# PAPER

View Article Online View Journal

Cite this: DOI: 10.1039/c3nj00456b

Received (in Montpellier, France) 1st May 2013, Accepted 30th May 2013

DOI: 10.1039/c3nj00456b

www.rsc.org/njc

# Introduction

Dye-sensitized solar cells (DSSCs) based on dye sensitizers (organic dyes or metal complex dyes) have received considerable attention as one of the most promising sustainable photovoltaic devices because of their interesting construction and operational principles, high incident-solar-light-to-electricity conversion efficiency, colorful and decorative nature, and low cost of production.<sup>1-3</sup> However, one of the challenges to further improve the photovoltaic performances of DSSCs lies in the enhancement of light-harvesting efficiency (LHE) in the red/ near-IR (NIR) region (600-1000 nm) of the solar spectrum. As a successful strategy to enhance LHE of dye sensitizers, it would be very useful to use red/NIR dye skeletons, which can provide good absorption of light in the red/NIR region of the solar spectrum. There have been some reports on DSSCs based on red/NIR dye sensitizers, such as squaraine dyes,<sup>4</sup> phthalocyanine dyes,<sup>5</sup> porphyrin dyes,<sup>6</sup> and boron dipyrromethene (BODIPY) dyes,<sup>7</sup> with absorption maxima at around 600–750 nm, and the design and development of effective red/NIR photosensitizers are therefore currently a hot topic in DSSC studies. Recently, a new series of donor (D)-acceptor (A)-substituted squaraine dyes,

Hiroshima University, Higashi-Hiroshima 739-8527, Japan.

# Photovoltaic performance of dye-sensitized solar cells based on $D-\pi$ -A type BODIPY dye with two pyridyl groups

Yousuke Ooyama,\* Yuta Hagiwara, Tomonobu Mizumo, Yutaka Harima and Joji Ohshita\*

D- $\pi$ -A type boron dipyrromethene (BODIPY) dye **YH-1**, which has two pyridyl groups as electronwithdrawing-anchoring groups at the end of the 3- and 5-positions and a carbazole-diphenylamine moiety as an electron donor at the 8-position on the BODIPY core, was designed and developed as a photosensitizer for dye-sensitized solar cells (DSSCs). It was found that the dye **YH-1** possesses a good light-harvesting efficiency (LHE) in the red/near-IR (NIR) region and good adsorption ability on TiO<sub>2</sub> film. We demonstrate that the expansion of the  $\pi$ -conjugated system by the introduction of not only the carbazole-diphenylamine moiety and the thiophene unit at the 8-position but also two thienylpyridines at the 3- and 5-positions on the BODIPY core can lead to red-shift and broadening of the absorption band in the red/NIR region. DSSCs based on **YH-1** exhibit incident photon-to-current conversion efficiency of *ca.* 10% over a range of 500 to 700 nm, with an onset at 800 nm.

> phthalocyanine dyes, and porphyrin dyes have been designed and synthesized; this has led to enhancement of LHE in the red/NIR region and a dramatic increase in electron-injection efficiency from the photoexcited dye to the conduction band (CB) of the TiO<sub>2</sub> electrode. As a result, the DSSCs based on these three type red/NIR dyes exhibited the solar energy-to-electricity conversion yield ( $\eta$ ) of up to 7.3,<sup>4b</sup> 5.5,<sup>5b</sup> and 11%,<sup>6a</sup> respectively.

> On the other hand, until very recently, there have been only a few reports on D-A-substituted BODIPY dye sensitizers. Song et al. reported photovoltaic performances of DSSCs based on a series of D- $\pi$ -A BODIPY dye sensitizers, which have triphenylamine as an electron donor at the 6-position and cyanoacrylic acid as an electron acceptor at the 2-position.<sup>7a,b</sup> The incident photon-to-current conversion efficiency (IPCE) for the D- $\pi$ -A BODIPY dye exhibits a high plateau at ca. 20% in the range of 400 to 600 nm, with an onset at 650 nm. On the other hand, Akkaya et al. have designed and synthesized a series of D-Asubstituted BODIPY dye sensitizers, which have two triphenylamines as electron donors at the 3- and 5-positions and carboxylic acid or cyanoacrylic acid as an electron acceptor at the 8-position.<sup>7c-e</sup> The IPCE for the D-A-substituted BODIPY dye exhibits a high plateau at ca. 30% in the range of 400 to 800 nm, with an onset at 900 nm. The DSSC based on the D-Asubstituted BODIPY dye showed the  $\eta$  value of up to 2.46%.<sup>7e</sup> To provide a new direction for the molecular design of efficient BODIPY dye sensitizers, further fundamental studies to obtain

Department of Applied Chemistry, Graduate School of Engineering,

 $<sup>\</sup>label{eq:email: yooyama@hiroshima-u.ac.jp, jo@hiroshima-u.ac.jp; Fax: +81-82-424-5494$ 



**Scheme 1** Chemical structure of  $D-\pi$ -A type BODIPY dye **YH-1**.

useful knowledge about the effects of the photophysical and electrochemical properties and molecular structures of the BODIPY dye sensitizers, and the molecular orientation and arrangement of the dyes on the  $TiO_2$  surface on the photovoltaic performances of DSSCs are therefore necessary.

In this work, to explore effective BODIPY dye sensitizers possessing a high LHE in the red/NIR region, we have designed and synthesized D– $\pi$ –A type BODIPY dye sensitizer **YH-1** with two pyridyl groups as electron-withdrawing-anchoring groups at the end of the 3- and 5-positions and a carbazole-diphenylamine moiety as an electron donor at the 8-position on the BODIPY core (Scheme 1). Moreover, the expansion of the  $\pi$ -conjugated system by the introduction of thiophene units as spacers at the 3-, 5-, and 8-positions onto the BODIPY core can lead to red-shift and broadening of the absorption band in the red/NIR region. We have demonstrated that the dye **YH-1** possesses good LHE and adsorption abilities on TiO<sub>2</sub> film, resulting in IPCE of *ca.* 10% over a range of 500 to 700 nm, with an onset at 800 nm.

