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Synthesis, optical and electrochemical properties, and photovoltaic performance of a panchromatic and near-infrared $(D)_2$–π–A type BODIPY dye with pyridyl group or cyanoacrylic acid†

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$(D)_2$–π–A type boron dipyrromethene (BODIPY) dyes **OMK-PY** and **OMK-CA** bearing a pyridyl group or cyanoacrylic acid group, respectively, at the end of 8-positions on the BODIPY core, as an electron-withdrawing anchoring group to adsorb onto the TiO_2 electrode and two diphenylamine–thienylcarbazole moieties as an electron-donating unit at the 3- and 5-positions on the BODIPY core, were designed and developed as a photosensitizer for dye-sensitized solar cells (DSSCs). It was found that the two BODIPY dyes adsorbed on a TiO_2 film show a strong and broad absorption band in the range of 600 to 850 nm, and the onset of the absorption band reached 900 nm, that is, **OMK-PY** and **OMK-CA** possess the near-infrared (NIR) adsorption ability as well as the panchromatic adsorption ability, and good adsorption ability onto the TiO_2 electrode. Moreover, cyclic voltammetry demonstrated that the two BODIPY dyes show two reversible oxidation waves, thus indicating that the redox processes of **OMK-PY** and **OMK-CA** are very stable. On the basis of the experimental results and density functional theory calculation, we propose that the $(D)_2$–π–A BODIPY structure with two diphenylamine–thienylcarbazole moieties as strong electron-donating units at the 3- and 5-positions on the BODIPY core is an effective strategy to lead a high light-harvesting efficiency (LHE) in the range of visible light to NIR light, although the DSSCs based on $(D)_2$–π–A type BODIPY dyes that have been developed in this current stage showed low photovoltaic performances.

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Introduction

Dye-sensitized solar cells (DSSCs) employing dye-adsorbed TiO_2 electrodes have made a hopeful impact on chemists, physicists, and engineers as one of the most promising new renewable photovoltaic cells in the last quarter of a century,[1–8] since Grätzel and co-workers reported high-performance DSSCs employing a Ru-complex dye-adsorbed TiO_2 electrode in 1991.[9] In particular, much effort has been made on the development of various types of D–π–A organic dye sensitizers which are constructed of a diphenyl- or dialkylamino group as the electron donor (D) and a carboxyl group,[10–16] 2-(1,1-dicyanomethylene) rhodanine,[17] pyridine,[18–21] or 8-hydroxylquinoline[22] as the electron acceptor (A) and anchor linked by π-conjugated bridges, and there has been a gradual accumulation of information about the relationship between the chemical structures and the photovoltaic performances of DSSCs. As a result, DSSCs have achieved a solar energy-to-electricity conversion yield (η) of up to 13%.[11c,d] However, one of the challenges to further improve the photovoltaic performances of DSSCs lies in the enhancement of light-harvesting efficiency (LHE) in the near-infrared (NIR) region (780–1000 nm) as well as visible region of the solar spectrum. Some boron dipyrromethene (BODIPY) dyes which are electrochemically modified through the introduction of electron-donating and electron-accepting groups onto the BODIPY core, possess panchromatic absorption ability because of their high photoabsorption coefficient in the visible region of the solar spectrum.[23–25] Actually, Akkaya *et al.* have designed and developed a series of D–A-substituted BODIPY dye sensitizers, which have two triphenylamines as electron donors at the 3- and 5-positions and benzoic acid as electron acceptor at the 8-position. The D–A-substituted BODIPY dyes showed a strong and broad absorption band in the range of 650 to 850 nm with the absorption maxima at around 720–760 nm (molar extinction coefficient (ε) = 60 000–70 000 M^{-1} cm^{-1}).[23d] However, almost all BODIPY photosensitizers reported so far show the photoabsorption band in wavelength region shorter than 700 nm.

Thus, in this work, to explore effective BODIPY dye sensitizers possessing a high LHE in the range of visible light to NIR light, we have designed and developed $(D)_2$–π–A type BODIPY dyes **OMK-PY** and **OMK-CA** bearing pyridyl group and

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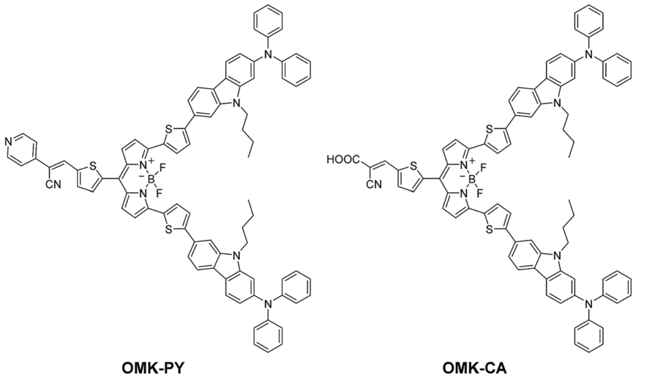


