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Structural optimization of thiophene-(*N*-aryl)pyrrole-thiophenebased metal-free organic sensitizer for the enhanced dye-sensitized solar cell performance

Vellaiappillai Tamilavan^a, A-Young Kim^b, Hye-Bin Kim^a, Misook Kang^b, Myung Ho Hyun^{a,*}

^a Department of Chemistry, Chemistry Institute for Functional Materials, Pusan National University, Busan 690-735, Republic of Korea ^b Department of Chemistry, Yeungnam University, Gyeongsan 712-749, Republic of Korea

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ABSTRACT

In this study, we prepared thiophene-(*N*-aryl)pyrrole-thiophene (TPT)-based two new metal-free organic sensitizers (**TPTDYE 2** and **TPTDYE 3**) with the aim of improving the dye-sensitized solar cell (DSSC) performance of recently reported TPT-based organic sensitizer (**TPTDYE 1**). The molecular structure of **TPTDYE 1** was tuned by decreasing the distance between the donor and acceptor groups (**TPTDYE 2**) or by introducing a fluoride atom on the phenyl ring near to the electron accepting cyanoacrylic acid group (**TPTDYE 3**). The photophysical and electrochemical studies of the newly synthesized sensitizers revealed that their absorption and energy levels were significantly altered compared to those of **TPTDYE 1**. The DSSC performance of each of sensitizers **TPTDYE 2** and **TPTDYE 3** was investigated with and without coadsorbent and compared with those of **TPTDYE 1** and standard **N719**. Between the two DSSCs, the one sensitized by **TPTDYE 2** offered greatly improved solar to electrical energy conversion efficiency of 6.85% without coadsorbent and 7.06% with coadsorbent. The overall conversion efficiency of the DSSC sensitized by **TPTDYE 2** without and with tot of the DSSC sensitized by **TPTDYE 2** without and with coadsorbent was found to be improved by 32% and 20%, respectively, compared with that of the DSSC sensitized by **TPTDYE 1** and almost equal (98.7%) to that of the standard cell prepared from **N719** under an identical condition.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are considered as one of the promising green energy production to solve world energy needs due to their high incident solar light to electrical energy conversion efficiency and easy device fabrication at low cost.¹ In DSSCs, typically four important components such as mesoporous semiconducting metal oxide (TiO₂), a sensitizer, an electrolyte/hole transporter, and counter electrode are employed in the solar light to electrical energy conversion process.¹ Currently, several research groups are devoting many efforts to enhance the DSSC performance through the utilization of any one of the optimized four components mentioned above or enhancing the light absorption of the DSSCs by making tandem structured or co-sensitized DSSCs. For example, the standard TiO₂ was replaced or modified with ZnO,^{2,3} structurally new sensitizers were developed,^{4–6} standard I³/I⁻ electrolyte was replaced with cobalt electrolyte^{7,8} and the DSSCs constructed with

two different sensitizers show their absorption band at different intervals of the solar spectra (co-sensitization).^{9,10} Among them developing structurally new sensitizers for DSSCs is believed to be an attractive and essential research area, since the sensitizers play a crucial role in determining the conversion efficiency as well as the stability of the DSSCs. In this instance, recently variety of organometallic complex sensitizers based on ruthenium-polypyridyl¹¹ and zinc–porphyrin complexes¹² and metal-free organic sensi-tizers based on coumarin,^{13,14} indoline,^{15,16} phenothiazine,^{17,18} carbazole,^{19,20} fluorene,^{21,22} tetrahydroquinoline,^{23,24} squaraine,^{9,25} cyanine,^{10,26} ullazine,^{27,28} triphenylamine,^{29–33} perylene,^{34,35} spirobifluorene,^{36,37} stilbene,³⁸ anthracene,^{39,40} dithienothiophene,⁴¹ dithienosilole,^{42,43} cyclopentadithiophene,^{44,45} dithienopyrrole,^{29,46} benzothiadiazole,^{47,48} and diketopyrrolopyrrole^{49,50} were reported. At present, the organometallic complex-based DSSCs were found to show a maximum conversion efficiency in the range of 12–13%^{7,8,51} while the DSSCs made from metal-free organic sensitizers offered a maximum efficiency in the range of 9–10%.^{7,23–33,47,49} The overall energy conversion efficiency of the DSSCs made from organic sensitizers is guite close to that of the organometallic complex-based DSSCs. The high energy conversion







^{*} Corresponding author. Tel.: +82 51 510 2245; fax: +82 51 516 7421; e-mail address: mhhyun@pusan.ac.kr (M.H. Hyun).