## **Results and discussion**

### Synthesis of YH-1

The BODIPY dye **YH-1** was synthesized according to the stepwise synthetic protocol illustrated in Scheme 2. Compound **1**  was prepared from 4,4'-dibromo-2-nitrobiphenyl and 5-formyl-2-thienylboronic acid through Suzuki coupling. The conversion from **1** to the corresponding acetal **2** was conducted to protect a carbonyl group during subsequent Buchwald–Hartwig C–N coupling of **2** with diphenylamine to produce compound **3**. Cadogan reductive cyclization of **3** gave the compound **4**. The reaction of **4** with 1-iodobutane by using sodium hydride yielded compound **5**. Compound **5** is hydrolyzed by treatment with acid to generate aldehyde **6**. Dipyrromethane 7 was prepared by condensation of compound **6** with pyrrole with TFA added as a catalyst. The dichlorinated compound **8** was prepared by chlorination of **7** with *N*-chlorosuccinimide (NSC) followed by oxidation with DDQ. Compound **8** was reacted with NEt<sub>3</sub> and treated with BF<sub>3</sub>–OEt<sub>2</sub> to afford the BODIPY **9**. The BODIPY dye **YH-1** was prepared by Stille coupling of **9** with 2-(4-pyridyl)-5-tributylstannanylthiophene.

### Spectroscopic properties of YH-1 in solution

The absorption and fluorescence spectra of YH-1 in 1,4-dioxane are shown in Fig. 1a and their spectral data are summarized in Table 1. The dye YH-1 in 1,4-dioxane shows a strong and broad absorption band in the range of 500 to 700 nm, which is assigned to contribution from both the  $S_0 \rightarrow S_1$  transition of the BODIPY core and the intramolecular charge-transfer (ICT) excitation from the electron donor moiety (carbazole-diphenylamine) to the electron acceptor moiety (BODIPY core containing thienylpyridines). The molar extinction coefficient ( $\varepsilon$ ) at the absorption peak wavelength ( $\lambda_{abs}$  = 673 nm) is *ca.* 81 000 M<sup>-1</sup> cm<sup>-1</sup>. A strong absorption peak at around 380 nm with the  $\varepsilon$  value of *ca.* 73 000  $M^{-1}$  cm<sup>-1</sup>, which can be assigned to the ICT band due to the thienylcarbazole-diphenylamine moiety, was also observed. The dye YH-1 in 1,4-dioxane exhibits a weak fluorescence property ( $\Phi_{\rm f}$  = 0.07), although the corresponding fluorescence maximum ( $\lambda_{em}$ ) occurs at 696 nm. This result is attributed to radiationless relaxation of the photoexcited dye, which is



Scheme 2 Synthetic route to D-π-A type BODIPY dye YH-1.



**Fig. 1** (a) Absorption and fluorescence spectra of **YH-1** ( $\lambda_{ex}$  = 673 nm) in 1,4-dioxane and (b) absorption spectra of **YH-1** adsorbed on TiO<sub>2</sub> film (9 µm) with and without CDCA as coadsorbent.

accelerated by free rotation of the thienyl group at the 8-position on the BODIPY core.<sup>8</sup>

### Theoretical calculations

To examine the electronic structure of **YH-1**, the molecular orbitals of the two dyes were calculated using density functional theory (DFT) at the B3LYP/6-31G(d) level. The DFT calculations indicate that the sulfur atoms of thiophene rings at the 3- and 5-positions turn outward from the BF<sub>2</sub> of the BODIPY core, which may be due to the steric interaction or C-H···F interaction between the thiophene rings and the BF<sub>2</sub>.<sup>9</sup> The HOMO and HOMO – 1 are mostly localized on the carbazole-diphenylamine moiety and the BODIPY core containing the two thienyl groups at the 3- and 5-positions, respectively, and the LUMO and the LUMO + 1 are mostly localized on the BODIPY core and the two thienylpyridine moieties, respectively (Fig. 2). Accordingly, these results reveal that dye excitations upon light irradiation induce a strong ICT from the carbazole-diphenylamine moiety to the pyridyl group through the BODIPY core.

### **Electrochemical properties of YH-1**

The electrochemical properties of **YH-1** were investigated by cyclic voltammetry (Fig. 3). Two reversible oxidation peaks were observed at 0.42 and 0.62 V *versus* ferrocene/ferrocenium (Fc/Fc<sup>+</sup>), corresponding to the oxidations of the diphenylamino group and the BODIPY core, respectively. This result shows that the oxidized states of **YH-1** are very stable. The HOMO energy level of the BODIPY core was evaluated from the half-wave potential for oxidation ( $E_{1/2}^{ox} = 0.59$  V, Table 1). The HOMO energy level was 1.22 V *vs.* a normal hydrogen electrode (NHE), which indicated that it is more positive than the  $I_3^-/I^-$  redox potential (0.4 V).







Fig. 3 Cyclic voltammogram of YH-1 in acetonitrile containing 0.1 M  $Bu_4NCIO_4$  at a scan rate of 100 mV s<sup>-1</sup>. The arrow denotes the direction of the potential scan.

