Dyes and Pigments 94 (2012) 553-560

Contents lists available at SciVerse ScienceDirect

# Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

# Panchromatic donor—acceptor—acceptor sensitizers based on 4H-cyclopenta [2,1-*b*:3,4-*b*']dithiophen-4-one as a strong acceptor for dye-sensitized solar cells

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#### ARTICLE INFO

Article history: Received 25 January 2012 Received in revised form 3 March 2012 Accepted 5 March 2012 Available online 20 March 2012

Keywords: Ketones Donor–acceptor system Organic dye Near-infrared absorption Dye-sensitized solar cells

#### ABSTRACT

Three new donor–acceptor–acceptor near-infrared organic dyes based on 4H-cyclopenta[2,1-b:3,4-b'] dithiophen-4-one as an additional acceptor were developed and used in dye-sensitized solar cells. By virtue of the simple donor–acceptor–acceptor configuration and systematic tuning of the electron-donating ability of the donor moiety, the absorption spectrum of **HIQ3** on TiO<sub>2</sub> extended to 900 nm. Remarkably, DSCs sensitized with **HIQ3** showed broad incident monochromatic photon-to-current conversion efficiency spectra across the entire visible range and extending into the near-infrared region as far as 1100 nm.

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# 1. Introduction

In the past decade, dye-sensitized solar cells (DSCs) have received increasing attention owing to their potential use in lowcost production of renewable energy and in large-area, flexible, colorful, lightweight devices [1]. Overall solar-to-electric energy conversion efficiencies exceeding 11% have been achieved under standard AM 1.5 conditions with DSCs based on ruthenium sensitizers because of their broad and intense metal-to-ligand charge transfer absorption across the entire visible range and extending to the near-infrared (NIR) [2]. Because the supply of ruthenium is limited, metal-free organic dyes have attracted considerable attention in the past several years [3]. Among these, donor- $\pi$ bridge-acceptor  $(D-\pi-A)$  compounds are particularly attractive because of their large molar extinction coefficients, readily tuned HOMO-LUMO levels, and low-cost, easy synthesis [4]. However, the overall conversion efficiencies of DSCs based on metal-free organic dyes are lower than those of DSCs based on ruthenium dyes, owing to the narrow coverage of the solar spectrum. Thus, there is growing interest in developing NIR sensitizers for applications in DSCs [5].

Recently, additional acceptor chromophores have been introduced between the donor and the  $\pi$ -bridge, leading to a D-A- $\pi$ -A architecture that facilitates intramolecular charge transfer and adjusts the bandgap energy for harvesting more NIR light [6]. However, the resulting absorption spectra and incident monochromatic photon-to-current conversion efficiency (IPCE) spectra are inefficient at reaching to the NIR region because the additional acceptors are only weakly electron withdrawing. A feasible strategy for extension of the absorption and IPCE spectra into the NIR region would be to use a more strongly electron-withdrawing acceptor between the donor moiety and cyanoacetic acid moiety to form a D-A-A architecture. The 4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one unit is a good candidate acceptor; owing to the presence of the electron-withdrawing ketone group, the HOMO-LUMO energy of this acceptor ( $\lambda_{max} = 474$  nm) is narrower than bithiophene  $(\lambda_{\text{max}} = 302 \text{ nm})$  and cyclopenta[2,1-*b*:3,4-*b'*]dithiophene  $(\lambda_{\text{max}} = 312 \text{ nm})$  [7]. In this study, we first introduced this strongly electron-withdrawing acceptor into the D-A-A configuration and synthesized three novel sensitizers, HIQ1, HIQ2 and HIQ3 (Fig. 1), for harvesting visible and NIR light. HIQ1 has the simplest structure, with triphenylamine as the donor and 2-cyano-2-propenoic acid as the acceptor/anchor. Two different spacers, thiophene in HIQ2 and ethylenedioxythiophene in HIQ3, were also introduced into the molecular backbone between the donor and the additional acceptor to further increase the electron-donating strength of the





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Fig. 1. Chemical structures of HIQ1, HIQ2 and HIQ3.

donor moiety. The performance of DSCs based on these NIR organic dyes is reported.