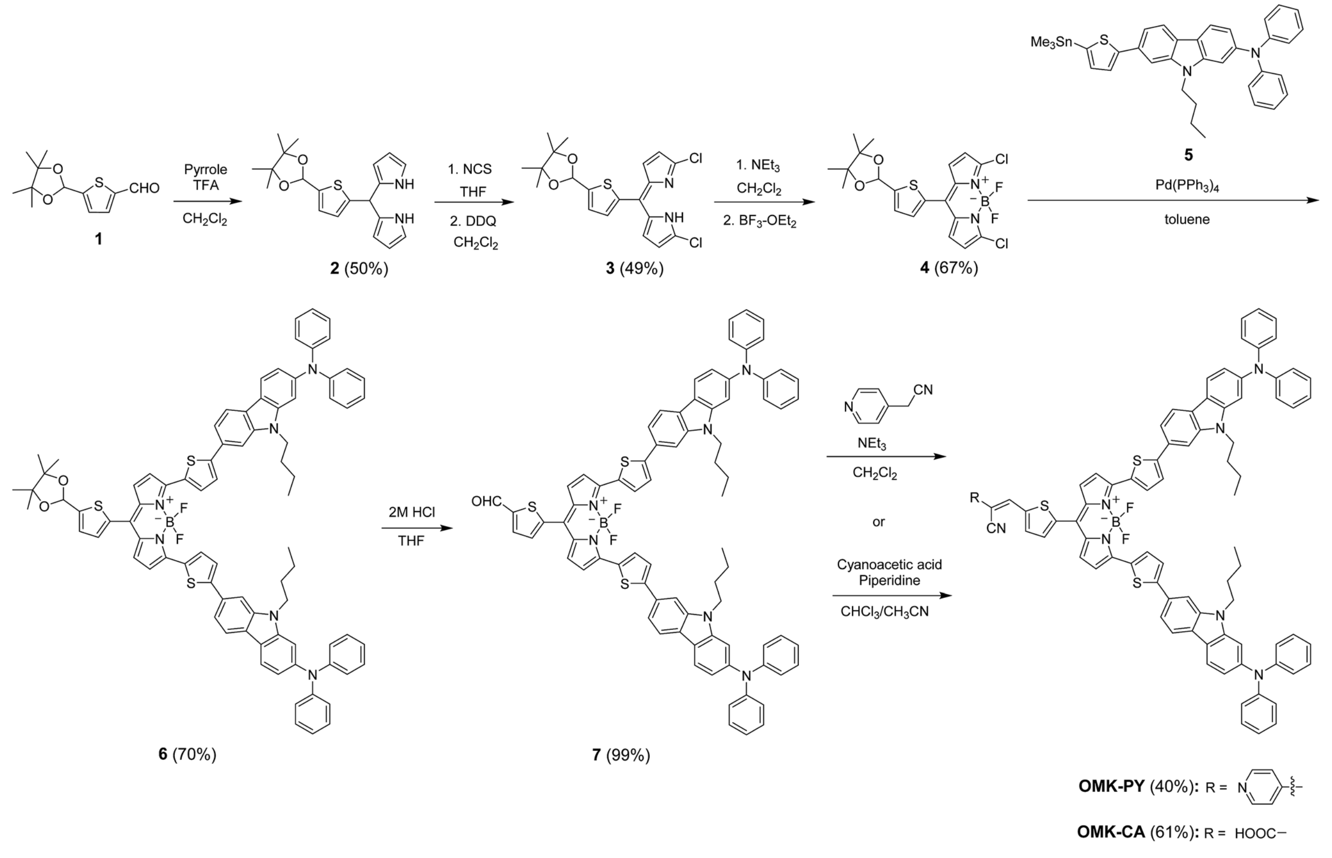
Fig. 1 Chemical structures of $(D)_2$–π–A type BODIPY dyes **OMK-PY** and **OMK-CA**.

cyanoacrylic acid group, respectively, at the end of 8-positions on the BODIPY core, as an electron-withdrawing anchoring group to adsorb onto the TiO_2 electrode and two diphenylamine–thienylcarbazole moieties as an electron-donating unit at the 3- and 5-positions on the BODIPY core (Fig. 1). Here we reveal the photophysical and electrochemical properties of the $(D)_2$–π–A BODIPY dye sensitizers and their photovoltaic performances in DSSCs, based on photoabsorption (dye solution and dye-adsorbed TiO_2 film) and electrochemical measurements (cyclic voltammetry), density functional theory (DFT) calculation, FT-IR spectroscopy of the dye-adsorbed TiO_2 film, photocurrent–voltage (*I*–*V*) curves, and incident photon-to-current conversion efficiency (IPCE) spectra. We demonstrate that the $(D)_2$–π–A type BODIPY dyes possess the NIR adsorption ability as well as the panchromatic adsorption ability.

Results and discussion

Synthesis

$(D)_2$–π–A BODIPY dye sensitizers **OMK-PY** and **OMK-CA** studied in this work were synthesized according to a stepwise synthetic protocol (Scheme 1). Indeed, the $(D)_2$–π–A BODIPY dyes were successfully prepared by using Stille coupling to introduce the electron-donating unit (two diphenylamine–thienylcarbazole moieties), and then by using Knoevenagel condensation to introduce the electron-withdrawing anchoring group (pyridyl group or cyanoacrylic acid group). Dipyrromethane **2** was prepared by condensation of compound **1** (ref. 26) with pyrrole with TFA added as a catalyst. The dichlorinated compound **3** was prepared by chlorination of **2** with *N*-chlorosuccinimide (NCS) followed by oxidation with DDQ. Compound **3** was reacted with NEt_3 and treated with BF_3–OEt_2 to afford the BODIPY **4**. Compound **6** was prepared by Stille coupling of **4** with stannanyl compound **5** (ref. 18*g*). Compound **6** is hydrolyzed by treatment with acid to generate the aldehyde **7**. BODIPY dye **OMK-PY** was prepared by reacting 4-pyridylacetonitrile hydrochloride with the compound **7** in the presence of NEt_3.[27] BODIPY dye **OMK-CA**



Scheme 1 Synthesis of **OMK-PY** and **OMK-CA**.