This assures an efficient regeneration of the oxidized dyes by electron transfer from I<sup>-</sup> ions in the electrolyte. The LUMO energy level of the BODIPY core was estimated from  $E_{1/2}^{\text{ox}}$  and an intersection of absorption and fluorescence spectra (688 nm; 1.80 eV). The LUMO energy level was -0.58 V. Evidently, the LUMO energy level is higher than the energy level of the CB of TiO<sub>2</sub> (-0.5 V), suggesting that an electron injection into the CB of TiO<sub>2</sub> is thermodynamically possible.

### Absorption properties of YH-1 adsorbed on TiO<sub>2</sub> nanoparticles

The absorption spectra of the dye **YH-1** adsorbed on  $\text{TiO}_2$  nanoparticles are shown in Fig. 1b. Compared with that in 1,4-dioxane, the longest wavelength absorption band in the range of 500 to 800 nm is significantly broadened, and the onset of the absorption band reached 850 nm. When chenodeoxy-cholic acid (CDCA) was employed as coadsorbent to prevent dye

Table 1	able 1 Optical and electrochemical data, HOMO and LUMO energy levels, and DSSC performance parameters of YH-1										
Dye	$\lambda_{\max}^{abs}/nm (\epsilon/M^{-1} cm^{-1})^a$	$\lambda_{\max}^{\mathrm{fl}}/\mathrm{nm} \ (\Phi_{\mathrm{f}})^{b}$	$E_{1/2}^{\mathrm{ox}\ c}/\mathrm{V}$	HOMO <sup>d</sup> /V	LUMO <sup>d</sup> /V	Molecules cm <sup>-2</sup> e	$J_{\rm sc}{}^f/{\rm mA~cm^{-2}}$	$V_{\rm oc}{}^f/{\rm mV}$	$\mathrm{ff}^f$	$\eta^f(\%)$	
YH-1	377 (72 600), 673 (80 900)	696 (0.07)	0.59	1.22	-0.58	$\begin{array}{l} 1.28 \times 10^{17g} \\ 1.19 \times 10^{17h} \\ 1.08 \times 10^{17i} \\ 1.04 \times 10^{17j} \end{array}$	$0.66^{g}$ $1.19^{h}$ $1.41^{i}$ $1.85^{j}$	$352^g$ $320^h$ $320^i$ $320^j$	$0.53^{g}$ $0.53^{h}$ $0.54^{i}$ $0.67^{j}$	$0.12^{g}$ $0.20^{h}$ $0.25^{i}$ $0.39^{j}$	

<sup>*a*</sup> In 1,4-dioxane. <sup>*b*</sup> In 1,4-dioxane. Fluorescence quantum yields ( $\Phi_f$ ) were determined by using a calibrated integrating sphere system ( $\lambda_{ex} = 673$  nm). <sup>*c*</sup> Half-wave potential for the oxidation ( $E_{1/2}^{ox}$ ) vs. Fc/Fc<sup>+</sup> was recorded in acetonitrile–Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) solution. <sup>*d*</sup> vs. Normal hydrogen electrode (NHE). <sup>*e*</sup> Adsorption amount per unit area of the TiO<sub>2</sub> electrode. <sup>*f*</sup> Under a simulated solar light (AM 1.5, 100 mW cm<sup>-2</sup>). <sup>*g*</sup> 0.1 mM dye solution in acetonitrile. <sup>*h*</sup> 0.1 mM dye and 5 mM CDCA solution. <sup>*i*</sup> 0.1 mM dye and 10 mM CDCA solution.

Fig. 4 (a) Photographs of YH-1 in 1,4-dioxane and (b) YH-1 adsorbed on  $TiO_2$  film, and (c) FTIR spectra of the dye powders and dyes adsorbed on  $TiO_2$  nanoparticles for YH-1.

aggregation on the TiO<sub>2</sub> surface, the longest wavelength absorption band decreases in the width with increasing CDCA concentration. This result indicates that under the condition without CDCA the dye **YH-1** forms strong  $\pi$ -stacked aggregates on the TiO<sub>2</sub> surface. As shown in Fig. 4a and b, the color of **YH-1** in 1,4-dioxane is dark blue, but the color of **YH-1** adsorbed on TiO<sub>2</sub> film is almost black, which is desirable for LHE. Thus, these results indicate that the dye **YH-1** with two thienyl-pyridines and a carbazole-diphenylamine moiety on the BODIPY core possesses panchromatic absorption ability.

### FTIR spectra of YH-1

To elucidate the adsorption states of dye YH-1 on TiO<sub>2</sub> nanoparticles, we measured the FTIR spectra of the dye powders and the dyes adsorbed on TiO<sub>2</sub> nanoparticles (Fig. 4c). For the powders of YH-1, the characteristic stretching bands for C=N or C=C were clearly observed at around 1598 and 1486  $\text{cm}^{-1}$ . When the dye YH-1 was adsorbed on the TiO<sub>2</sub> surface, a new band appeared at around 1613 cm<sup>-1</sup>, which can be assigned to the pyridyl group coordinated to the Lewis acid sites (exposed  ${\rm Ti}^{n+}$  cations) on the TiO<sub>2</sub> surface, although the stretching band at around 1598 cm<sup>-1</sup> still remains; this suggests the presence of a pyridyl group hydrogen-bonded to Brønsted acid sites (surfacebound hydroxyl groups, Ti-OH) on the TiO<sub>2</sub> surface.<sup>10,11</sup> Consequently, this result indicates that the dye YH-1 is adsorbed on the TiO<sub>2</sub> surface through the coordinate bonding at Lewis acid sites and/or the hydrogen bonding at Brønsted acid sites, which is associated with the molecular structure with two thienylpyridine moieties outward from the BF2 of the BODIPY core.