# 2. Experimental section

### 2.1. Materials

All chemicals and reagents were used as received from suppliers without further purification. THF and toluene were dried over molecular sieves and distilled under argon from sodium benzo-phenone ketyl immediately prior to use. 4H-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one was synthesized according to the reported method [8]. Column chromatography was performed using Wakogel-C300 as a stationary phase.

### 2.2. Analytical instruments

UV-vis-NIR N.Nspectra were measured in dimethylformamide (DMF) solution or on a TiO<sub>2</sub> film (thickness = 4  $\mu$ m) with a UV-vis-NIR spectrophotometer (UV-3600, Shimadzu). <sup>1</sup>H (600 MHz) and <sup>13</sup>C NMR (150 MHz) spectra were measured with a DRX-600 spectrometer (Bruker BioSpin). Mass spectra were measured on a Shimadzu Biotech matrix-assisted laser desorption ionization (MALDI) mass spectrometer. Cyclic voltammetry was performed on a CH Instruments 624D potentiostat/galvanostat system with a three-electrode cell consisting of a Ag/AgCl reference electrode, a working electrode, and a platinum wire counter-electrode. The redox potentials of the dyes absorbed on TiO<sub>2</sub> were measured in CH<sub>3</sub>CN containing 0.1 M tetra-nbutylammonium hexafluorophosphate. Electrochemical measurements were performed at a scan rate of 50 mV s<sup>-1</sup>.

### 2.3. Cell fabrication and characterization

The DSCs were fabricated as follows. A double-layer TiO<sub>2</sub> photoelectrode (thickness 15  $\mu$ m; area 0.25 cm<sup>2</sup>) was used as a working electrode. A 10  $\mu$ m main transparent layer with titania particles (~20 nm) and a 5  $\mu$ m scattering layer with titania particles (~400 nm) were screen-printed on the fluorine-doped tin oxide conducting glass substrate [9]. A solution of **HIQ1**, **HIQ2** or **HIQ3** (3 × 10<sup>-4</sup> M) in acetonitrile/tert-butyl alcohol (1/1, v/v) was used to coat the TiO<sub>2</sub> film with the dye. Deoxycholic acid (20 mM) was added to the dye solution as a co-adsorbent to prevent aggregation of the dye molecules. The electrodes were immersed in the dye solutions and then kept at 25 °C for 24 h to adsorb the dye onto the

TiO<sub>2</sub> surface. Photovoltaic measurements were performed in a twoelectrode sandwich-type sealed-cell configuration. The dye-coated TiO<sub>2</sub> film was used as the working electrode, and platinum-coated conducting glass was used as the counter-electrode. The two electrodes were separated by a Surlyn spacer (50 µm thick) and sealed up by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide, 0.05 M I<sub>2</sub> and 1.0 M LiI in acetonitrile. The current–voltage characteristics were measured using a black metal mask with an aperture area of 0.25 cm<sup>2</sup> under standard AM 1.5 sunlight (100 mW cm<sup>-2</sup>, WXS-155S-10: Wacom Denso Co., Japan) [10]. Monochromatic incident photon-to-current conversion efficiency spectra were measured with monochromatic incident light of  $1 \times 10^{16}$  photons cm<sup>-2</sup> under 100 mW cm<sup>-2</sup> in director current mode (CEP-2000BX, Bunko-Keiki).