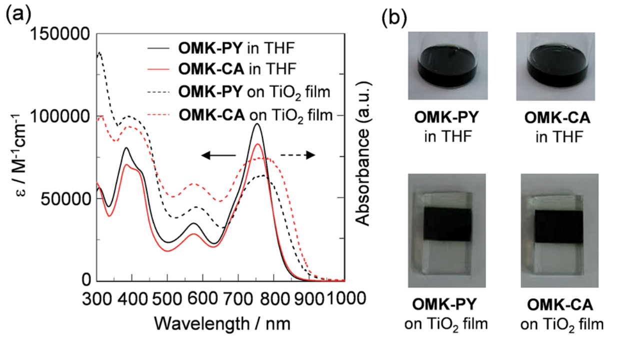


Fig. 2 (a) Photoabsorption spectra of OMK-PY and OMK-CA in THF and adsorbed on TiO_2 film. (b) Photographs of the dyes in THF and adsorbed on TiO_2 film.

was prepared by typical Knoevenagel condensation of the compound 7 with cyanoacetic acid in the presence of piperidine.

Photophysical properties

The photoabsorption spectra of **OMK-PY** and **OMK-CA** in THF and adsorbed on the TiO_2 film are shown in Fig. 2a and their optical data are summarized in Table 1. The two dyes in THF show a strong and broad absorption band in the range of 600 to 800 nm, which is assigned to the intramolecular charge-transfer (ICT) excitation from the electron donor moiety (two diphenylamine–thienylcarbazole moieties) through the BODIPY core to the electron acceptor moiety (2-(pyridin-4-yl)acrylonitrile moiety for **OMK-PY** and cyanoacetic acid group for **OMK-CA**, respectively). For **OMK-PY** the molar extinction coefficient (ε) at the absorption peak wavelength ($\lambda_{abs} = 753$ nm) is 95 400 M^{-1} cm^{-1}, which is higher than that of **OMK-CA** ($\varepsilon = 83\ 100$ M^{-1} cm^{-1} at $\lambda_{abs} = 754$ nm). Moreover, for the two dyes a strong absorption peak at around 400 nm with the ε value of *ca.* 70 000–80 000 M^{-1} cm^{-1}, which can be assigned to the ICT band due to the diphenylamine–thienylcarbazole moiety, was also observed. Interestingly, for the absorption spectra of **OMK-PY** and **OMK-CA** adsorbed on TiO_2 film the longest wavelength absorption band in the range of 600 to 850 nm is significantly broadened, and the onset of the absorption band reached 900 nm, compared with that in THF. As shown in Fig. 2b, the colors of the two dyes in THF are blackish green and the color of dye-adsorbed TiO_2 film is almost black. Thus, this result indicates that the $(D)_2$–π–A type BODIPY dyes possess a good LHE in the range of visible light to NIR light and good adsorption ability onto TiO_2 electrode, that is, **OMK-PY** and **OMK-CA** possess the NIR adsorption ability as well as the panchromatic adsorption ability.

Electrochemical properties

The electrochemical properties of **OMK-PY** and **OMK-CA** were determined by cyclic voltammetry (CV) in DMF containing 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) (Fig. 3). The potentials were referenced to ferrocene/ferrocenium (Fc/Fc^+) as the internal reference. Two oxidation waves were observed at 0.34 V and 0.48 V for **OMK-PY** and 0.33 V and 0.48 V for **OMK-CA**, corresponding to the oxidations of the BODIPY core and the diphenylamino group, respectively. The corresponding reduction wave to the first oxidation wave appeared at 0.22 V for **OMK-PY** and 0.25 V for **OMK-CA**, respectively, whereas for the two dyes the corresponding reduction wave (*ca.* 0.42 V) to the second oxidation wave was not clearly observed. These results show that for the two dyes the first redox process is electrochemically reversible, but the second redox process is electrochemically irreversible. The HOMO energy levels of the two dyes were evaluated from the half-wave potential for oxidation ($E^{ox}_{1/2} = 0.28$ V for **OMK-PY** and 0.29 V for **OMK-CA**, respectively, Table 1). The HOMO energy level was 1.00 V for **OMK-PY** and 1.01 V for **OMK-CA**, respectively, *versus* the normal hydrogen electrode (NHE). Thus, the two dyes have comparable HOMO energy levels. This result shows that the HOMO energy levels of the two dyes are more positive than the I_3^-/I^- redox potential (0.4 V), and thus this ensures an efficient regeneration of the oxidized dyes by electron transfer from the I_3^-/I^- redox couple in the electrolyte. The LUMO energy level was estimated from the $E^{ox}_{1/2}$ and the onset of photoabsorption spectra (860 nm; 1.44 eV for both **OMK-PY** and **OMK-CA**) in THF. The LUMO energy level was −0.44 V for **OMK-PY** and −0.43 V for **OMK-CA**, respectively, and thus the two dyes have comparable LUMO energy levels. However, the LUMO energy levels of the two dyes are lower than the energy level (E_{cb}) of the conduction band (CB) of TiO_2 electrode (−0.5 V). This suggests that the electron injection from the photoexcited dye to the CB of TiO_2 electrode is thermodynamically difficult.

Theoretical calculations

To examine the electronic structures of **OMK-PY** and **OMK-CA**, the molecular orbitals of the two dyes were calculated using density functional theory (DFT) at the B3LYP/6-31G(d,p) level.[28] As shown in Fig. 4, for the two dyes the HOMO and HOMO−1 are mostly localized on the BODIPY core containing the two diphenylamine–thienylcarbazole moieties and the two diphenylamine–carbazole moieties, respectively. The LUMO is mostly localized on the

Table 1 Optical and electrochemical data, HOMO and LUMO energy levels, and DSSC performance parameters of OMK-PY and OMK-CA

Dye	λ^{abs}_{max}/nm (ε^a/M^{-1} cm^{-1})	$E^{ox}_{1/2}$ ^{b}/V	HOMO^c/V	LUMO^c/V	Molecules^d/cm^{-2}	J_{sc} ^{e}/mA cm^{-2}	V_{oc} ^{e}/mV	ff^e	η^e (%)
OMK-PY	385 (80 800), 574 (35 000), 753 (95 400)	0.28	1.00	−0.44	6.9×10^{16}	1.08	335	0.53	0.19
OMK-CA	385 (70 600), 574 (28 500), 754 (83 100)	0.29	1.01	−0.43	1.0×10^{17}	0.68	319	0.51	0.11

[a] In THF. [b] Half-wave potentials *versus* Fc/Fc^+ of oxidation ($E^{ox}_{1/2}$) for **OMK-PY** and **OMK-CA** were recorded in DMF/Bu_4NClO_4 (0.1 M) solution. [c] *Versus* normal hydrogen electrode (NHE). [d] Adsorption amount of dye molecules per unit area of the TiO_2 electrode, when the 9 μm thick TiO_2 electrode was immersed into 0.1 mM dye solution in THF. [e] Under a simulated solar light (AM 1.5, 100 mW cm^{-2}).