### Photovoltaic performances of DSSCs based on YH-1

The DSSCs were prepared by using the dye-adsorbed  $\text{TiO}_2$  electrode, Pt-coated glass as a counter electrode, and an acetonitrile solution with iodine (0.05 M), lithium iodide (0.1 M), and 1,2-dimethyl-3-propylimidazolium iodide (0.6 M) as an electrolyte. The photocurrent–voltage (*I–V*) characteristics were measured under simulated solar light (AM 1.5, 100 mW cm<sup>-2</sup>). The IPCE spectra and the *I–V* curves are shown in Fig. 5. The photovoltaic performance parameters are collected in Table 1. Interestingly, when CDCA was employed as a coadsorbent to prevent dye aggregation on the TiO<sub>2</sub> surface, the IPCE at around 700 nm and the short-circuit photocurrent density (*J*<sub>sc</sub>) value dramatically



Fig. 5 (a) IPCE spectra and (b) *I–V* curves of DSSCs based on **YH-1** with and without CDCA as coadsorbent.

increased with increasing CDCA concentration. Under the adsorption conditions of 0.05 mM dye and 10 mM CDCA, the IPCE value of YH-1 is a high plateau in the range of 500 to 700 nm (ca. 10%), with an onset at 800 nm. The  $J_{\rm sc}$  and  $\eta$  values for YH-1 are 1.85 mA cm<sup>-2</sup> and 0.39%, respectively. This result shows that the BODIPY core forms strong  $\pi$ -stacked aggregates on the TiO<sub>2</sub> surface, leading to a reduction in direct electron-injection from the BODIPY core to the CB of the TiO<sub>2</sub> electrode. Consequently, the coadsorption of CDCA can effectively prevent the  $\pi$ -stacked aggregation between BODIPY cores, resulting in an increase in the electron-injection yield. On the other hand, the relatively high IPCE value at around 400 nm is attributed to direct electron-injection from the thienylcarbazole-diphenylamine moiety to the CB of the TiO<sub>2</sub> electrode. The open-circuit photovoltage  $(V_{oc})$  of BODIPY dye sensitizers is lower than that of the conventional organic dye sensitizers.<sup>7</sup> It is assumed that the low  $V_{\rm oc}$  value (ca. 350 mV) for YH-1 is attributed to faster charge recombination between the injected electrons in the CB of TiO2 and  $I_3^-$  ions in the electrolyte, arising from the approach of  $I_3^$ ions to the TiO2 surface due to the electrostatic interactions between the BODIPY core and  $I_3^-$  ions. Accordingly, the relatively low photovoltaic performance of YH-1 is due to not only formation of strong  $\pi$ -stacked aggregates, the lower LUMO level and the radiationless relaxation of the photoexcited dye, leading to a reduction in the electron-injection yield, but also faster charge recombination between the injected electrons and I<sub>3</sub> ions, leading to a decrease in the Voc value. Thus, this work indicates that the introduction of alkyl groups on the BODIPY core can effectively prevent not only the  $\pi$ -stacked aggregation and the charge recombination, but also the radiationless relaxation of the photoexcited dye by restriction of the free rotation of the thienyl group at the 8-position. Further studies to ensure these findings are now in progress by using the alkylated BODIPY dye sensitizers with two pyridyl groups and will be reported in a subsequent paper.

# Conclusions

As an effective BODIPY dye sensitizer possessing a high LHE in the red/NIR region, we have designed and synthesized D– $\pi$ –A type BODIPY dye **YH-1** with two pyridyl groups as electronwithdrawing-anchoring groups and a carbazole-diphenylamine moiety as an electron donor. We demonstrate that the expansion of the  $\pi$ -conjugated system by the introduction of not only the carbazole-diphenylamine moiety and the thiophene unit at the 8-position but also two thienylpyridines at the 3- and 5-positions on the BODIPY core can lead to red-shift and broadening of the absorption band in the red/NIR region, although the DSSCs based on the dye **YH-1** showed low photovoltaic performances.

# **Experimental section**

Melting points were measured using a Yanaco micro-melting point apparatus MP model. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer using the ATR method. High-resolution mass spectral data were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. <sup>1</sup>H NMR spectra were recorded on a Varian-400 (400 MHz) or Varian-500 (500 MHz) FT NMR spectrometer. Absorption spectra were observed using a Hitachi U-2910 spectrophotometer and fluorescence spectra were measured using a HORIBA Fluoro-Max-4 spectrofluorometer. The fluorescence quantum yields in solution were determined by a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system ( $\lambda_{ex}$  = 673 nm). Cyclic voltammetry (CV) curves were recorded in acetonitrile-Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) solution with a three-electrode system consisting of Ag/Ag<sup>+</sup> as a reference electrode, Pt plate as a working electrode, and Pt wire as a counter electrode by using a AMETEK Versa STAT 4 potentiostat. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of YH-1 were evaluated from the spectral analyses and the CV data. The HOMO energy level was evaluated from the  $E_{1/2}^{\text{ox}}$ . The LUMO energy level of YH-1 was estimated from the  $E_{1/2}^{ox}$  and an intersection of absorption and fluorescence spectra (688 nm; 1.80 eV), which correspond to the energy gap between the HOMO and the LUMO.

### Synthesis

5-(4'-Bromo-2-nitro-[1,1'-biphenyl]-4-yl)thiophene-2-carbaldehyde (1). To a mixture of 4,4'-dibromo-2-nitro-biphenyl (1.14 g, 3.20 mmol), 5-formyl-2-thiopheneboronic acid (0.5 g, 3.20 mmol), and  $Pd(PPh_3)_4$  (0.26 g, 0.22 mmol) under an argon atmosphere was added aqueous 1 M Na<sub>2</sub>CO<sub>3</sub> (2.5 ml) and DMF (15 ml) and stirred for 16 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was dried over MgSO4, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane-hexane = 2:1 as eluent) to give 1 (0.26 g, yield 21%) as a light yellow solid; m.p. 172–173 °C; IR (ATR):  $\tilde{\nu}$  = 1633, 1515, 1343, 1222 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, acetone-d<sub>6</sub>, TMS)  $\delta$  = 7.39 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 4.0 Hz, 1H), 8.07 (d, J = 4.0 Hz, 1H), 8.18 (dd, J = 2.0 and 8.0 Hz, 1H), 8.38 (d, J = 2.0 Hz, 1H), 10.02 (s, -CHO) ppm; HRMS (APCI): m/z (%): (M + H<sup>+</sup>) calcd for C<sub>17</sub>H<sub>11</sub>NO<sub>3</sub>SBr, 387.96375; found 387.96371.