#### 2.4. Synthesis

# 2.4.1. 4H-Cyclopenta[2,1-b:3,4-b']dithiophen-4-one-2-carbaldehvde

To a cold solution of 4H-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-4one (4.51 g, 23.4 mmol) and DMF (1.86 g, 25.74 mmol) in 1,2dichloroethane (60 mL) at 0 °C was added phosphorus oxychloride (3.95 g, 25.74 mmol). The reaction solution was heated to 80 °C and stirred for 6 h, and then saturated aqueous sodium acetate (100 mL) was added. The mixture was stirred at room temperature for an additional 30 min. The crude product was extracted into dichloromethane, and the organic layer was washed with brine and water and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (ethyl acetate/ hexane, 1/10, v/v) to yield a deep red solid (4.7 g, 91% yield). <sup>1</sup>H NMR  $(600 \text{ MHz}, \text{CDCl}_3) \delta$ : 9.79 (s, 1H), 7.62 (s, 1H), 7.34 (d, J = 4.8 Hz, 1H), 7.15 (d, J = 4.8 Hz, 1H) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 182.19, 181.17, 157.51, 147.62, 145.74, 145, 142.1, 131.34, 123.6, 122.19 ppm. MALDI-MS calcd: 219.97, found: 219.85.

# 2.4.2. 6-Bromo-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one-2-carbaldehyde

To a solution of 4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one-2-carbaldehyde (4.6 g, 20.9 mmol) in DMF (50 mL) under argon was added N-bromosuccinimide (NBS; 4.1 g, 23 mmol) in the dark. The resulting solution was stirred for 12 h at room temperature under argon and then extracted with dichloromethane (200 mL  $\times$  3) and water (50 mL). The combined organic layers were dried over

anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatog-raphy on silica gel (ethyl acetate/hexane, 1/10, v/v) to give a pale red solid (6.0 g, 96% yield). <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 9.79 (s, 1H), 7.91 (s, 1H), 7.38 (s, 1H) ppm. <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 182.04, 180.05, 157.05, 147.27, 146.14, 143.56, 140.61, 129.44, 124.76, 118.15 ppm. MALDI-MS calcd: 297.88, found: 297.98.

# 2.4.3. 6-{4-[N,N-Bis(4-methylphenyl)amino]phenyl}-4H-cyclopenta[2,1-b:3,4-b'] dithiophen-4-one-2-carbaldehyde

A mixture of 6-bromo-4H-cyclopenta[2,1-*b*:3,4-*b*']dithiophen-4-one-2-carbaldehyde (0.1 g, 0.35 mmol), 4-tributylstannyl-N,Nbis(4-methylphenyl)aniline (0.22 g, 0.4 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg) and anhydrous toluene (20 mL) was refluxed for 24 h under argon. The crude product was extracted into dichloromethane, and the organic layer was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (ethyl acetate/hexane, 1/8, v/v) to yield a black-red solid (0.12 g, 73% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.76 (s, 1H), 7.58 (s, 1H), 7.36 (dd, *J* = 6.6, 1.8 Hz, 4H), 7.16 (s, 1H), 7.11 (d, *J* = 8.4 Hz, 4H), 7.03 (m, 4H), 6.99 (m, 2H), 2.33 (s, 6H) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$ : 181.94, 181.76, 158.76, 152.41, 149.15, 145.9, 145.07, 144.45, 143.81, 141.03, 133.68, 130.13, 129.44, 126.29, 125.35, 125.3, 121.29, 115.98, 20.88 ppm.

# 2.4.4. 2-Cyano-3-{6-{4-[N,N-bis(4-methylphenyl)amino]phenyl}-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one-2-yl}acrylic acid (**HIQ1**)

To a stirred solution of 6-{4-[N,N-bis(4-methylphenyl)amino] phenyl}-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one-2-

carbaldehyde (27 mg, 0.55 mmol) and cyanoacetic acid (94 mg, 1.1 mmol) in chloroform (5 mL) was added piperidine (188 mg, 2.2 mmol). The reaction mixture was refluxed under argon for 12 h and then acidified with 2 M aqueous hydrochloric acid (10 mL). The crude product was extracted into chloroform, and the organic layer was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography with chloroform and methanol/chloroform (1/10, v/v) in turn as eluents to yield a black powder (23 mg, 76% yield). FT-IR (KBr,  $v_{max}/cm^{-1}$ ): 3416, 3026, 2919, 2853, 2219, 1709, 1578, 1430, 1359, 1320, 1259, 1212, 1093, 816, 767. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>) δ: 8.15 (s, 1H), 7.65 (s, 1H), 7.51 (s, 2H), 7.37 (s, 2H), 7.14(d, J = 7.8 Hz, 4H), 6.96 (d, J = 7.8 Hz, 4H), 6.85(d, J = 7.8 Hz, 2H), 2.27 (s, 6H) ppm. <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) δ: 182.12, 163.99, 155.87, 151.12, 148.49, 145.86, 144.52, 143.02, 140.77, 140.02, 133.6, 130.67, 128.94, 126.66, 125.92, 125.47, 121.25, 119.14, 116.56, 79.65, 20.91 ppm. HRMS (FAB<sup>+</sup>, m/z): calcd for C<sub>33</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>, 558.1072; found, 558.1061.