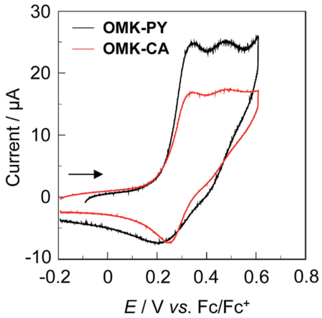


Fig. 3 Cyclic voltammograms of **OMK-PY** and **OMK-CA** in DMF containing 0.1 M Bu_4NClO_4. The arrow denotes the direction of the potential scan.

BODIPY core containing thiophene-2-(pyridin-4-yl)acrylonitrile moiety for **OMK-PY** and thiophene–cyanoacetic acid group for **OMK-CA**, respectively, and the LUMO+1 is mostly localized on thiophene-2-(pyridin-4-yl)acrylonitrile moiety for **OMK-PY** and thiophene–cyanoacetic acid group for **OMK-CA**, respectively. Accordingly, the DFT calculations reveal that for both **OMK-PY** and **OMK-CA** the dye excitations upon light irradiation induce a strong ICT from the electron donor moiety (two diphenylamine–carbazole moieties) through the BODIPY core to the electron acceptor moiety (2-(pyridin-4-yl)acrylonitrile moiety for **OMK-PY** and cyanoacetic acid group for **OMK-CA**, respectively).

FT-IR spectra

To elucidate the adsorption states of **OMK-PY** and **OMK-CA** on TiO_2 nanoparticles, we measured the FTIR spectra of the dye powders and the dyes adsorbed on TiO_2 film (Fig. 5). For the dye powder of **OMK-PY** the C═N stretching band of the pyridyl group was observed at around 1590 cm^{-1}. When **OMK-PY** was adsorbed on the TiO_2 film, the C═N stretching band was slightly shifted by 1 cm^{-1}, to higher wavenumber compared with the dye powders, that is, the band can be assigned to the hydrogen-bonded pyridyl group to Brønsted acid sites on the TiO_2 surface.[18] For the dye powder of **OMK-CA**, the C═O stretching band of the carboxyl group was observed at around 1690 cm^{-1}. On the other hand, in the FTIR spectrum of **OMK-CA** adsorbed onto TiO_2 film showed that the C═O stretching bands of the carboxyl group disappeared completely; this indicates the formation of a bidentate bridging linkage between the carboxyl group of the dye and the Brønsted acid site on the TiO_2 surface. Consequently, this result demonstrates that **OMK-PY** and **OMK-CA** was adsorbed on the TiO_2 film through the hydrogen bond and bidentate bridging linkage, respectively, at the Brønsted-acidic sites on the TiO_2 surface.

Photovoltaic performances

The DSSCs based on **OMK-PY** and **OMK-CA** were fabricated by using the dye-adsorbed TiO_2 electrode (9 μm), 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 the electrolyte. The *I–V* characteristics were measured under simulated solar light (AM 1.5, 100 mW cm^{-2}). The IPCE spectra and the *I–V* curves are shown in Fig. 6. The photovoltaic performance parameters (a short circuit photocurrent density (J_{sc}), an open-circuit photovoltage (V_{oc}), a fill factor (ff) and a solar energy-to-electricity conversion yield (η)) are collected in Table 1. The adsorption amount (1.0×10^{17} molecules per cm^2) of **OMK-CA** adsorbed on TiO_2 electrode is larger than that of **OMK-PY** (6.9×10^{16} molecules per cm^2). The high adsorption ability of **OMK-CA** relative