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efficiency of organic sensitizers induced us to develop new organic sensitizers for DSSCs because they have many advantages over organometallic complexes such as easy preparation and purification, higher molar extinction coefficient, easier structural modification, and unlimited resources because they do not contain noble metals.

Recently, we reported the synthesis and DSSC applications of a series of 1-(2.6-diisopropylphenyl)-2-(5-phenylthiophen-2-yl)-5-(thiophen-2-yl)pyrrole (thiophene-(*N*-aryl)pyrrole-thiophene, TPT)-based metal-free organic sensitizers.^{52,53} Among them, a DSSC sensitized by **TPTDYE 1** (Fig. 1) was found to give high solar to electrical energy conversion efficiency (η) of 6.71% using $I^3/I^$ electrolyte.⁵² The high molar absorptivity, planar structure and high energy conversion efficiency of TPTDYE 1 induced us to optimize its molecular structure. The sensitizers obtained through the structural modification of TPTDYE 1 are expected to show different opto-electrical properties, which might enhance their photovoltaic performances. In this instance, in this study, we prepared two new TPT-based organic sensitizers such as TPTDYE 2 and TPTDYE 3 (Fig. 1), studied their opto-electrical properties and compared their photovoltaic properties with those of TPTDYE 1 and the most successful inorganic sensitizer N719 (Fig. 1) as a standard.

2. Results and discussions

2.1. Synthesis and characterization

In this study, we devoted our efforts to improve the photovoltaic properties of TPT-based sensitizers through the structural optimization of **TPTDYE 1**. The π -conjugation distance between the donor and acceptor group of **TPTDYE 1** is found to be considerably wider than that of the organic sensitizers showing high conversion efficiency.^{4–6,13–50} In order to facilitate the electron flow from donor to acceptor group of **TPTDYE 1**, we intended to decrease the π -conjugation distance or introduce an electron attracting fluoride atom on the phenyl group near to the cyanoacrylic acid. In this instance, **TPTDYE 2** was prepared by removing the phenyl ring in between the TPT and cyanoacrylic acid unit of **TPTDYE 1**. On the other hand, **TPTDYE 3** was prepared by introducing a fluoride atom on the phenyl ring near to the cyanoacrylic acid group of **TPTDYE 1**. The synthetic routes to TPT-based organic sensitizers, **TPTDYE 2** and **TPTDYE 3**, are outlined in Fig. 2.

The key intermediates, **1** and **5**, were synthesized by treating 1-(2,6-diisopropylphenyl)-2,5-di(thiophen-2-yl)pyrrole with 1 or 2 equiv of NBS, respectively, according to the known



Fig. 1. Molecular structures of sensitizers TPTDYE 1, TPTDYE 2, TPTDYE 3, and N719.



Fig. 2. Scheme for the preparation of sensitizers TPTDYE 2 and TPTDYE 3.

procedures.^{52–55} The formylation of compound **1** was performed by treating compound **1** with *n*-BuLi and then DMF to afford compound **2**. The bromination of compound **2** by using NBS offered compound **3**. Then, the Suzuki coupling reaction between compound **3** and 4-(diphenylamino)phenylboronic acid yielded compound **4**. On the other hand, compound **6** was obtained from the Suzuki coupling reaction of compound **5** with 4-(diphenylamino) phenylboronic acid. The Knoevenagel condensation reactions of each of compounds **4** and **6** with cyanoacetic acid in the presence of piperidine afforded **TPTDYE 2** and **TPTDYE 3**, respectively, in good yields.