# 2.4.5. 6-{5-{4-[N,N-Bis(4-methylphenyl)amino]phenyl}thiophene-2-yl}-4H-cyclopenta

2.4.5.1. [2,1-b:3,4-b']dithiophen-4-one-2-carbaldehyde. A mixture of 6-bromo-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one-2-carbaldehyde (0.19 g, 0.65 mmol), 4-(2-(tributylstannyl)thiophene-5-yl)-N,N-bis(4-methylphenyl)aniline (0.52 g, 0.8 mmol), Pd(PPh\_3)<sub>4</sub> (10 mg) and anhydrous toluene (20 mL) was refluxed for 24 h under argon. The crude product was extracted into dichloromethane, and the organic layer was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (ethyl acetate/hexane, 1/8, v/v) to yield black-red solid (0.28 g, 75% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$ : 9.77 (s, 1H), 7.40 (d, *J* = 6.6 Hz, 2H), 7.18 (d, *J* = 3.6 Hz, 2H), 7.13 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 4H), 7.03 (m, 6H), 2.32 (s, 6H) ppm. <sup>13</sup>C NMR

(150 MHz, CDCl<sub>3</sub>) δ: 181.94, 181.23, 158.19, 148.42, 145.59, 145.57, 145.46, 144.87, 144.74, 144.08, 141.23, 133.52, 133.24, 130.03, 129.4, 126.46, 126.07, 125.82, 125.07, 122.7, 121.87, 117.84, 20.86 ppm.

### 2.4.6. 2-Cyano-3-{6-{2-{4-[N,N-bis(4-methylphenyl)amino] phenyl}thiophene-5-yl}-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4one-2-yl}acrylic acid (**HIQ2**)

**HIQ2** was synthesized according to the procedure described for **HIQ1** and was obtained as a black powder (0.15 g, 60% yield). FT-IR (KBr,  $v_{max}/cm^{-1}$ ): 3420, 3025, 2917, 2852, 2210, 1709, 1676, 1575, 1430, 1262, 931, 813, 790, 761. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.06 (s, 1H), 7.58 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 4.2 Hz, 1H), 7.33 (d, J = 4.2 Hz, 1H), 7.29 (s, 1H), 7.13 (d, J = 8.4 Hz, 4H), 6.94 (d, J = 8.4 Hz, 4H), 6.87 (d, J = 8.4 Hz, 2H), 2.27 (s, 6H) ppm. <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 181.89, 163.91, 154.33, 148.01, 146.56, 144.7, 143.85, 143.76, 143.17, 141.3, 140.99, 140.91, 133.96, 133.32, 130.62, 127.73, 126.8, 126.6, 125.23, 124.02, 121.77, 119.79, 117.39, 79.66, 20.89 ppm. HRMS (FAB<sup>+</sup>, m/z): calcd for C<sub>37</sub>H<sub>24</sub>N<sub>2</sub>O<sub>3</sub>S<sub>3</sub>, 640.0949; found, 640.0925.