2-(5-(4'-Bromo-2-nitro-[1,1'-biphenyl]-4-yl)thiophen-2-yl)-1,3dioxolane (2). A solution of 1 (2.14 g, 5.51 mmol), ethylene glycol (0.77 ml, 13.78 mmol), and *p*-toluenesulfonic acid monohydrate (0.8 mg) in toluene (25 ml) was refluxed by using a Dean-Stark apparatus under an argon atmosphere. After 10 h, the reaction mixture was washed with 10% NaOH aq. and extracted with dichloromethane. The organic extract was dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane as eluent) to give 2 (2.11 g, yield 88%) as a light yellow solid; m.p. 146–153 °C; IR (ATR):  $\tilde{\nu} = 1534$ , 1358, 1202, 1080 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta = 4.01-4.15$  (m, 4H), 6.09 (s, 1H), 7.27 (d, J = 3.8 Hz, 1H), 7.37 (d, J = 8.7 Hz, 2H), 7.61–7.63 (m, 2H), 7.68 (d, J = 8.7 Hz, 2H), 8.02 (dd, J = 1.9 and 8.1 Hz, 1H), 8.22 (d, J = 1.9 Hz, 1H) ppm; HRMS (APCI): m/z (%): (M + H<sup>+</sup>) calcd for C<sub>19</sub>H<sub>15</sub>NO<sub>4</sub>SBr, 431.98997; found 431.99039.

4'-(5-(1,3-Dioxolan-2-yl)thiophen-2-yl)-2'-nitro-N,N-diphenyl-[1,1'-biphenyl]-4-amine (3). To a mixture of 2 (1.0 g, 2.28 mmol), diphenylamine (0.77 g, 4.56 mmol), Pd(OAc)<sub>2</sub> (0.03 g, 0.11 mmol), (t-Bu)<sub>3</sub>P (1 M in toluene, 0.23 ml, 0.23 mmol), and t-BuONa (0.27 g, 2.85 mmol) under an argon atmosphere was added toluene (60 ml) and stirred for 10 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane-hexane = 2:1 as eluent) to give 3(1.01 g, yield 85%) as an orange powder; m.p. 166–167 °C; IR (ATR):  $\tilde{\nu}$  = 1517, 1486, 1268, 1087 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 4.00–4.15 (m, 4H), 6.09 (s, 1H), 7.07 (d, J = 8.8 Hz, 2H), 7.09–7.14 (m, 6H), 7.26 (d, J = 3.7 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.33-7.38 (m, 4H), 7.58 (d, J = 3.7 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.97 (dd, J = 2.0 and 8.2 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H) ppm; HRMS (ESI): m/z (%): (M + H<sup>+</sup>) calcd for C<sub>31</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>S, 521.15295; found 521.15247.

**7-(5-(1,3-Dioxolan-2-yl)thiophen-2-yl)-***N*,*N***-diphenyl-9***H***-carbazol-2-amine (4).** To a mixture of 3 (1.0 g, 1.94 mmol) and PPh<sub>3</sub> (1.27 g, 4.85 mmol) under an argon atmosphere was added *o*-dichlorobenzene (18 ml) and stirred for 39 h at 160 °C. After concentrating under reduced pressure, the residue was chromatographed on silica gel (dichloromethane–hexane = 2:1 as eluent) to give 4 (0.73 g, yield 77%) as a light green solid; m.p. 236–239 °C; IR (ATR):  $\tilde{\nu}$  = 3396, 1588, 1487, 1240, 1087 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 4.00–4.14 (m, 4H), 6.06 (s, 1H), 6.94 (dd, *J* = 2.0 and 8.4 Hz, 1H), 7.01–7.06 (m, 2H), 7.07–7.12 (m, 4H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.27–7.32 (m, 4H), 7.37 (d, *J* = 3.6 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 10.25 (s, –NH) ppm; HRMS (ESI): *m/z* (%): (M + H<sup>+</sup>) calcd for C<sub>31</sub>H<sub>25</sub>N<sub>2</sub>O<sub>2</sub>S, 489.16313; found 489.16205.

7-(5-(1,3-Dioxolan-2-yl)thiophen-2-yl)-9-butyl-N,N-diphenyl-9Hcarbazol-2-amine (5). A solution of 4 (0.30 g, 0.61 mmol) in DMF (50 ml) was treated with sodium hydride (60%, 0.08 g, 1.82 mmol) and stirred for 1 h at room temperature. 1-Iodobutane (0.346 ml, 3.04 mmol) was added dropwise over 30 min and the solution was stirred at room temperature for 24 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane–hexane = 2:1 as eluent) to give 5 (0.32 g, yield 96%) as a yellow solid; M.p. 148–150 °C; IR (ATR):  $\tilde{\nu}$  = 1592, 1452, 1262, 1068 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 0.86 (t, *J* = 7.3 Hz, 3H), 1.26–1.35 (m, 2H), 1.74–1.81 (m, 2H), 4.00–4.15 (m, 4H), 4.35 (t, *J* = 7.0 Hz, 2H), 6.06 (s, 1H), 6.92 (dd, *J* = 1.9 and 8.4 Hz, 1H), 7.01–7.06 (m, 2H), 7.10–7.15 (m, 4H), 7.20 (d, *J* = 3.7 Hz, 1H), 7.22 (d, *J* = 1.9 Hz, 1H), 7.28–7.33 (m, 4H), 7.47 (d, *J* = 3.7 Hz, 1H), 7.51 (dd, *J* = 1.6 and 8.1 Hz, 1H), 7.80 (d, *J* = 1.6 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H) ppm; HRMS (APCI): *m*/*z* (%): (M + H<sup>+</sup>) calcd for C<sub>35</sub>H<sub>33</sub>N<sub>2</sub>O<sub>2</sub>S, 545.22573; found 545.22540.