2.2. Optical properties

The optical properties such as absorption and photoluminescence of sensitizers TPTDYE 1. TPTDYE 2. and TPTDYE 3 were measured in 1.0×10^{-5} M tetrahydrofuran (THF) solution and their corresponding spectra are presented in Fig. 3a. The relatively less π -conjugated sensitizer (TPTDYE 2) showed red-shifted absorption band with maximum absorption at 512 nm (e \sim 4.8×10⁴ M⁻¹ cm⁻¹) compared with that of **TPTDYE 1** (maximum absorption at 455 nm, $\varepsilon = 5.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).⁵² On the other hand, quite similarly structured sensitizer TPTDYE 3 containing a fluoride atom showed narrower absorption band than that of TPTDYE 1 with maximum absorption at 423 nm ($\epsilon = 5.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The absorption bands of the sensitizers are expected to be originated from the overlap of the π - π * transition and the donor-acceptor intramolecular charge transfer (ICT) between the donor and the cyanoacrylic acid anchoring moiety.⁵² The latter phenomenon was evidently documented for sensitizer TPTDYE 1 using solvent-

dependent absorption behaviors as reported previously.⁵² The red-shifted absorption of TPTDYE 2 compared with that of TPTDYE **1** is expected to be originated from the efficient ICT between the donor and acceptor group because the ICT usually improves when the distance between the donor and acceptor group is decreased. On the contrary, the introduction of fluoride group on the phenyl ring of **TPTDYE 1** seems to diminish the ICT in THF. resulting in the narrow and blue shifted absorption band for TPTDYE 3. To make sure the blue shifted absorption of TPTDYE 3, we measured the absorption spectra of all three sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3 in chloroform (CHCl₃) as shown in Fig. 3b-d. Interestingly, the absorption range of **TPTDYE 3** was much broader in CHCl₃ than in THF while the absorption ranges of TPTDYE 1 and **TPTDYE 2** in CHCl₃ were almost identical with those in THF. The change of solvent from THF to CHCl₃ seems to enhance the ICT in **TPTDYE 3** even though the reason is not clear and, consequently, improve the absorption range of **TPTDYE 3** significantly in CHCl₃.

The absorption spectra of sensitizers **TPTDYE 1**, **TPTDYE 2**, and **TPTDYE 3** adsorbed on TiO₂ with and without chenodeoxycholic acid (DCA) are also displayed in Fig. 3b–d, respectively. The absorption bands of sensitizers **TPTDYE 1**, **TPTDYE 2**, and **TPTDYE 3** adsorbed on TiO₂ were found to be significantly broadened and red shifted compared with those in solution and the absorption bands appeared in the range of 350 nm–600 nm for **TPTDYE 1** and 350–650 nm for **TPTDYE 2** and **TPTDYE 3**. The absorption maxima of **TPTDYE 1** and **TPTDYE 3** adsorbed on TiO₂ were found to be 475 and 500 nm, respectively, while the absorption maximum of **TPTDYE 2** appeared quite broad from 390 nm to 540 nm. The red-shifted absorption of dyes adsorbed on TiO₂ might be attributed to the formation of a J-type aggregate.⁵⁶



Fig. 3. UV–visible absorption spectra of sensitizers **TPTDYE 1**, **TPTDYE 2**, and **TPTDYE 3** measured in THF (1.0×10^{-5} M). Inset: Normalized absorption and photoluminescence (excited at their absorption maxima) spectra of **TPTDYE 1**, **TPTDYE 2**, and **TPTDYE 3** in THF solution (a). UV–visible absorption and photoluminescence (PL) spectra of **TPTDYE 1** (b), **TPTDYE 2** (c), and **TPTDYE 3** (d). UV–visible absorption spectra were measured in chloroform (CHCl₃), as film adsorbed on TiO₂ or as film adsorbed on TiO₂ with DCA. Photoluminescence (PL) spectra were measured in chloroform.

