions raises the HOMO energy levels of the DAP chromophores by 0.24–0.50 eV. The appreciable difference in the Eox⁺ values of 11 and 12 implies that the HOMO energy levels of the D–π–A dyes can also be controlled by the N-substituents, as suggested by DFT calculations on 13-m and 14-m (see above). With the optical HOMO–LUMO gaps and Eox⁺ values in hand, we next calculated the exited-state oxidation potentials (Eox*⁺) of 4, 11, and 12 to be −0.71, −0.59, and −0.78 eV (versus a normal hydrogen electrode (NHE)), respectively. Under our measurement conditions, the redox potentials of carboxylic acids 5, 13, and 14 could not be determined accurately because of their low solubility. Therefore, we estimated the driving forces for electron injection (ΔG inj) from the excited states of these carboxylic acids to the CB of TiO₂ (−0.50 eV vs. NHE) from the Eox*⁺ values of their ester counterparts 4, 11, and 12. The ΔG inj values thus estimated are in the order 11 (−0.09 eV) > 4 (−0.21 eV) > 12 (−0.28 eV).

Finally, we fabricated DSSCs by using new DAP dyes 2, 5, 13, and 14, and examined their cell performances under standard AM1.5 conditions to reveal the effects of the β substituents on the PCE. The DAP-modified TiO₂ (DAP/TiO₂) electrodes were prepared by immersing a double (for 2, 5) or triple (for 13, 14) layer TiO₂ electrode into 0.2 M ethanol (for 2, 5) or ethanol/THF (for 13, 14) solutions of DAP at room temperature (for details, see the Experimental Section). The cell performances discussed below were obtained under optimized measurement conditions (Figures S6–S8 in the Supporting Information). The current–voltage (I–V) curves for the DSSCs are shown in Figure 5, and the short-circuit currents (Jsc), open-circuit voltages (Voc), fill factors (FFs), and PCEs are summarized in Table 2.

As expected, the introduction of amorphous groups at the periphery of the DAP ring considerably improved the cell performances of the DAP/TiO₂ electrodes; the PCE values increased in the order 2/TiO₂ (0.10) < 5/TiO₂ (1.1) < 13/TiO₂ (1.7) < 14/TiO₂ (2.0). The effect of the β substituent on the Jsc value was greater than its effect on the Voc and FF values. As a result, the difference in PCE values among the four cells stems mostly from the difference in their Jsc values. The spectral features of the photocurrent action spectra of the four cells (Figure 6a) match well with those of the absorption spectra of the corresponding DAP dyes adsorbed on TiO₂ (Figure 6b). The incident photon–to-current efficiency (IPCE) values of the 5/TiO₂, 13/TiO₂, and 14/TiO₂ cells were considerably larger than those of the 2/TiO₂ cell in all wavelength regions; this suggests that the D–π–A structure is indispensable for the achievement of high Jsc values.

The IPCE values of cells fabricated by using the D–π–A dyes increased in the order 5/TiO₂ < 13/TiO₂ < 14/TiO₂ (Figure 6a), which agrees with the order of their absorptivities (Figure 6b). The IPCE is divided into three components: light-harvesting efficiency (LHE), quantum yield of electron injection from the dye-excited singlet state to the CB of the TiO₂ electrode, and charge collection efficiency. The driving force for electron injection in the 13/TiO₂ cell seems to be smaller than that for the 5/TiO₂ cell. Therefore, the marked difference in the IPCE values of these two cells is probably attributed to the higher LHE and/or charge collection efficiency of 13/TiO₂ compared with those of 5/TiO₂. In contrast, the difference in the IPCE values of the 13/TiO₂ and 14/TiO₂ cells can be attributed to different LHE values and/or driving forces for the electron injec-

Table 1. Optical and electrochemical data for DAPs.