# 2.4.7. 6-{5-{4-[N,N-Bis(4-methylphenyl)amino]phenyl}-3,4ethylenedioxythiophene-2-yl}-4H-cyclopenta[2,1-b:3,4-b'] dithiophen-4-one-2-carbaldehyde

A mixture of 6-bromo-4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one-2-carbaldehyde (0.1 g, 0.35 mmol), 4-[5-tributylstannyl-3,4ethylenedioxythiophene-2-yl]-N,N-bis(4-methylphenyl)aniline (0.28 g, 0.4 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg) and anhydrous toluene (20 mL) was refluxed for 24 h under argon. The crude product was extracted into dichloromethane, and the organic laver was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (ethyl acetate/ hexane, 1/5, v/v) to yield a black-red solid (0.15 g, 68% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ: 9.74 (s, 1H), 7.53 (m, 3H), 7.16 (s, 1H), 7.08 (d, J = 7.8 Hz, 4H), 7.02 (m, 6H), 4.41 (s, 2H), 4.36 (s, 2H), 2.32 (s, 6H)ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ: 181.84, 181.56, 159.14, 147.5, 145.28, 144.84, 144.79, 143.23, 142.7, 141.08, 139.61, 137.22, 133.02, 129.96, 129.46, 126.93, 124.94, 124.88, 121.94, 117.69, 115.89, 107.95, 65.15, 64.62, 20.85 ppm.

# 2.4.8. 2-Cyano-3-{6-{2-{4-[N,N-bis(4-methylphenyl)amino] phenyl}-3,4-ethylenedioxy thiophen-5-yl}-4H-cyclopenta[2,1-b:3,4b']dithiophen-4-one-2-yl}acrylic acid (**HIQ3**)

**HIQ3** was synthesized according to the procedure described for **HIQ1** and was obtained as a black powder (52 mg, 55% yield). FT-IR (KBr,  $v_{max}/cm^{-1}$ ): 3397, 3024, 2920, 2857, 2211, 1713, 1578, 1493, 1437, 1360, 1280, 1082, 813, 762. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 8.08 (s, 1H), 7.61 (s, 1H), 7.50 (s, 2H), 7.12 (m, 5H), 6.93 (m, 6H), 4.45 (s, 2H), 4.37 (s, 2H), 2.27 (s, 6H) ppm. <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 181.84, 163.6, 155.8, 147.08, 145.69, 144.79, 143.55, 142.46, 141.33, 140.83, 140.2, 139.82, 138.03, 130.58, 128.52, 127.13, 125.25, 125.02, 121.97, 119.37, 115.7, 115.52, 107.81, 79.65, 65.67, 65.06, 20.88 ppm. HRMS (FAB<sup>+</sup>, *m/z*): calcd for C<sub>39</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>S<sub>3</sub>, 698.1004; found, 698.1011.

### 3. Results and discuss

### 3.1. Synthesis

The general synthetic routes to **HIQ1**, **HIQ2** and **HIQ3** are depicted in Fig. 2. 4H-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one was formyla ted with phosphorus oxychloride in DMF to afford 4H-cyclopenta[2,1*b*:3,4-*b'*]dithiophen-4-one-2-carbaldehyde in excellent yield. The carb aldehyde was brominated with NBS to give 6-bromo-4H-cyclopenta [2,1-*b*:3,4-*b'*]dithiophen-4-one-2-carbaldehyde in high yield.4-tribu



Fig. 2. Synthesis of HIQ1, HIQ2 and HIQ3: (i) POCl<sub>3</sub>, DMF, 1,2-dichloroethane reflux, (ii) NBS, DMF, rt, (iii) Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, reflux, (iv) CNCH<sub>2</sub>COOH, piperidine, CHCl<sub>3</sub>, reflux.

tylstannyl-N,N-bis(4-methylphenyl)aniline, 4-[5-(tributylstannyl)thio phene-2-yl]-N,N-bis(4-methylphenyl)aniline, and 4-[5-tributylstann yl-3,4-ethylenedioxythiophene-2-yl]-N,N-bis(4-methylphenyl)aniline were allowed to react separately with 6-bromo-4H-cyclopenta[2,1b:3,4-b']dithiophen-4-one-2-carbaldehyde via a Pd(PPh<sub>3</sub>)<sub>4</sub>-catalyzed Stiller coupling reaction to afford the three dye precursors in moderate yields. Finally, **HIQ1**, **HIQ2** and **HIQ3** were obtained through Knoevenagel condensation between the precursors and cyanoacetic acid. All the compounds, including the three dyes, were characterized by NMR and MS.