All three sensitizers adsorbed on TiO₂ along with DCA showed slightly blue shifted absorption bands compared with those of the sensitizers adsorbed on TiO₂ without DCA. The absorption maxima of TPTDYE 1 and TPTDYE 3 adsorbed on TiO₂ with DCA were found to be 471 nm and 497 nm, respectively, while the absorption maximum of **TPTDYE 2** was appeared guite broad from 390 nm to 540 nm. DCA added is expected to compete with the sensitizers to bind on TiO₂ surface, and consequently, the aggregation of the sensitizers on TiO₂ is reduced, which leads blue shift in their absorption bands.⁵⁷

The normalized photoluminescence (PL) spectra of TPTDYE 1, TPTDYE 2, and TPTDYE 3 in THF (inset of Fig. 3a) and in CHCl₃ (excited at their absorption maximum, Fig. 3b-d) are displayed in Fig. 3. The PL maxima of TPTDYE 1, TPTDYE 2, and TPTDYE 3 are appeared at 615, 661, and 575 nm, respectively, in CHCl₃ and their band gaps (E_{0-0}) were estimated from the wavelength at the intersection of absorption and emission spectra to be 2.34, 2.08, and 2.42 eV, respectively. The optical properties of sensitizers TPTDYE 1, **TPTDYE 2**, and **TPTDYE 3** are summarized in Table 1.



Fig. 4. Cyclic voltammograms of sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3 adsorbed on TiO₂ in 0.1 M Bu₄NBF₄/acetonitrile at 100 mV/s, potential versus Ag/AgCl.

Table 1

Optical and electrochemical properties of TPTDYE 1, TPTDYE 2, and TPTDYE 3

Sensitizer	λ _{max,soln} a (nm)	ε ^b	λ _{max,dye film} ^c (nm)	$\lambda_{max,dye+DCA film}^{d}$ (nm)	PL max ^e (nm)	E_{0-0}^{f} (eV)	E _{ox} ^g (V)	E _{LUMO} h (V)
TPTDYE 1	455	5.8×10 ⁴	475	471	615	2.34	0.96	-1.38
TPTDYE 2 TPTDYE 3	512 423	4.8×10^4 5.4×10^4	390—540 500	390–540 497	661 575	2.08 2.42	1.02 0.95	-1.06 -1.47

^a Measurements from dye dissolved in THF (1×10^{-5} M).

^b Molar extension coefficient (M^{-1} cm⁻¹) of the dyes measured in THF (1×10⁻⁵ M).

Measurements from dye adsorbed on TiO₂.

^d Measurements from dye and DCA adsorbed on TiO₂. ^e Measurements from dye dissolved in CHCl₃ (1x10⁻⁵ M).

^f The optical band gap (E_{0-0}) estimated at the intersection of absorption and emission spectra in CHCl₃ solution.

^g The onset oxidation potentials were estimated from cyclic voltammetry analysis.

^h The E_{LUMO} level was calculated using the following equation, $E_{LUMO} = E_{ox} - E_{0-0}$.

2.3. Electrochemical properties

The CV analysis is one the most common and simplest method to determine the energy levels including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the sensitizers. It is essential to determine the energy levels of the sensitizers to ensure their suitability for DSSC applications. To ensure the efficient electron injection from sensitizer to TiO₂ and from electrolyte (I_3^-/I^-) to sensitizer, the HOMO level of the sensitizer should be positioned below the redox potential of electrolyte (0.4 V, $I_3^{-}/I^{-})$ while the LUMO energy of the sensitizer should be positioned above the LUMO level of TiO₂ (-0.5 V).^{52,53} Cyclic voltammetry (CV) experiments were conducted for the sensitizers adsorbed on TiO₂ as an working electrode, platinum wire as a counter electrode and Ag/AgCl as an reference electrode in acetonitrile (ACN) containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) at room temperature and ambient atmosphere. Based on the CV analysis shown in Fig. 4, the E_{ox} (oxidation potential) values reflecting the HOMO levels of sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3 were estimated to be 0.96, 1.02, and 0.95 V, respectively. On the other hand, the LUMO levels of the sensitizers were calculated by using the known equation $(E_{LUMO} = E_{ox} - E_{0-0})$, ^{52,53} where E_{ox} is the oxidation potential or HOMO energy level and E_{0-0} is the band gap of the sensitizers. The LUMO energy levels of sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3 were calculated to be -1.38, -1.06, and -1.47 V, respectively. The CV analysis indicates the HOMO energy level of **TPTDYE 2** was slightly higher than that of **TPTDYE 1**, but the LUMO energy level of TPTDYE 2 was significantly lowered than that of TPTDYE 1. On the contrary, the HOMO level of TPTDYE 3 was almost identical with that of TPTDYE 1, but the LUMO energy level of