<table>
<thead>
<tr>
<th>DAP</th>
<th>λmax [nm]a</th>
<th>λem [nm]b</th>
<th>Eox⁺ [V]c</th>
<th>ΔG inj [eV]c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>596 (4.87)</td>
<td>609 (0.03)</td>
<td>+0.76</td>
<td>2.06</td>
</tr>
<tr>
<td>4</td>
<td>619 (4.65)</td>
<td>772 (0.08)</td>
<td>+0.50, +0.71</td>
<td>1.85</td>
</tr>
<tr>
<td>5</td>
<td>623 (4.32)</td>
<td>774 (0.07)</td>
<td>n.m.</td>
<td>1.85</td>
</tr>
<tr>
<td>11</td>
<td>654 (4.39)</td>
<td>783 (0.07)</td>
<td>+0.53, +0.76</td>
<td>1.76</td>
</tr>
<tr>
<td>13</td>
<td>654 (4.47)</td>
<td>784 (0.04)</td>
<td>n.m.</td>
<td>1.76</td>
</tr>
<tr>
<td>12</td>
<td>670 (4.45)</td>
<td>805 (0.03)</td>
<td>+0.27, +0.66</td>
<td>1.69</td>
</tr>
<tr>
<td>14</td>
<td>669 (n.m.)</td>
<td>802 (0.02)</td>
<td>n.m.</td>
<td>1.69</td>
</tr>
<tr>
<td>9</td>
<td>610 (4.79)</td>
<td>621 (0.02)</td>
<td>+0.77</td>
<td>2.01</td>
</tr>
</tbody>
</table>

[a] Absorption maxima in the range > 500 nm in CH₂Cl₂. Data in parentheses are log ε. [b] Emission maxima in CH₂Cl₂. Data in parentheses are fluorescence quantum yields. [c] Oxidation potentials versus the ferrocene/ferrocenium couple (Fc/Fc⁺), as determined by cyclic voltammetry (CV; in THF with 0.1 M Bu₄NPF₆). [d] Optical HOMO–LUMO gaps. [e] Data from Ref. [6a]; n.m. = not measured because of low solubility.

Figure 5. Photocurrent–voltage characteristics of 2/TiO₂ (---), 5/TiO₂ (--), 13/TiO₂ (----), and 14/TiO₂ (-----).

Table 2. Photovoltaic parameters of DSSCs.d

<table>
<thead>
<tr>
<th>Cell</th>
<th>Jsc [mA cm⁻²]</th>
<th>Voc [V]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/TiO₂</td>
<td>0.39</td>
<td>0.38</td>
<td>0.69</td>
<td>0.10</td>
</tr>
<tr>
<td>5/TiO₂</td>
<td>2.71</td>
<td>0.55</td>
<td>0.72</td>
<td>1.1</td>
</tr>
<tr>
<td>13/TiO₂</td>
<td>4.35</td>
<td>0.54</td>
<td>0.74</td>
<td>1.7</td>
</tr>
<tr>
<td>14/TiO₂</td>
<td>5.35</td>
<td>0.52</td>
<td>0.72</td>
<td>2.0</td>
</tr>
</tbody>
</table>

[a] Measured under white-light illumination (AM1.5, 100 mW cm⁻²).
these compounds, the present results clearly show that the DAP chromophore could be used as the electron-accepting π unit in various D–π–A-type functional dyes. Further studies on DAP-based dyes, which are now underway in our laboratory, should provide new insight into the development of azaporphyrin-based materials.

**Experimental Section**

**General**

All melting points were recorded on a Yarazu micro melting point apparatus and are uncorrected. 1H NMR spectra were recorded on a Varian 400 or 700 MHz spectrometer by using CDCl3 or CD2Cl2 as solvents. Chemical shifts are reported in ppm as relative values versus tetramethylsilane. HRMS results were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer. UV/Vis absorption spectra were measured at room temperature on a JASCO V-530 spectrometer. Electrochemical measurements were performed at room temperature on a CH Instruments model 650E electrochemical workstation by using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag+ (0.1 M AgNO3, 0.1 M Bu4NPF6, (MeCN)) reference electrode. The scan rate was 60 mV s⁻¹ and the potentials were calibrated with Fe/Fe2+ (0.64 V vs. NHE). Compound 1 was prepared according to reported procedures. Other chemicals and solvents were of reagent-grade quality and used without further purification, unless otherwise noted. TLC was performed with Alt. 5554 DC-Alufolien Kieselgel 60 F254 (Merck) plates, and preparative column chromatography was performed by using Silica Gel 60 (spherical, neutrality; Nacalai Tesque). All reactions were performed under an argon or nitrogen atmosphere. The synthetic procedures and characterization data of new compounds are described below.