#### 3.2. Optical properties

The absorption spectra of all three dyes in DMF solution exhibited strong and broad absorption over the entire visible region extending to the NIR region (Fig. 3). The absorption spectra of **HIQ1**, **HIQ2** and **HIQ3** were characterized by two prominent bands: the band between 280 and 500 nm was attributed to the  $\pi$ - $\pi$ \* transitions of the conjugated aromatic moieties, and the band at longer wavelength (around 600 nm) was attributed to the intramolecular

charge transfer transitions between the donor moiety and the acceptor unit [11]. Because the 4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one moiety possesses substantial guinoidal character within a conjugated backbone, it allows for stable electron delocalization [7]. The absorption peaks at 398 and 597 nm of HIQ1 were slightly red-shifted to 417 nm and 600 nm in HIQ2 and to 430 and 627 nm in HIQ3, owing to the increase in electron-donating ability imparted by the thiophene and ethylenedioxythiophene groups. HIQ3 had moderate molar extinction coefficients ( $\varepsilon$ ) of  $3.6 \times 10^4$  and  $7.3 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> at 430 and 627 nm, respectively. The  $\varepsilon$  values of the three dyes increase in the order HIQ1 < HIQ2 < HIQ3 (Table 1). All these features make HIQ1, HIQ2 and HIQ3 attractive sensitizers for nanocrystalline TiO2 DSCs in a range covering the entire visible region and extending into the NIR region. When adsorbed on a transparent TiO<sub>2</sub> electrode, all three dyes showed broad absorption spectra, and the absorption peaks were slightly red-shifted compared with the corresponding peaks of their solution absorption spectra, owing to interaction of the anchoring group with surface titanium anions (Fig. 4). Moreover, the onset of absorption of HIQ3 occurred at about 900 nm,



Fig. 3. UV-vis-NIR absorption spectra of HIQ1, HIQ2 and HIQ3 in DMF.

making this dye a good candidate as a NIR sensitizer for DSCs. The D-A-A configuration, with its strongly electron-withdrawing additional acceptor, showed a spectrum with a large red-shift relative to the spectra observed with previously reported D- $\pi$ -A configuration dyes [12].

### 3.3. Electrochemical properties

To evaluate the thermodynamics of electron injection from the excited-state of the dye to the conduction band of the TiO<sub>2</sub> electrode and dye regeneration via electron donation from the electrolyte, a cyclic voltammetry was obtained in a typical threeelectrode electrochemical cell with the dye-sensitized TiO<sub>2</sub> films as the working electrodes and 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte (Table 1). The reference electrode was Ag/AgCl calibrated with Fc<sup>+</sup>/Fc as an internal reference. All dyes exhibited a guasi-reversible oxidative wave. The ground-state oxidation potential values,  $S^{+/0}$ , of **HIQ1**, HIQ2 and HIQ3 were measured to be 1.18, 1.10 and 0.99 V (versus NHE), respectively, and these values were low enough for efficient regeneration of the oxidized dyes through reaction with iodide (0.4 V; Fig. 5) [13]. The excited-state oxidation potential values, S<sup>+/\*</sup>, of the three dyes were calculated from the oxidation potential and the optical energy gaps,  $E_{0-0}$ , determined from the 10% maximum absorption intensity of the absorption spectra on transparent TiO<sub>2</sub> films [14]. The calculated S<sup>+/\*</sup> values of **HIQ1**, **HIQ2** and **HIQ3** were -0.66, -0.62 and -0.57 V, respectively, and were a little more negative than the conduction band level of TiO<sub>2</sub> (approximately

Table 1Absorption and electrochemical properties of HIQ1, HIQ2 and HIQ3.