TPTDYE 3 was more negatively shifted compared with that of **TPTDYE 1.** The LUMO energy levels of all three sensitizers are located well above the LUMO level of TiO₂ and the HOMO energy levels are positioned below the redox potential of electrolyte (I_3^-/I^-) . The HOMO and LUMO energy levels of **TPTDYE 2** and TPTDYE 3 revealed that they are also suitable candidates for DSSC applications. The electrochemical properties of sensitizers TPTDYE **1. TPTDYE 2.** and **TPTDYE 3** are summarized in Table 1.

2.4. Computational studies

The structures of sensitizers TPTDYE 2 and TPTDYE 3 were optimized by using B3LYP hybrid functional and 6-31G* basis sets with the aim of understanding the correlation between their structures, optical properties, and electronic distribution at valance (HOMO) and conduction (LUMO) bands. The optimized structures and their electronic distribution in the HOMO and LUMO levels of sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3 are shown in Fig. 5. The geometrically optimized structures of sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3 clearly indicate that the sensitizers exhibit planar structures except for the triphenylamine (TPA) unit. In addition, the dihedral angles between the aromatic groups are not much different for the three sensitizers. These results suggest that the planarity of **TPTDYE 1** is not much affected by the decreased distance between the electron donor and acceptor group or by the incorporation of fluoride atom on the back bone of TPTDYE 1.

The electron density was found to be distributed throughout the electron donor groups such as TPA and N-aryl TPT in the HOMO energy levels of the sensitizers while it was found to be distributed on the electron acceptor group (cyanoacrylic acid) along with benzene and N-aryl TPT in the LUMO energy levels. The electronic



Fig. 5. The optimized structures and frontier orbital plots of the HOMO and LUMO of sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3.

distribution over the *N*-aryl TPT unit in both HOMO and LUMO suggests that an effective ICT occurs from the donor to acceptor through the *N*-aryl TPT unit. In particular, the electronic overlap between the HOMO and LUMO level of the sensitizers was found to be excellent for relatively less π -conjugated sensitizer, **TPTDYE 2**, and these results suggest that the ICT can occur more efficiently for sensitizer **TPTDYE 2** than for sensitizer **TPTDYE 3** or **TPTDYE 1**.

2.5. Photovoltaic performance of DSSCs

The solar to electrical energy conversion ability of sensitizers TPTDYE 2 and TPTDYE 3 was tested by preparing DSSCs with each of the sensitizers. Under the identical condition DSSCs were also prepared with the reported sensitizer, TPTDYE 1, and the most successful ruthenium-polypyridyl complex, N719, as a standard to briefly compare their energy conversion efficiencies. The currentdensity/voltage (I-V) curves of the DSSCs sensitized by each of sensitizers TPTDYE 1, TPTDYE 2, TPTDYE 3, and N719 without DCA are shown in Fig. 6a and the detailed photovoltaic parameters such as open-circuit voltage (V_{oc}), short-circuit photocurrent density (J_{sc}) , fill factor (FF), and energy conversion efficiency (η) are summarized in Table 2. The DSSC performances were measured at 100 mW/cm² under simulated AM 1.5 G solar light conditions. The DSSC sensitized by TPTDYE 2 without DCA offered maximum energy conversion efficiency (η) of 6.85% with a V_{oc} of 0.73 V, a J_{sc} of 13.80 mA/cm² and an FF of 0.68, while the DSSC sensitized by **TPTDYE 3** without DCA gave a η of 2.63% with a V_{oc} of 0.65 V, a J_{sc} of 5.95 mA/cm², and an FF of 0.68. Under the identical condition, the DSSCs sensitized by **TPTDYE 1** and **N719** without DCA gave an η of 5.19% (V_{oc} =0.68 V, J_{sc} =11.93 mA/cm², and FF=0.64) and 7.15% $(V_{oc}=0.67 \text{ V}, J_{sc}=16.16 \text{ mA/cm}^2, \text{ and FF}=0.66)$, respectively.