5-(9-Butyl-7-(diphenylamino)-9H-carbazol-2-yl)thiophene-2carbaldehyde (6). To compound 5 (0.32 g, 0.58 mmol) under an argon atmosphere was added THF (20 ml) and 3 N HCl (7 ml), and refluxed for 30 min. The reaction mixture was cooled to room temperature, washed with 10% NaOH aq., and extracted with dichloromethane. The organic extract was dried over MgSO<sub>4</sub>, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane-hexane = 2:1 as eluent) to give 6 (0.29 g, yield 99%) as a yellow solid; m.p. 173–174 °C; IR (ATR):  $\tilde{\nu}$  = 1654, 1584, 1441, 1229 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 0.86 (t, *J* = 7.2 Hz, 3H), 1.26–1.35 (m, 2H), 1.75–1.82 (m, 2H), 4.35 (t, J = 7.8 Hz, 2H), 6.94 (dd, J = 2.0 and 8.4 Hz, 1H), 7.03-7.08 (m, 2H), 7.11-7.15 (m, 4H), 7.23 (d, J = 2.0 Hz, 1H), 7.28–7.33 (m, 4H), 7.63 (dd, J = 1.6 and 8.0 Hz, 1H), 7.76 (d, J = 4.0 Hz, 1H), 7.97 (d, J = 1.6 Hz, 1H), 7.98 (d, J = 4.0 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 9.95 (s, -CHO) ppm; HRMS (APCI): *m*/*z* (%):  $(M + H^{+})$  calcd for C<sub>33</sub>H<sub>29</sub>N<sub>2</sub>OS, 501.19951; found 501.19940.

9-Butyl-7-(5-(di(1H-pyrrol-2-yl)methyl)thiophen-2-yl)-N,N-diphenyl-9H-carbazol-2-amine (7). To a mixture of 6 (0.28 g, 0.56 mmol) and pyrrole (1.17 ml, 16.9 mmol) under an argon atmosphere was added trifluoroacetic acid (0.69 µl) and stirred for 10 h at room temperature. The reaction mixture was washed with Na2CO3 aq. and extracted with dichloromethane. The organic extract was dried over MgSO4, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane-hexane = 1:1 as eluent) to give 7 (0.29 g, yield 83%) as a reddish brown solid; m.p. 92–95 °C; IR (ATR):  $\tilde{\nu}$  = 3411, 1594, 1489, 1269 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 0.84 (t, J = 7.2 Hz, 3H), 1.24-1.31 (m, 2H), 1.72-1.79 (m, 2H), 4.32 (t, J = 6.8 Hz, 2H), 5.74 (s, 1H), 5.94–5.96 (m, 2H), 6.01–6.03 (m, 2H), 6.72–6.73 (m, 2H), 6.80 (d, J = 3.6 Hz, 1H), 6.91 (dd, J = 2.0 and 8.4 Hz, 1H), 7.01–7.06 (m, 2H), 7.10–7.12 (m, 4H), 7.21 (d, J = 2.0 Hz, 1H), 7.27-7.32 (m, 4H), 7.35 (d, J = 3.6 Hz, 1H), 7.44 (dd, J = 1.6 and 8.4 Hz, 1H), 7.71 (d, J = 1.6 Hz, 1H), 8.00–8.05 (m, 2H); HRMS (APCI): m/z (%): (M + H<sup>+</sup>) calcd for C<sub>41</sub>H<sub>37</sub>N<sub>4</sub>S, 617.27334; found 617.27319.

(*E*)-9-Butyl-7-(5-((5-chloro-1*H*-pyrrol-2-yl)(5-chloro-2*H*-pyrrol-2-ylidene)methyl)thioph-en-2-yl)-*N*,*N*-diphenyl-9*H*-carbazol-2-amine (8). To compound 7 (0.29 g, 0.47 mmol) under an argon atmosphere was added THF (4 ml) and then stirred at -80 °C. Next, a solution of *N*-chlorosuccinimide (0.13 g, 0.94 mmol) in THF was added dropwise and the solution was stirred at -80 °C for 2 h and then at room temperature for 24 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was dried over MgSO<sub>4</sub>, filtrated and concentrated. To the reaction mixture was added DDQ (0.13 g, 0.51 mmol) and dichloromethane (9 ml), and the solution was stirred at room temperature for 3 h. After concentrating under reduced pressure, the residue was chromatographed on silica gel (dichloromethane–hexane = 1:2 as eluent) to give **8** (0.15 g, yield 46%) as a reddish brown solid; IR (ATR):  $\tilde{\nu}$  = 1559, 1254, 1036 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 0.86 (t, *J* = 7.4 Hz, 3H), 1.26–1.35 (m, 2H), 1.75–1.83 (m, 2H), 4.37 (t, *J* = 7.0 Hz, 2H), 6.49 (d, *J* = 4.0 Hz, 2H), 6.94 (dd, *J* = 1.8 and 8.4 Hz, 1H), 7.03–7.08 (m, 2H), 7.11–7.14 (m, 4H), 7.18 (d, *J* = 4.0 Hz, 2H), 7.23 (d, *J* = 1.8 Hz, 1H), 7.27–7.34 (m, 4H), 7.53 (d, *J* = 3.8 Hz, 1H), 7.62 (dd, *J* = 1.6 and 8.2 Hz, 1H), 7.76 (d, *J* = 3.8 Hz, 1H), 7.96 (d, *J* = 1.6 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H); HRMS (APCI): *m*/z (%): (M + H<sup>+</sup>) calcd for C<sub>41</sub>H<sub>33</sub>N<sub>4</sub>SCl<sub>2</sub>, 683.17975; found 683.18054.