Dye	Absorption <sup>a</sup> [nm] ( $\epsilon$ [10 <sup>3</sup> M <sup>-1</sup> cm <sup>-1</sup> ])	S <sup>+/0 b</sup> [V]	$E_{0-0}^{c} [V]$	S <sup>+/*d</sup> [V]
HIQ1	398 (14.1), 597 (3.2)	1.18	1.83	-0.66
HIQ2	417 (29.8), 600 (6.1)	1.10	1.72	-0.62
HIQ3	430 (35.9), 627 (7.3)	0.99	1.56	-0.57

 $^a$  Absorption peaks and molar extinction coefficients (  $\epsilon)$  were measured in DMF (2  $\times$  10  $^{-5}$  M).

<sup>b</sup> Ground-state oxidation potentials, S<sup>+/0</sup>, were measured on TiO<sub>2</sub> containing 0.1 M (n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub> at a scan rate of 50 mV s<sup>-1</sup> (vs. NHE).

<sup>c</sup> Optical energy gaps,  $E_{0-0}$ , were estimated from the 10% maximum absorption intensity of the absorption spectra on transparent TiO<sub>2</sub>.

<sup>d</sup> Excited-state oxidation potentials, S<sup>+/\*</sup>, were calculated from the expression S<sup>+/\*</sup> = S<sup>+/0</sup> –  $E_{0-0}$ .



Fig. 4. UV-vis-NIR absorption spectra of HIQ1, HIQ2 and HIQ3 on TiO2 nanoparticles.

-0.5 V vs NHE) [15]. These results indicate that electron injection from the excited-state of the dye to the  $\rm TiO_2$  conduction band was possible.

### 3.4. Theoretical calculations

To gain insight into the molecular orbitals and molecular geometries of the dyes, we carried out time-dependent density functional theory calculations (Fig. 6). Molecular-orbital calculations demonstrated that the HOMO of HIQ1 was largely delocalized on the triphenylamino unit. In HIQ2 and HIQ3, the HOMOs were spread over the triphenylamino unit through the thiophene group and the ethylenedioxythiophene group, respectively. These results suggest that delocalization of the HOMO on the donor moiety may facilitate reduction of the oxidized dye by reaction with I<sup>-</sup>, making the dye suitable for highly efficient solar cells. The LUMOs of all three dyes were predominantly located on the cyanoacrylic units and extended to the 4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one moieties, facilitating electron injection from the photoexcited sensitizer to the TiO<sub>2</sub> semiconductor. HOMO-LUMO excitation moves the electron from the donor moiety to the cyanoacrylic acid moiety via the additional acceptor group. Such electron density distributions are beneficial for efficient charge separation and electron injection. Thus, both our electrochemical and theoretical results indicated that introducing a strongly electron-withdrawing



**Fig. 5.** Comparison of the conduction band (CB) of TiO<sub>2</sub>, the  $S^{+/0}$  and  $S^{+/*}$  values of the dyes, and the redox potential of  $I^-/I_3^-$ , as well as the optical energy gaps ( $E_{0-0}$ ).



Fig. 6. Frontier molecular orbital profiles of HIQ1, HIQ2 and HIQ3 at the B3LYP/6-31G<sup>\*</sup> level.

additional acceptor into the D-A-A configuration was a reasonable strategy.

### 3.5. Photovoltaic performance

The photovoltaic performance of DSCs sensitized with **HIQ1**, **HIQ2** and **HIQ3** was studied under standard AM 1.5 irradiation (100 mW cm<sup>-2</sup>). The short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factors (*FF*) and overall solar-to-electric energy conversion efficiencies ( $\eta$ ) for each dye–TiO<sub>2</sub> electrode are summarized in Table 2. IPCEs for the solar cells, plotted as a function of excitation wavelength, were calculated from Eq. (1),

$$IPCE(\lambda) = 1240(I_{sc}/\lambda\phi)$$
(1)

where  $I_{sc}$  is the photocurrent density at short circuit (mA cm<sup>-2</sup>) under monochromatic irradiation,  $\lambda$  is the wavelength of incident radiation (nm) and  $\phi$  is the incident radiative flux (W m<sup>-2</sup>). DSCs based on **HIQ1**, **HIQ2** and **HIQ3** showed moderate response in the visible region and extending into the NIR region (Fig. 7). The IPCE values gradually increased in the order **HIQ1** < **HIQ2** < **HIQ3** at wavelengths >800 nm. The IPCE at 900 nm was 1.9% for **HIQ1**, and the value doubled to 4% for **HIQ2** and reached 9.4% for **HIQ3** (Table 2). These results indicate that we not only achieved NIR absorption but also increased the absorption intensity in the longwavelength region by means of simple tuning of the electrondonating ability of the donor moiety in the D-A-A configuration containing a strongly electron-withdrawing additional acceptor. It is noteworthy that the IPCE response of **HIQ3** extended to 1100 nm,