Our previous studies revealed that the photovoltaic performances of TPTDYE-based DSSCs were significantly improved with the use of coadsorbent such as DCA.⁵³ To investigate the DCA influence on the performances of the DSSCs sensitized by TPTDYE 1, TPTDYE 2, and TPTDYE 3, we prepared the DSSCs from each of the sensitizers along with DCA (10 mM). The J-V curves of the DSSCs made from each of sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3 with DCA are shown in Fig. 6b, and those DSSCs were found to show maximum η value of 5.87% (V_{oc} =0.71 V, J_{sc} =12.72 mA/cm², and FF=0.65), 7.06% (V_{oc}=0.72 V, J_{sc}=14.86 mA/cm², and FF=0.66) and 4.42% (V_{oc}=0.65 V, J_{sc}=10.15 mA/cm², and FF=0.67), respectively. The DSSCs prepared with DCA from each of three sensitizers **TPTDYE 1**, **TPTDYE 2**, and **TPTDYE 3** showed improved η with quite similar V_{oc} and FF values and improved J_{sc} values compared with those of the DSSCs prepared without DCA. It is worth to notice that the bulky DCA molecules prevent the dye aggregation (dimer or trimer formation, whose electron injection efficiency is lower than that of the monomer) on the TiO₂, and consequently, increase the electron injection efficiency from the sensitizer into the TiO₂, resulting in the improved J_{sc} values.^{57–59} In contrast, the rate of recombination of the injected electrons in the DSSCs prepared with DCA seems to be quite similar with that in the DSSCs prepared without DCA and/or the influence of DCA on the conduction band movement of sensitizer-adsorbed TiO₂ might be negligible for the DSSCs based on sensitizers **TPTDYE 1**, **TPTDYE 2**, and **TPTDYE 3**,



Fig. 6. *J*–*V* Characteristics of the DSSCs made from each of sensitizers **TPTDYE 1**, **TPTDYE 2**, **TPTDYE 3**, and **N719** without (a) and with DCA (b) under AM 1.5 irradiation (100 mW/cm²).

Name of the sensitizer	Without DCA					With DCA				
	$\overline{V_{\rm oc}^{\rm a}(\rm V)}$	$J_{\rm sc}^{b}$ (mA/cm ²)	FF ^c (%)	η^{d} (%)	IPCE ^e (%)	$V_{\rm oc}^{\rm a}({\rm V})$	$J_{\rm sc}^{\rm b}$ (mA/cm ²)	FF ^c (%)	η ^d (%)	IPCE ^e (%)
TPTDYE 1	0.68	11.93	0.64	5.19	57	0.71	12.72	0.65	5.87	58
TPTDYE 2	0.73	13.80	0.68	6.85	65	0.72	14.86	0.66	7.06	68
TPTDYE 3	0.65	5.95	0.68	2.63	40	0.65	10.15	0.67	4.42	49
N719	0.67	16.16	0.66	7.15	64	—	_	—	—	—

Table 2 Photovoltaic properties of TPTDYE 1. TPTDYE 2. TPTDYE 3. and N719

Open-circuit voltage.

Short-circuit current density. ^c Fill factor.

^d Power conversion efficiency.

^e Incident photon to collected electron efficiency.

showing similar $V_{\rm oc}$ values in the DSSCs prepared with and without DCA.57-59