**Synthesis**

**Compound 2:** A mixture of 1 (29.8 mg, 0.0392 mmol), NaOH (558 mg, 13.9 mmol), MeOH (30 mL), THF (30 mL), and water (6 mL) was stirred at reflux temperature. After 11.5 h, the solvent was removed under reduced pressure. CH3Cl and a 3.5% aqueous solution of HCl were added to the solid residue, and the mixture was shaken vigorously. The organic phase was separated, dried over Na2SO4 and evaporated under reduced pressure to leave a solid residue, which was then reprecipitated from CH2Cl2/MeOH to give 2 as a green solid (22.6 mg, 0.0309 mmol, 78%). M.p. > 300 °C; Rf (CH3Cl/MeAcOEt/MeOH = 3/1): 0.85; 1H NMR (400 MHz, CD3Cl2/CD2OD): δ = 1.78 (s, 6H; o-Me); 1.81 (s, 6H; o-Me); 2.35 (s, 3H; p-Me); 2.56 (s, 3H; p-Me); 2.75 (s, 2H; m-Mes); 3.02 (d, J = 4.8 Hz, 2H; CNH(COOH), 8.60 (d, J = 4.8 Hz, 1H; pyrrole-β); 8.75 (d, J = 4.8 Hz, 1H; pyrrole-β); 8.78 (s, 1H; pyrrole-β); 8.85 (d, J = 8.4 Hz, 2H; CNH(COOH), 9.01 (d, J = 4.8 Hz, 1H; pyrrole-β); 9.02 (d, J = 4.8 Hz, 1H; pyrrole-β); 9.15 ppm (d, J = 4.8 Hz, 1H; pyrrole-β); COOH proton was not observed; HRMS (ESI): m/z calculated for C38H33N5O5Zn: 731.2107 [M+H]+; found: 731.2094.

**Compound 3:** NBS (12.7 mg, 0.071 mmol) was added to a solution of 1 (54.8 mg, 0.072 mmol) in CHCl3 (15 mL), and stirred at reflux. After 15.5 h, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH3Cl/MeAcOEt/pyridine = 100/1/1 as eluents. The green fraction (Rf = 0.40; CH3Cl/MeAcOEt = 100/1) was collected, concentrated, and...
reprecipitated from CH₂Cl₂/MeOH to give a mixture of 3-anti and dibrominated-1 (34.5 mg, 3-anti/Br-1: 10.03; 42% yield for 3-anti determined by NMR spectroscopy). A mixture of 3-syn (R: 0.22; CH₂Cl₂/AcOEt = 100/1) and 1 was obtained as a green fraction (27.5 mg, 3-syn: 1 = 2:1; 32% yield for 3-syn determined by NMR spectroscopy). Crude 3-anti was used for the synthesis of 4 without further purification. **3-anti**: m.p. > 300°C; 1H NMR (700 MHz, CDCl₃): δ = 1.45 (t, J = 7.0 Hz, 3H x 2); COOH(CH₃), 1.84 (s, x 2, 6H x 2); o-Me, 1.86 (s, x 2, 6H x 2); o-Me, 2.64 (s, x 3, 3H x 2), 4.38 (q, J = 7.0 Hz, 2H x 2); COOH(CH₃), 7.31 (s, x 2, 2H x 2, m-Mes), 7.33 (s, x 2, 2H x 2, m-Mes), 8.28 (d, x 2, J = 7.7 Hz, 2H x 2), C₆H₄(COEt), 8.84-8.90 (m, x 3, 3H x 2); pyrrole-β, 9.00-9.05 (m, x 2, 3H x 2); pyrrole-β = C₆H₄(COEt), 9.27-9.32 ppm (m, x 2, 2H x 2; pyrrole-β).