Table 2	
Current-voltage characteristics of DSCs sensitized	with <b>HIQ1</b> , <b>HIQ2</b> and <b>HIQ3</b> .

Dye	IPCE [%] at 900 nm	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	$V_{\rm oc}$ [V]	FF	η (%)
HIQ1	1.9	7.76	0.34	0.64	1.69
HIQ2	4.0	8.11	0.30	0.56	1.37
HIQ3	9.4	9.21	0.29	0.49	1.31

which is the longest-wavelength response among all NIR dyes reported to date.

The current–voltage characteristics ( $J_{sc}$ ,  $V_{oc}$ , FF, and  $\eta$ ) of the **HIQ1** cell were 7.76 mA cm<sup>-2</sup>, 0.34 V, 0.64 and 1.69%, respectively, under AM 1.5 irradiation at 100 mW cm<sup>-2</sup> (Fig. 8 and Table 2). The  $J_{sc}$  of the DSC based on **HIQ2** (8.11 mA cm<sup>-2</sup>) was slightly higher than that of the DSC based on **HIQ1**, owing to the higher light-harvesting efficiency of **HIQ2** compared to that of **HIQ1**. However, both  $V_{oc}$  and FF of **HIQ2** were lower than those of **HIQ1**, resulting in a lower  $\eta$  (1.37%) for **HIQ1**. Among the three sensitizers, **HIQ3** showed the highest  $J_{sc}$  (9.21 mA cm<sup>-2</sup>), this result agrees well with the proceeding IPCE measurements and absorption spectra. Thus, we were able to increase the photocurrent simply by introducing a more strongly electron-donating donor into the D-A-A configuration based on 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one as the additional acceptor. Although the  $\eta$  and IPCE values were not



Fig. 7. IPCE spectra of DSCs based on HIQ1, HIQ2 and HIQ3.



Fig. 8. J-V curves of DSCs sensitized with HIQ1, HIQ2 and HIQ3.

ideal, owing to the low excited-state oxidation potentials of the three dyes, adopting this type of D-A-A configuration is a simple, feasible approach to the construction of NIR dyes. Further studies on 4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one involving, for example, optimization of the structure, tuning of the energy levels and electron injection efficiency, and optimization of the electrolyte solution and the redox couple are likely to result in more-efficient NIR dyes. Additionally, co-sensitization with other dyes to cover a broad solar spectrum may also be a good option.

### 4. Conclusion

By introducing a strongly electron-withdrawing additional acceptor in a D-A-A configuration, we synthesized novel NIR dye sensitizers, HIO1, HIO2 and HIO3, which have 4H-cyclopenta[2,1b:3,4-b' dithiophen-4-one as the additional acceptor and cyanoacetic acid as an acceptor/anchor group. By systematically tuning the electron-donating ability of the donor moiety simultaneously, we were able to achieve, with HIQ3 on TiO2, a very broad absorption spectrum extending to 900 nm, which was suitable for a NIR DSC. DSCs sensitized with HIQ3 showed an overall conversion efficiency up to 1.31%. It is noteworthy that the IPCE spectrum showed a broad response from the visible region extending into the NIR area up to 1100 nm. These results demonstrate the great potential of compounds containing 4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-one-based D-A-A structures as NIR sensitizers. We are carrying out additional studies to tune the energy levels by molecular engineering of the D-A-A structure with the goal of developing efficient DSCs based on NIR dyes.

### Acknowledgments

This work was supported by NIMS Saint-Gobain Center of Excellence for Advanced Materials, and Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Agency.

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