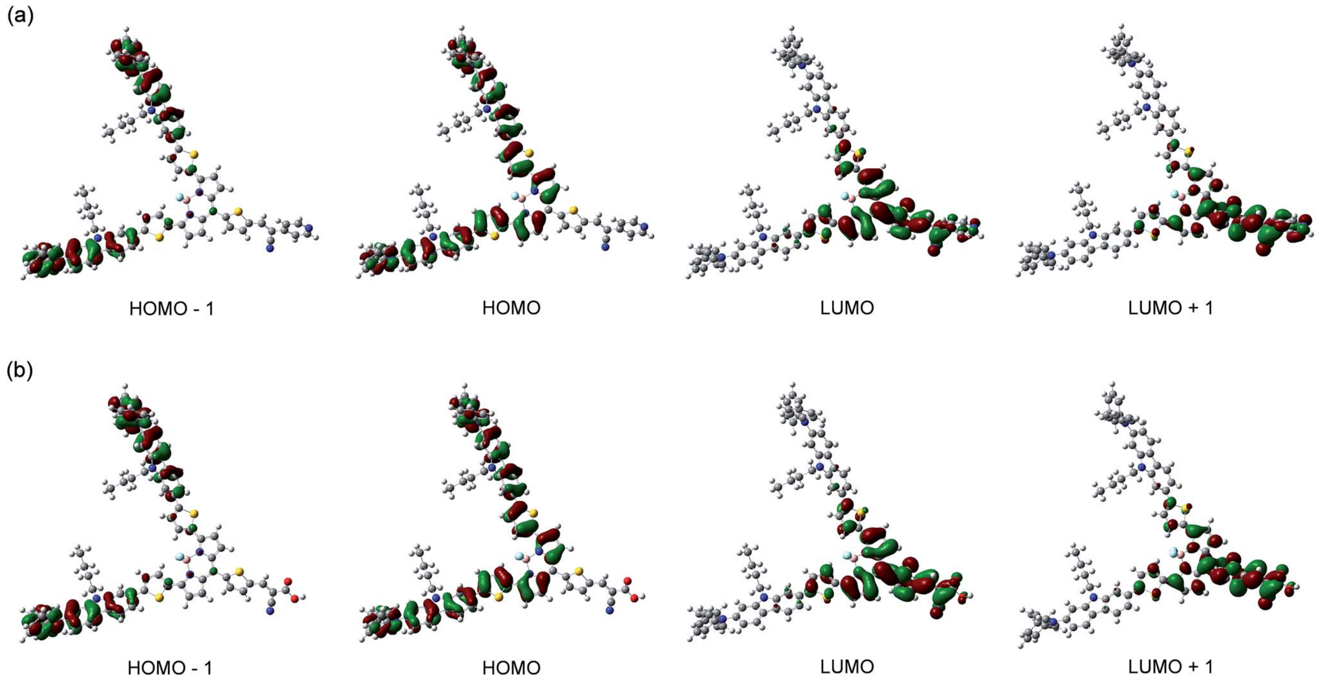


Fig. 4 HOMO−1, HOMO, LUMO and LUMO+1 of (a) **OMK-PY** and (b) **OMK-CA** derived from the DFT calculations at B3LYP/6-31G(d,p) level.

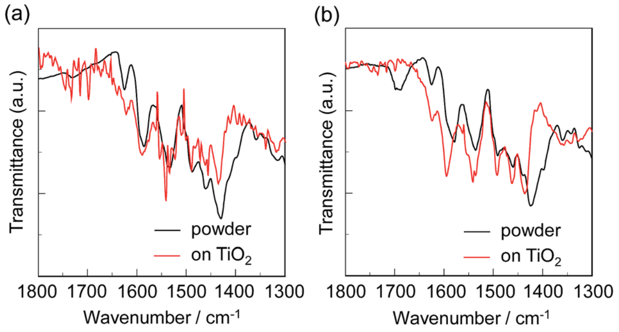


Fig. 5 FTIR spectra of the dye powder and the dye-adsorbed TiO_2 film. (a) OMK-PY and (b) OMK-CA.

to **OMK-PY** is attributed to the formation of the bidentate bridging linkage between the carboxyl group of **OMK-CA** and the Brønsted acid sites on the TiO_2 surface. The IPCE spectra showed that the maximum IPCE values of **OMK-PY** and **OMK-CA** are 13% and 9%, respectively. It is worth mentioning here that for the two dyes the IPCE value in the range of 600 to 800 nm is notably much lower than that at around 400 nm, that is, the ICT band from the electron donor moiety through the BODIPY core to the electron acceptor moiety make little contribution to the IPCE spectra. The *I–V* curves show that the J_{sc} and η values are 1.08 mA cm^{-2} and 0.19% for **OMK-PY** and 0.68 mA cm^{-2} and 0.11% for **OMK-CA**, respectively. Accordingly, the relatively low photovoltaic performances of **OMK-PY** and **OMK-CA** are due to the low LUMO level which makes it thermodynamically difficult for the photoexcited dye to inject the electron into the CB of TiO_2 electrode. In addition, the V_{oc} value of BODIPY dye sensitizers is generally lower than that of the conventional organic dye sensitizers.[23] It is assumed that the low V_{oc} value (*ca.* 330 mV) for **OMK-PY** and **OMK-CA** is attributed to faster charge recombination between the injected electrons in the CB of TiO_2 electrode and I_3^- ions in the electrolyte, arising from the approach of I_3^- ions to the TiO_2 surface due to the electrostatic interactions between the BODIPY core and I_3^- ions. Consequently, the low photovoltaic performances of DSSCs based on **OMK-PY** and **OMK-CA** are attributed to the low electron-injection efficiency due to the low LUMO level and the faster charge recombination due to the BODIPY core, leading to the low J_{sc} and V_{oc} values, respectively.

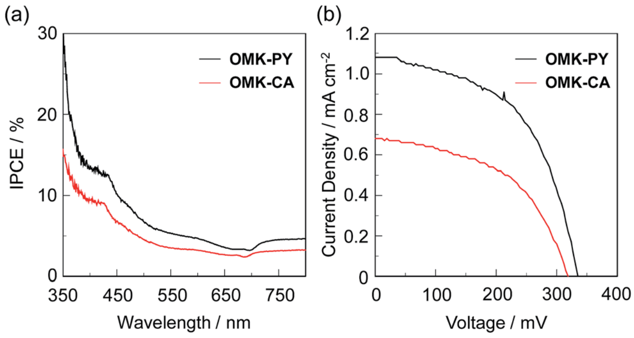


Fig. 6 (a) IPCE spectra and (b) *I–V* curves of DSSCs based on OMK-PY and OMK-CA.