**Compound 4**: Compound 3-syn (34.5 mg, 0.030 mmol; a mixture with 0.009 mmol of Br₂-I), Pd(OAc)₂ (1.7 mg, 0.0076 mmol), Cy-JohnPhos (5.6 mg, 0.016 mmol), K₂CO₃ (17.8 mg, 0.129 mmol), p(N,N-diphenylaminomethyl)boronic acid (59.3 mg, 0.205 mmol), 1,4-dioxiane (6 mL), and distilled water (0.6 mL) were heated at 80°C. After 4 h, CH₂Cl₂ and water were added, and the combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to leave a solid residue, which was then purified by column chromatography on silica gel with CH₂Cl₂ as an eluent. The green fraction (R: 0.36; CH₂Cl₂) was collected, concentrated, and reprecipitated from CH₂Cl₂/MeOH to give 4 as a green solid (18.1 mg, 0.018 mmol, 60%). M.p. > 300°C; UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 404 (4.96), 619 nm (4.65); 1H NMR (700 MHz, CDCl₃): δ = 1.49 (t, J = 7.4 Hz, 3H x 2); COOH(CH₃), 1.86-1.91 (s, x 4, 6H x 4; o-Me), 2.64-2.65 (s, x 4, 3H x 4; p-Me), 4.46-4.49 (q, x 2, J = 7.4 Hz, 2H x 2); C₆H₄(COEt), 7.13 (t, x 2, J = 7.7 Hz, 2H x 2; Ph-P), 7.28 (d, x 2, J = 7.7 Hz, 4H x 2; o-Ph), 7.32-7.35 (s, x 4, 2H x 4; m-Mes), 7.37 (pseudo-t-x, x 2, J = 7.7 Hz, 4H x 2; m-Phe), 7.41 (d, x 2, J = 9.1 Hz, 2H x 2, C₆H₄(NH₂), 8.38 (d, x 2, J = 8.4 Hz, 2H x 2, C₆H₄(COEt), 8.76-8.77 (m, x 2, 2H x 2; pyrrole-β), 8.79-8.80 (s, x 2, 1H x 2; pyrrole-β), 8.85-8.87 (m, x 2, 2H x 2, C₆H₄(NH₂)), 8.97 (s, x 2, 1H x 2; pyrrole-β), 9.04-9.06 (d, x 2, J = 8.4 Hz, 2H x 2, C₆H₄(COEt), 9.18-9.19 (d, x 2, J = 4.2 Hz, 1H x 2; pyrrole-β), 9.20-9.23 ppm (d, x 2, J = 4.2 Hz, 1H x 2; pyrrole-β); HRMS (ESI): m/z calc for C₅H₄N₄O₂: 202.0345 [M+H]⁺; found: 202.0345.