In comparison with the DSSC sensitized by TPTDYE 1, the photovoltaic parameters such as Voc, Jsc, and FF were found to be higher for the DSSC sensitized by TPTDYE 2 with and without DCA. We expect that the positive effects such as red-shifted absorption maximum along with broad absorption ability (more effective light harvesting than TPTDYE 1 and TPTDYE 3) and the enhanced electron injection from sensitizer **TPTDYE 2** to TiO_2 as well as the electron regeneration efficiency from electrolyte to sensitizer **TPTDYE 2** due to its suitable HOMO and LUMO energy levels might offer significantly improved device performances compared with that of TPTDYE 1. The DSSC sensitized by TPTDYE 3 was found to give the FF and V_{oc} values similar with those of the DSSC prepared from TPTDYE 1 with and without DCA. However, the DSSC sensitized by **TPTDYE 3** was found to give significantly lower *I*sc value compared with that of the DSSC prepared from TPTDYE 1 with and without DCA. The exact reason for the lower J_{sc} value of the DSSC sensitized by TPTDYE 3 is not clear, but might be due to the relatively increased recombination process. There are two possible reasons for the increased recombination process in the DSSC sensitized by **TPTDYE 3**. The first reason is that the relatively high energy difference ($\Delta E_g = 0.97$ V) between the LUMO levels of **TPTDYE 3** and TiO_2 might reduce the electron injection from the LUMO level of TPTDYE 3 to the LUMO level of TiO₂, and consequently, increases the recombination process. The second reason is that the presence of fluoride atom having the tendency of strong electron affinity might restrict the electron transfer process as previous reports evidently documented that the incorporation of electron withdrawing moiety near to the cyanoacrylic acid increases the recombination process or jeopardize the electron injection to TiO₂.^{47,60}

The solar to electrical energy conversion efficiency of the DSSC sensitized by TPTDYE 2 without and with DCA was found to be improved by 32% and 20%, respectively, compared to that of the DSSC sensitized by TPTDYE 1. In addition, the overall photovoltaic performance of the DSSC sensitized by TPTDYE 2 was found to be quite similar (98.7%) to that of the DSSC sensitized by N719. These results reveal that TPTDYE 2 is a promising candidate for DSSC applications.

The monochromatic IPCEs (Incident-Photon-to-electron Conversion Efficiencies) of the DSSCs are presented in Fig. 7. The IPCE spectra of DSSCs prepared with each of sensitizers TPTDYE 1, TPTDYE 2, TPTDYE 3, and N719 without DCA were found to show the maximum IPCE value of 57% at 450 nm, 65% at 480 nm, 40% at 415 nm, and 64% at 550 nm, respectively, while those of the corresponding DSSCs made from each of sensitizers TPTDYE 1, TPTDYE 2, and TPTDYE 3 with DCA were found to show the increased IPCE maximum values of 58% at 465 nm, 68% at 485 nm, and 49% at 465 nm, respectively. The IPCE maximum value was found to be 10% higher for the DSSC sensitized by TPTDYE 2 and 9% lower for the



Fig. 7. IPCE characteristics for the DSSCs made from each of sensitizers TPTDYE 1, TPTDYE 2, TPTDYE 3, and N719 without (a) and with DCA (b).

DSSC sensitized by TPTDYE 3 compared to that for the DSSC sensitized by TPTDYE 1. The relatively broader IPCE spectrum and higher IPCE maximum value of the DSSC sensitized by TPTDYE 2 evidently support its higher energy conversion efficiency compared with that of the DSSC sensitized by TPTDYE 1 or TPTDYE 3.

3. Conclusions

We prepared 1-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole-based two new metal-free organic sensitizers TPTDYE 2 and **TPTDYE 3** with the aim of improving the DSSC performance of reported TPTDYE 1 through the structural modifications. New sensitizers **TPTDYE 2** showing less π -conjugation distance between the donor and acceptor units and TPTDYE 3 containing fluoride

atom near to the cyanoacrylic acid group showed the red-shifted absorption bands compared with that of **TPTDYE 1** in chloroform and as film on TiO₂. The electrochemical study indicates that the HOMO and LUMO energy levels of TPTDYE 2 were significantly compressed than those of **TPTDYE 1**, while the HOMO energy level of **TPTDYE 3** was found to be almost identical with that of **TPTDYE** 1, but the LUMO energy level was more negatively shifted. We found that the incorporation of electron attracting fluoride atom near to the cyanoacrylic acid group of **TPTDYE 1** is not satisfactory in terms of increasing the energy conversion efficiency. Interestingly, the energy conversion efficiency was notably enhanced when the π -conjugation distance between donor and acceptor units was decreased. The maximum energy conversion efficiency of 7.06% and 4.42% was achieved for the DSSCs made from the sensitizers **TPTDYE 2** and **TPTDYE 3**, respectively, along with DCA. The maximum conversion efficiency of the DSSC sensitized by TPTDYE **2** with DCA was found to be 20% higher than that of the DSSC sensitized by TPTDYE 1 and almost equal (98.7%) to that of the DSSC sensitized by N719 prepared under the identical device preparation condition