Conclusions

To explore effective BODIPY dye sensitizers possessing a high LHE in the range of visible light to NIR light, we have designed and developed $(D)_2$–π–A type BODIPY dyes **OMK-PY** and **OMK-CA** bearing pyridyl group and cyanoacrylic acid group, respectively, at the end of 8-positions on the BODIPY core, as an electron-withdrawing anchoring group to adsorb onto the TiO_2 electrode and two diphenylamine–thienylcarbazole moieties as an electron-donating unit at the 3- and 5-positions on the BODIPY core. It was found that for the absorption spectra of **OMK-PY** and **OMK-CA** adsorbed on TiO_2 film the two dyes show a strong and broad absorption band in the range of 600 to 850 nm, and the onset of the absorption band reached 900 nm, that is, **OMK-PY** and **OMK-CA** possess the NIR adsorption ability as well as the panchromatic adsorption ability. Consequently, we demonstrate that $(D)_2$–π–A BODIPY structure having two diphenylamine–thienylcarbazole moieties as strong electron-donating units at the 3- and 5-positions on the BODIPY core is an effective strategy to lead a high LHE in the range of visible light to NIR light, although the DSSCs based on $(D)_2$–π–A type BODIPY dyes that have been developed in this current stage showed low photovoltaic performances due to the low LUMO level.

Experimental

General

Melting points were measured with a Yanaco micro melting point apparatus MP model. IR spectra were recorded on a SHIMADZU IRAffinity-1 spectrometer by ATR method. High-resolution mass spectral data were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian-400 (400 MHz) or a Varian-500 (500 MHz) FT NMR spectrometer. Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer. Cyclic voltammetry (CV) curves were recorded in DMF/Bu_4NClO_4 (0.1 M) solution with a three-electrode system consisting of Ag/Ag^+ as reference electrode, Pt plate as working electrode, and Pt wire as counter electrode by using a AMETEK Versa STAT 4 potentiostat. The potentials were referenced to ferrocene/ferrocenium (Fc/Fc^+) as the internal reference. The HOMO and LUMO energy levels of **OMK-PY** and **OMK-CA** were evaluated from the spectral analyses and the CV data. Thus, the HOMO energy level was evaluated from the $E^{ox}_{1/2}$. The LUMO energy level was estimated from the $E^{ox}_{1/2}$ and the onset of photoabsorption spectra (860 nm; 1.44 eV for both **OMK-PY** and **OMK-CA**) in THF, that is, the LUMO energy level was obtained through eq. $-[E_{0-0} - \mathrm{HOMO}]$, where E_{0-0} transition energy is the onset of photoabsorption spectra corresponding to the energy gap between HOMO and LUMO.

Synthesis

2,2′-((5-(4,4,5,5-Tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl)methylene)bis(1*H*-pyrrole) (2). To a dichloromethane solution (40 ml) of **1** (ref. 26) (0.1 g, 0.42 mmol) and pyrrole (0.06 ml, 0.88 mmol) under an argon atmosphere was added trifluoroacetic acid (0.0005 ml) and stirred for 2 h at room temperature. The reaction mixture was diluted with water, and then the solution was extracted with dichloromethane. The dichloromethane extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane–ethyl acetate = 9 : 1 as eluent) to give **2** (0.07 g, yield 50%) as a yellow viscous solid; IR (ATR): $\tilde{\nu} = 3358$, 2976, 1670, 1553 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 1.29$ (d, 12H), 5.71 (s, 1H), 6.04 (br, 2H), 6.12 (s, 1H), 6.14–6.16 (m, 2H), 6.69–6.70 (m, 2H), 6.74 (d, $J = 3.6$ Hz, 1H), 7.00 (d, $J = 3.6$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 22.22$, 24.54, 39.54, 83.17, 96.86, 107.22, 108.59, 117.54, 125.30, 126.43, 131.74, 142.59, 146.80 ppm; HRMS (ESI): m/z (%): [M + H^+] calcd for $C_{20}H_{25}N_2O_2S$, 357.16313; found 357.16336.

(*E*)-2-Chloro-5-((5-chloro-2*H*-pyrrol-2-ylidene)(5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl)methyl)-1*H*-pyrrole (3). To compound **2** (2.68 g, 7.52 mmol) under an argon atmosphere was added THF (40 ml) and then stirred at −75 °C. Next, a solution of *N*-chlorosuccinimide (2.01 g, 15.1 mmol) in THF (30 ml) was added dropwise and the solution was stirred at −75 °C for 1 h and then at room temperature for 2 h. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. To the dichloromethane extract (150 ml) was added DDQ (1.71 g, 7.52 mmol) and the solution was stirred at room temperature for 2 h. After concentrating under reduced pressure, the residue was chromatographed on silica gel (dichloromethane as eluent) to give **3** (1.54 g, yield 49%) as a reddish brown solid; mp 89–91 °C; IR (ATR): $\tilde{\nu} = 2967$, 1560, 1420 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) $\delta = 1.33$ (d, 12H), 6.21 (s, 1H), 6.29 (d, $J = 4.3$ Hz, 2H), 6.90 (d, $J =$ 4.3 Hz, 2H), 7.19 (br, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) $\delta =$ 22.20, 24.40, 83.57, 96.58, 117.18, 126.28, 130.33, 131.53, 132.40, 136.98, 138.44, 142.12, 147.64 ppm; HRMS (ESI): m/z (%): [M + H^+] calcd for $C_{20}H_{21}N_2O_2Cl_2S$, 423.06953; found 423.06921.

3,7-Dichloro-5,5-difluoro-10-(5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinine (4). To a compound **3** (1.5 g, 3.55 mmol) under an argon atmosphere was added dichloromethane (100 ml) and triethylamine (4.72 ml, 35.5 mmol) and stirred for 30 min at room temperature. Next, BF_3–OEt_2 (6.25 ml, 53.3 mmol) was added dropwise and the solution was stirred at room temperature for 12 h. The reaction mixture was washed with water and extracted with dichloromethane. The dichloromethane extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane–hexane = 1 : 2 as eluent) to give **4** (1.11 g, yield 67%) as a dark red solid; mp 185–187 °C; IR (ATR): $\tilde{\nu} = 2982$, 1545, 1381 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) $\delta = 1.31$ (s, 12H), 6.26 (s, 1H), 6.71 (d, $J =$ 4.4 Hz, 2H), 7.42 (d, $J = 3.8$ Hz, 1H), 7.43 (d, $J = 4.4$ Hz, 2H), 7.65 (d, $J = 3.8$ Hz, 1H) ppm; ^{13}C NMR (125 MHz, acetone-d_6) $\delta =$ 22.34, 24.51, 84.17, 96.90, 119.96, 128.16, 133.17, 133.34, 133.95, 134.73, 144.76, 152.63, 153.81 ppm; HRMS (ESI): m/z (%): [M + Na^+] calcd for $C_{20}H_{19}N_2O_2BF_2Cl_2SNa$, 493.04976; found 493.04974.