**Compound 5**: A mixture of 4 (17.1 mg, 0.017 mmol), NaOH (302 mg, 7.56 mmol), MeOH (15 mL), THF (15 mL), and water (3 mL) was stirred at reflux. After 5.5 h, the solvent was removed under reduced pressure. CH₂Cl₂ and a 3.5% aqueous solution of HCl were added to the solid residue, and the mixture was shaken vigorously. The organic phase was separated, washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure to leave a solid residue, which was then reprecipitated from CH₂Cl₂/MeOH to give 5 as a green solid (13.0 mg, 0.013 mmol, 78%). M.p. > 300°C; UV/Vis (CH₂Cl₂): λₘₐₓ (log ε) = 400 (4.67), 623 nm (4.32); R (hexane/AcOEt = 5/2): 0.18; 1H NMR (700 MHz, CDCl₃/CDOD): δ = 1.82-1.92 (s, x 4, 6H x 4; o-Me), 2.64-2.65 (s, x 4, 3H x 4; p-Me), 7.14 (t, x 2, J = 7.7 Hz, 2H x 2; Ph-P), 7.28 (d, x 2, J = 7.7 Hz, 4H x 2; o-Ph), 7.32-7.35 (s, x 4, 2H x 4; m-Mes), 7.37 (pseudo-t-x, x 2, J = 7.7 Hz, 4H x 2; m-Phe), 7.42 (d, x 2, J = 8.4 Hz, 2H x 2; CI₂H₄(NH₂)), 8.40 (d, x 2, J = 8.4 Hz, 2H x 2; CI₂H₄(COEt), 8.76-8.80 (m, x 2, 2H x 2; pyrrole-β), 8.94-8.95 (s, x 2, 1H x 2; pyrrole-β), 8.96-9.00 (m, x 2, 2H x 2; CI₂H₄(NH₂)), 8.97 (s, x 2, 1H x 2; pyrrole-β), 9.02-9.04 (d, x 2, J = 8.4 Hz, 2H x 2; CI₂H₄(COEt), 9.17-9.19 (d, x 2, J = 4.2 Hz, 1H x 2; pyrrole-β), 9.20-9.23 ppm (d, x 2, J = 4.2 Hz, 1H x 2; pyrrole-β); COOH proton was not observed; HRMS (ESI): m/z calc for C₅H₄N₄O₂: 974.3131 [M+H]⁺; found: 974.3140.
(45.1 mg; 9.1 = 1.015; 56% yield determined by NMR spectroscopy). Crude product 9 was used for the synthesis of 11 without further purification. Compound 9 could be separated from 1 by repeating column chromatography (CH₂Cl₂/acetone/pyridine = 100:1:1), and the spectral data of 9 were measured by using this purified sample. M.p. 245–250 °C (decomp); Rf (CH₂Cl₂/acetone = 100:1) = 0.15; UV/Vis (CH₂Cl₂): λmax (log ε) = 425 (5.03), 610 nm (4.79); 1H NMR (700 MHz, CDCl₃): δ = 1.49 (t, J = 7.0 Hz, 6H; COOHCH₂CH₃), 1.83 (s, 12H; o-Me), 2.64 (s, 6H; p-Me), 4.49 (q, J = 7.0 Hz, 4H; COOHCH₂CH₃), 7.29 (s, 4H; m-Mes), 8.33 (d, J = 8.4 Hz, 4H; CH₃COOEt), 8.76 (d, J = 4.8 Hz, 2H; pyrrole-ći); HRMS (ESI): m/z calc for C₈H₁₀N₂O₄Zn: 907.2945 [M+H]⁺; found: 907.2932.

**Compound 10**: NBS (8.3 mg, 0.047 mmol) was added to a solution of 9 (20.2 mg, 0.020 mmol; a mixture with 0.003 mmol of 1) in CHCl₃ (5 mL), and the resulting mixture was stirred at reflux. After 14.5 h, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂/acetone = 100:1 as eluents. The green fraction (Rf = 0.31; CH₂Cl₂/acetone = 100:1) was collected, concentrated, and recrystallized from CH₂Cl₂/MeOH to give a mixture of 10 and tribromobenzene (1.5 mL) were used as the transparent layer of the photoanode, according to procedures reported in the literature. The preparation of TiO₂ paste was coated onto the FTO glass by screen printing, followed by standing in a clean box for a few minutes, and drying at 125 °C for 6 min; this process was repeated to attain a final thickness of 12 μm (12 μm thickness of the film or 6 min in this process was used for H, C, N, and O, and the Wachters-Hay all-electron basis set[14] supplemented with one f-function (exponent: 1.62) was used for Zn. The functional of DFT was the Becke three-parameter Lee–Yang–Parr (B3LYP) exchange-correlation functional.[15] The Cartesian coordinates are summarized in Table S2 in the Supporting Information. Selected Kohn–Sham orbitals and their energies are summarized in Figure 4. All calculations were performed by using the Gaussian 09 suite of programs.[16] Fabrication of dye-sensitized TiO₂ electrodes