10-(5-(9-Butyl-7-(diphenylamino)-9H-carbazol-2-yl)thiophen-2-yl)-3,7-dichloro-5,5-diflu-oro-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (9). To compound 8 (0.15 g, 0.22 mmol) under an argon atmosphere was added dichloromethane (8.5 ml) and triethylamine (0.29 ml, 2.16 mmol) and stirred for 30 min at room temperature. Next, BF<sub>3</sub>-OEt<sub>2</sub> (0.42 ml, 3.24 mmol) was added dropwise and the solution was stirred at room temperature for 66 h. The reaction mixture was washed with water and extracted with dichloromethane. The organic extract was dried over MgSO4, filtered, and concentrated. The residue was chromatographed on silica gel (dichloromethane-hexane = 1:2 as eluent) to give 9 (0.14 g, yield 89%) as a purple solid; IR (ATR):  $\tilde{\nu}$  = 1525, 1385, 1259, 1107 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 0.86 (t, J = 7.6 Hz, 3H), 1.26-1.35 (m, 2H), 1.76-1.83 (m, 2H), 4.38 (t, J = 7.0 Hz, 2H), 6.74 (d, J = 4.4 Hz, 2H), 6.95 (dd, J = 2.0 and 8.4 Hz, 1H), 7.03-7.08 (m, 2H), 7.12-7.15 (m, 4H), 7.23 (d, J = 2.0 Hz, 1H), 7.28–7.34 (m, 4H), 7.61 (d, J = 4.4 Hz, 2H), 7.67 (dd, J = 1.6 and 8.4 Hz, 1H), 7.84 (d, J = 3.6 Hz, 1H), 7.90 (d, J = 3.6 Hz, 1H), 8.04 (d, J = 1.6 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H) ppm; HRMS (ESI): m/z (%): (M + Na<sup>+</sup>) calcd for C<sub>41</sub>H<sub>31</sub>BN<sub>4</sub>F<sub>2</sub>NaSCl<sub>2</sub>, 753.15998; found 753.16034.

10-(5-(9-Butyl-7-(diphenylamino)-9H-carbazol-2-yl)thiophen-2-yl)-5,5-difluoro-3,7-bis(5-(pyridin-4-yl)thiophen-2-yl)-5H-dipyrrolo-[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (YH-1). A solution of 9 (0.09 g, 0.12 mmol), 4-(5-tributylstannanyl-thiophen-2-yl)-pyridine (0.17 g, 0.37 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.01 g, 8  $\times$  10<sup>-3</sup> mmol) in toluene (15 ml) was stirred for 8 h at 110 °C under an argon atmosphere. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The organic extract was concentrated. The residue was chromatographed on reverse-phase silica gel (dichloromethanemethanol = 1:1 as eluent) to give YH-1 (0.01 g, yield 8%) as a black solid; IR (ATR):  $\tilde{\nu}$  = 1589, 1529, 1467 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>)  $\delta$  = 0.86 (t, J = 7.4 Hz, 3H), 1.26–1.36 (m, 2H), 1.76–1.83 (m, 2H), 4.37 (t, J = 6.8 Hz, 2H), 6.95 (dd, J = 1.8 and 8.4 Hz, 1H), 7.04-7.09 (m, 2H), 7.12-7.16 (m, 6H), 7.23 (d, J = 1.8 Hz, 1H), 7.28-7.34 (m, 4H), 7.53 (d, J = 4.4 Hz, 2H), 7.66 (dd, J = 1.6 and 8.2 Hz, 1H), 7.70 (d, J = 6.1 Hz, 4H), 7.76 (d, J = 3.8 Hz, 1H), 7.86 (d, J = 3.8 Hz, 1H), 7.88 (d, J = 4.0 Hz, 2H), 8.01 (d, J = 1.6 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 8.26 (d, J = 4.0 Hz, 2H), 8.64 (d, J = 6.1 Hz, 4H) ppm; HRMS (ESI): m/z (%): (M + H<sup>+</sup>) calcd for C<sub>59</sub>H<sub>44</sub>BN<sub>6</sub>F<sub>2</sub>S<sub>3</sub>, 981.28452; found 981.28467.

Preparation of dye-sensitized solar cells based on dye YH-1. The TiO<sub>2</sub> paste (JGC Catalysts and Chemicals Ltd., PST-18NR) was deposited on a fluorine-doped-tin-oxide (FTO) substrate by doctor-blading, and sintered for 50 min at 450  $^\circ$ C. The 9  $\mu$ m thick TiO<sub>2</sub> electrode (0.5  $\times$  0.5 cm<sup>2</sup> in photoactive area) was immersed into 0.1 mM or 0.05 mM dye solution in acetonitrile for a number of hours enough to adsorb the photosensitizer. The DSSCs were fabricated by using the TiO<sub>2</sub> electrode thus prepared, Pt-coated glass as a counter electrode, and a solution of 0.05 M iodine, 0.1 M lithium iodide, and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in acetonitrile as an electrolyte. The photocurrent-voltage characteristics were measured using a potentiostat under a simulated solar light (AM 1.5, 100 mW cm $^{-2}$ ). IPCE spectra were measured under monochromatic irradiation with a tungsten-halogen lamp and a monochromator. The amount of adsorbed dye on TiO2 nanoparticles was determined by absorption spectral measurement of the concentration change of the dve solution before and after adsorption. Absorption spectra of the dyes adsorbed on TiO<sub>2</sub> nanoparticles were recorded on the dye-adsorbed  $TiO_2$  film (thickness of 9  $\mu$ m) in the transmission mode using a calibrated integrating sphere system.