7,7′-((5,5-Difluoro-10-(5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl)-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinine-3,7-diyl)bis(thiophene-5,2-diyl))bis(9-butyl-*N*,*N*-diphenyl-9*H*-carbazol-2-amine) (6). A solution of **4** (1.0 g, 2.13 mmol), **5** (ref. 18*g*) (2.71 g, 4.25 mmol), and $Pd(PPh_3)_4$ (2.94 g, 2.54 mmol) in toluene (270 ml) was stirred for 12 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 dichloromethane extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was chromatographed on silica gel (chloroform–hexane = 1 : 2 as eluent) to give **6** (1.99 g, yield 70%) as a blackish green solid; mp 176–177 °C; IR (ATR): $\tilde{\nu} = 2955$, 1591, 1431 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6) $\delta = 0.88$ (t, $J =$ 7.4 Hz, 6H), 1.32–1.34 (m, 16H), 1.77–1.84 (m, 4H), 4.37 (t, $J =$ 7.0 Hz, 4H), 6.29 (s, 1H), 6.94 (dd, $J = 1.8$ and 8.4 Hz, 2H), 7.04–7.08 (m, 4H), 7.13–7.14 (m, 10H), 7.23 (d, $J = 1.8$ Hz, 2H), 7.30–7.34 (m, 10H), 7.40 (d, $J = 3.8$ Hz, 1H), 7.55 (d, $J = 3.7$ Hz, 1H), 7.64 (dd, $J = 1.5$ and 8.1 Hz, 2H), 7.76 (d, $J = 4.1$ Hz, 2H), 7.95 (d, $J =$ 1.2 Hz, 2H), 8.06 (d, $J = 8.4$ Hz, 2H), 8.15 (d, $J = 8.0$ Hz, 2H), 8.31 (d, $J = 4.1$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, acetone-d_6) $\delta =$ 14.18, 21.02, 22.38, 24.60, 31.84, 43.07, 84.02, 97.12, 105.79, 106.95, 117.90, 118.44, 119.25, 121.22, 121.60, 122.04, 123.65, 124.26, 124.88, 126.15, 126.47, 127.67, 130.18, 130.79, 131.21, 132.77, 133.72, 133.91, 135.69, 137.40, 142.26, 143.43, 147.74, 149.12, 150.10, 150.32, 150.98 ppm; HRMS (ESI): m/z (%): [M + Na^+] calcd for $C_{84}H_{73}N_6O_2BF_2S_3Na$, 1365.49105; found 1365.49304.

5-(3,7-Bis(5-(9-butyl-7-(diphenylamino)-9*H*-carbazol-2-yl)thiophen-2-yl)-5,5-difluoro-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-10yl)thiophene-2-carbaldehyde (7). To a solution of **6** (1.85 g, 1.38 mmol) in THF (20 ml) was added 2 N HCl (13.8 ml) and refluxed for 12 h. The reaction mixture was washed with water and extracted with dichloromethane. The dichloromethane extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane–hexane = 1 : 1 as eluent) to give **7** (1.71 g, yield 99%) as a dark green solid; mp 171–172 °C; IR (ATR): $\tilde{\nu} =$ 2953, 1665, 1585 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) $\delta = 0.88$ (t, $J = 7.4$ Hz, 6H), 1.29–1.36 (m, 4H), 1.78–1.83 (m, 4H), 4.37 (t, J = 6.9 Hz, 4H), 6.94 (dd, $J = 1.9$ and 8.4 Hz, 2H), 7.05–7.07 (m, 4H), 7.13–7.15 (m, 8H), 7.17 (d, $J = 4.8$ Hz, 2H), 7.23 (d, $J =$ 1.8 Hz, 2H), 7.28–7.33 (m, 10H), 7.65 (dd, $J = 1.5$ and 8.1 Hz, 2H), 7.78 (d, $J = 4.0$ Hz, 2H), 7.81 (d, $J = 3.5$ Hz, 1H), 7.96 (d, $J =$ 1.0 Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 8.15 (d, $J = 8.1$ Hz, 2H), 8.18 (d, $J = 3.5$ Hz, 1H), 8.35 (d, $J = 3.8$ Hz, 2H), 10.12 (s, –CHO) ppm; ^{13}C NMR (125 MHz, acetone-d_6) $\delta = 14.18$, 21.02, 31.85, 43.08, 105.77, 107.01, 117.91, 118.46, 119.21, 121.24, 122.07, 123.67, 124.37, 124.89, 126.29, 130.18, 130.56, 131.11, 133.53, 133.82, 137.44, 137.61, 142.25, 143.46, 143.57, 147.81, 149.10, 150.99, 151.65, 184.42 ppm (four aromatic carbon signals were not observed owing to overlapping resonances); HRMS (ESI): m/z (%): [M + H^+] calcd for $C_{76}H_{62}N_6OBF_2S_3$, 1243.42029; found 1243.42139.