The preparation of TiO₂ electrodes and the fabrication of the sealed cells for photovoltaic measurements was performed according to procedures reported in the literature.[17,18] Nanocrystalline TiO₂ particles (d = 20 nm, CCIC:PT323NR, JGC-CCCIC; d = 20 nm, CCIC:PT18NR, JGC-CCCIC; and d = 30 nm, CCIC:PT30NRD, JGC-CCCIC) were used as the transparent layer of the photoanode, whereas sub-microcrystalline TiO₂ particles (d = 400 nm, CCIC:PT400C, JGC-CCCIC) were used as the light-scattering layers of the photoanode. The working electrode was prepared by cleaning fluorine-doped tin oxide (FTO) glass (solar 4 mm thickness, 10 Ω/□, Nippon Sheet Glass) with a solution of detergent in an ultrasonic bath for 15 min, rinsing with distilled water and ethanol, and drying in air. The electrode was subjected to UV/O₂ irradiation for 18 min, immersed in a 40 mM freshly prepared aqueous solution of TiCl₄ at 70 °C for 30 min, washed with distilled water and ethanol, and dried. Nanocrystalline TiO₂ paste was coated onto the FTO glass by screen printing, followed by standing in a clean box for a few minutes, and drying at 125 °C for 6 min; this process was repeated to attain a final thickness of 12 μm (12 μm thickness of the film or 6 min in this process was used for H, C, N, and O, and the Wachters-Hay all-electron basis set[14] supplemented with one f-function (exponent: 1.62) was used for Zn. The functional of DFT was the Becke three-parameter Lee–Yang–Parr (B3LYP) exchange-correlation functional.[15] The Cartesian coordinates are summarized in Table S2 in the Supporting Information. Selected Kohn–Sham orbitals and their energies are summarized in Figure 4. All calculations were performed by using the Gaussian 09 suite of programs.[16]
The counter electrode was prepared by drilling a small hole in FTO glass (1 mm thickness, 10 Ω/☐. Nippon Sheet Glass), rinsing with distilled water and ethanol, followed by treatment with 1 M HCl in 2-propanol by using an ultrasonic bath for 15 min. After heating in air for 15 min at 400 °C, platinum was deposited on the FTO glass by coating with a drop of a solution of H2PtCl6 (2 mg in 1 mL of ethanol) twice. Finally, the FTO glass was heated at 400 °C for 15 min to obtain the counter Pt electrode.

A sandwich cell was prepared by using the dye-anchored TiO2 film as a working electrode and a counter Pt electrode, which were assembled with a hot-melt ionomer film Surlyn polymer gasket (DuPont, 50 μm), and the superimposed electrodes were tightly held and heated at 110 °C to seal the two electrodes. The aperture of the Surlyn frame was 2 mm larger than that of the area of the TiO2 film, and its width was 1 mm. The hole in the counter Pt electrode was sealed by a film of Surlyn. A hole was then made in the Surlyn film covering with a needle. A drop of an electrolyte was put on the hole in the back of the counter Pt electrode. It was introduced into the cell by vacuum back-filling. Finally, the hole was sealed with Surlyn film and a cover glass (0.13–0.17 mm thickness).

A solder was applied on each edge of the FTO electrodes. The electrolyte solution used was 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M I−, 0.05 M Li+, 0.10 M guanidinium thiocyanate, and 0.50 M 4-t-butylpyridine in a mixture of acetonitrile and valeronitrile (85:15).

The IPCE and I–V performances were measured on an action spectral measurement setup (CEP-2000RR, BUNKOUKEIKI) and a solar simulator (PEC-L10, Peccell Technologies) with an simulated sunlight (AM 1.5 (100 mW cm−2)).

Conflicts of interest

The authors declare no conflict of interest.

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