# Acknowledgements

This work was supported by A-STEP (AS242Z00243J) from Japan Science and Technology Agency (JST), by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) (24102005 and 24550225) and by The Kao Foundation for Arts and Sciences.

# Notes and references

- (a) B. O'Regan and M. Grätzel, *Nature*, 1991, 353, 737;
   (b) M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopolous and M. Grätzel, *J. Am. Chem. Soc.*, 1993, 115, 6382.
- 2 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595.
- 3 (a) A. Mishra, M. K. R. Fischer and P. Bäuerle, Angew. Chem., Int. Ed., 2009, 48, 2474; (b) Z. Ning and H. Tian, Chem. Commun., 2009, 5483; (c) Y. Ooyama and Y. Harima, Eur. J. Org. Chem., 2009, 2903; (d) Y. Ooyama and Y. Harima, Chem-PhysChem, 2012, 13, 4032; (e) Y. Ooyama, J. Ohshita and Y. Harima, Chem. Lett., 2012, 1384; (f) N. Robertson, Angew. Chem., Int. Ed., 2006, 45, 2338; (g) F. Odobel, L. L. Pleux,

Y. Pellegrin and E. Blart, Acc. Chem. Res., 2010, 43, 1063;
(h) J.-H. Yum, E. Baranoff, S. Wenger, M. K. Nazeeruddin and M. Grätzel, Energy Environ. Sci., 2011, 4, 842; (i) Z. Ning, Y. Fu and H. Tian, Energy Environ. Sci., 2010, 3, 1170; (j) J. Mao, N. He, Z. Ning, Q. Zhang, F. Guo, L. Chen, W. Wu, J. Hua and H. Tian, Angew. Chem., Int. Ed., 2012, 51, 9873; (k) L.-L. Li and E. W.-G. Diau, Chem. Soc. Rev., 2013, 42, 291.

- 4 (a) J.-H. Yum, P. Walter, S. Huber, S. Rentsch, T. Geiger, F. Nüesch, F. D. Angelis, M. Grätzel and M. K. Nazeeruddin, J. Am. Chem. Soc., 2007, 129, 10320; (b) J. H. Delcamp, Y. Shi, J.-H. Yum, T. Sajoto, E. Dell'Orto, S. Barlow, M. K. Nazeeruddin, S. R. Marder and M. Grätzel, Chem.-Eur. J., 2013, 19, 1819.
- 5 (a) M. Kimura, H. Nomoto, N. Masaki and S. Mori, Angew. Chem., Int. Ed., 2012, 51, 4371; (b) M.-E. Ragoussi, J.-J. Cid, J.-H. Yum, G. De La Torre, D. D. Censo, M. Grätzel, M. K. Nazeeruddin and T. Torres, Angew. Chem., Int. Ed., 2012, 51, 4375.
- 6 (a) T. Bessho, S. M. Zakeeruddin, C.-Y. Yeh, E. W.-G. Diau and M. Grätzel, Angew. Chem., Int. Ed., 2010, 49, 6646;
  (b) A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin and M. Grätzel, Science, 2011, 334, 629.
- 7 (a) M. Mao, J.-B. Wang, Z.-F. Xiao, S.-Y. Dai and Q.-H. Song, *Dyes Pigm.*, 2012, 94, 224; (b) J.-B. Wang, X.-Q. Fang, X. Pan, S.-Y. Dai and Q.-H. Song, *Chem.–Asian J.*, 2012, 7, 696; (c) S. Erten-Ela, M. D. Yilmaz, B. Icli, Y. Dede, S. Icli and E. U. Akkaya, *Org. Lett.*, 2008, 10, 3299; (d) S. Kolemen, Y. Cakmak, S. Erten-Ela, Y. Altay, J. Brendel, M. Thelakkat and E. U. Akkaya, *Org. Lett.*, 2010, 12, 3812; (e) S. Kolemen, O. A. Bozdemir, Y. Cakmak, G. Barin, S. Erten-Ela, M. Marszalek, J.-H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin, M. Grätzel and E. U. Akkaya, *Chem. Sci.*, 2011, 2, 949.
- 8 R. Hu, E. Larger, A. Aguilar-Aguilar, J. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Zhong, K. S. Wong, E. Peña-Cabrera and B. Z. Tang, *J. Phys. Chem. C*, 2009, **113**, 15845.
- 9 S. Rihn, P. Retailleau, N. Bugsaliewicz, A. De Nicola and R. Ziessel, *Tetrahedron Lett.*, 2009, **50**, 7008.
- 10 M. I. Zaki, M. A. Hasan, F. A. Al-Sagheer and L. Pasupulety, Colloids Surf., A, 2001, 190, 261.
- 11 (a) Y. Ooyama, S. Inoue, T. Nagano, K. Kushimoto, J. Ohshita, I. Imae, K. Komaguchi and Y. Harima, *Angew. Chem., Int. Ed.*, 2011, **50**, 7429; (b) Y. Ooyama, T. Nagano, S. Inoue, I. Imae, K. Komaguchi, J. Ohshita and Y. Harima, *Chem.-Eur. J.*, 2011, **17**, 14837.