3-(5-(3,7-Bis(5-(9-butyl-7-(diphenylamino)-9*H*-carbazol-2-yl)thiophen-2-yl)-5,5-difluoro-5*H*-4dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-10-yl)thiophen-2-yl)-2-(pyridin-4-yl)acrylonitrile (OMK-PY). To a solution of 4-pyridylacetonitrile hydrochloride (0.05 g, 0.322 mmol) in dichloromethane (3 ml) was added triethylamine (0.21 ml, 1.61 mmol) and stirred for

20 min at 0 °C. Next, **7** (0.4 g, 0.322 mmol) was added and the solution was stirred at room temperature for 5 days. The reaction mixture was washed with water and extracted with dichloromethane. The dichloromethane extract was dried over $MgSO_4$, filtrated, and concentrated. The residue was chromatographed on silica gel (dichloromethane and then ethyl acetate as eluent) to give **OMK-PY** (0.171 g, yield 40%) as a dark green solid; mp 169–170 °C; IR (ATR): $\tilde{\nu} = 2924, 1585, 1429\ \mathrm{cm}^{-1}$; ^{1}H NMR (500 MHz, acetone-d$_6$) $\delta = 0.88$ (t, $J = 7.4$ Hz, 6H), 1.30–1.35 (m, 4H), 1.79–1.82 (m, 4H), 4.37 (t, $J = 6.6$ Hz, 4H), 6.94 (d, $J = 8.3$ Hz, 2H), 7.04–7.07 (m, 4H), 7.13–7.14 (m, 8H), 7.18 (br, 2H), 7.23 (s, 2H), 7.30–7.33 (m, 10H), 7.64 (d, $J = 8.9$ Hz, 2H), 7.75–7.78 (m, 5H), 7.96 (s, 2H), 8.05–8.07 (m, 3H), 8.15 (d, $J = 8.9$ Hz, 2H), 8.34 (br, 2H), 8.58 (s, 1H), 8.73 (d, $J = 5.9$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, acetone-d$_6$) $\delta = 14.18$, 21.02, 31.85, 43.09, 105.78, 107.01, 117.49, 117.74, 117.92, 118.46, 119.22, 120.53, 121.25, 122.07, 123.67, 124.36, 124.89, 125.99, 126.28, 129.64, 130.18, 130.51, 131.15, 133.63, 133.77, 134.27, 137.93, 142.26, 143.46, 147.80, 149.11, 151.65 ppm (seven aromatic carbon signals were not observed owing to overlapping resonances); HRMS (ESI): *m*/*z* (%): $[M + H^+]$ calcd for $C_{85}H_{66}N_8BF_2S_3$, 1343.46282; found 1343.46300.

3-(5-(3,7-Bis(5-(9-butyl-7-(diphenylamino)-9*H*-carbazol-2-yl)thiophen-2-yl)-5,5-difluoro-5*H*-dipyrrolo[1,2-*c*:2′,1′-*f*][1,3,2]diazaborinin-10-yl)thiophen-2-yl)-2-cyanoacrylic acid (OMK-CA). A solution of **7** (0.4 g, 0.322 mmol), cyanoacetic acid (0.11 g, 0.644 mmol) and piperidine (0.032 ml, 0.322 mmol) in chloroform/acetonitrile (1 : 1, 65 ml) was refluxed for 22 h. After concentrating under reduced pressure, the resulting residue was chromatographed on silica gel (ethyl acetate and then ethyl acetate containing 5% acetic acid as eluent) to give the mixture **OMK-CA** and unreacted cyanoacetic acid. The mixture was dissolved in dichloromethane and washed with water. The dichloromethane extract was dried over $MgSO_4$, filtrated, and concentrated to give **OMK-CA** (0.256 g, yield 61%) as a dark green solid; mp 176–179 °C; IR (ATR): $\tilde{\nu} = 2922, 1688, 1578, 1424\ \mathrm{cm}^{-1}$; ^{1}H NMR (500 MHz, DMSO-d$_6$) $\delta = 0.79$ (t, $J = 7.5$ Hz, 6H), 1.17–1.23 (m, 4H), 1.62–1.68 (m, 4H), 4.29 (t, $J = 6.8$ Hz, 4H), 6.87 (dd, $J = 1.6$ and 8.5 Hz, 2H), 7.03–7.08 (m, 12H), 7.15 (d, $J = 1.5$ Hz, 2H), 7.26 (d, $J = 4.5$ Hz, 2H), 7.29–7.33 (m, 10H), 7.60 (d, $J = 9.1$ Hz, 2H), 7.84 (d, $J = 3.9$ Hz, 1H), 7.90 (d, $J = 4.1$ Hz, 2H), 7.95 (s, 2H), 8.07 (d, $J = 8.5$ Hz, 2H), 8.13–8.15 (m, 3H), 8.24 (d, $J = 4.2$ Hz, 2H), 8.58 (br, –COOH) ppm; unfortunately, it was difficult to obtain the ^{13}C NMR spectrum of **OMK-CA** because of its poor solubility in deuterated solvent; HRMS (ESI): *m*/*z* (%): $[M^+]$ calcd for $C_{81}H_{62}N_7O_2BF_2S_3$, 1309.41827; found 1309.42188.

Preparation of DSSCs

The TiO_2 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 °C. The 9 μm thick TiO_2 electrode was immersed into 0.1 mM dye solution in THF for 15 hours enough to adsorb the dye sensitizers (**OMK-PY** and **OMK-CA**). The DSSCs were fabricated by using the TiO_2 electrode (0.5 × 0.5 cm^2 in photoactive area) 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 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 dye molecules adsorbed on TiO_2 film was determined form the calibration curve by absorption spectral measurement of the concentration change of the dye solution before and after adsorption. The quantification of dye was made based on the molar extinction coefficient for $\lambda_{\max}^{\mathrm{abs}}$ of dye in the above solution. Absorption spectra of the dyes adsorbed on TiO_2 film (3 μm) were recorded on the dyes-adsorbed TiO_2 film in the transmission mode with a calibrated integrating sphere system.

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