4. Experimental section

4.1. Materials and instruments

Reagents were received from Aldrich or TCI chemicals and used without further purification. The purification of the compounds was performed on silica gel (Merck Kieselgel 60, 70–230 mesh) column chromatography. The proton (¹H, 300 MHz) and carbon (¹³C, 75 MHz) NMR spectra were recorded using a Varian Mercury Plus spectrometer (300 MHz) in deuterated solvents. Infrared spectra were obtained on a Nicolet 380 FTIR spectrophotometer with samples prepared as KBr pellets. The absorption and photoluminescence spectra were recorded using JASCO V-570 and Hitachi F-4500 fluorescence spectrophotometer, respectively, at 25 $^{\circ}$ C. Sensitizer-adsorbed TiO₂ films were prepared as follows: TiO₂ coated FTO plates were prepared by using a doctor blade printing technique and then dried at 450 °C for 30 min. Subsequently, FTO/ TiO₂ substrates were immersed in 0.3 mM sensitizer solution (without or with 10 mM DCA) for 24 h. The dye-adsorbed TiO₂ plates were dried at 40 °C for 10 min and at rt for 3 h and then used for measurements. The cyclic voltammograms were recorded by using a CH Instruments Electrochemical Analyzer. The CV instrument calibration was performed by using the ferrocene/ferrocenium (FOC) redox couple as an external standard.

4.2. Fabrication and characterization of dye-sensitized solar cells (DSSCs)

Fluorine-doped tin oxide (FTO) glass plates (Hartford FTO, 30 Ω cm⁻², 80% transmittance in visible region) were cleaned in a detergent solution using an ultrasonic bath for 30 min and then rinsed with water and ethanol. Then, the plates were immersed in 40 mM TiCl₄ (aqueous) at 70 °C for 30 min and washed with water and ethanol. A transparent nanocrystalline layer was prepared on the FTO glass plates by using a doctor blade printing TiO₂ paste (Dyesol, DSL 18NR-T), which was then dried for 2 h at 25 °C. The TiO₂ electrodes were gradually heated under an air condition at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The thickness of the transparent layer was measured by using an Alpha-step 250 surface profilometer (Tencor Instruments, San Jose, CA). A paste containing 400 nm sized anatase particles (Dyesol. DSL 18NR-AO) was deposited by means of doctor blade printing to obtain the scattering layer, and then dried for 2 h at 25 °C. The TiO₂ electrodes were gradually heated under an air condition at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for

15 min, and at 500 °C for 15 min. The resulting film was composed of a 6.0 µm thick transparent layer and a 7.0 µm thick scattering layer. Then, they were immersed into the dye solution [0.3 mM solution of dye in ethanol or ethanol containing 0.3 mM of dye with 10 mM of 3α,7β-dihydroxy-5β-cholanic acid (chenodeoxycholic acid, DCA)] and kept at room temperature for 24 h. FTO plates for the counter electrodes were cleaned in an ultrasonic bath in H₂O and acetone, subsequently. The counter electrodes were prepared by Pt vacuum coating using a JEOL-400 vacuum evaporator $(7.5 \times 10^{-6}$ Torr, 20 V, 30 A, and 250 L/min) for 30 s on an FTO plate. The dye-adsorbed TiO₂ electrodes and the Pt counter electrodes were assembled into a sealed sandwich-type cell by heating at 80 °C using a hot-melt ionomer film (Solaronix Surlyn, Meltonix 1170-25, 25 μ m) as a spacer between the electrodes. A drop of the electrolyte solution was placed in the drilled hole of the counter electrode and was driven into the cell via vacuum backfilling. Finally, the hole was sealed using additional Surlyn and a cover glass. The electrolyte was then introduced into the cell, which is composed of 1.0 M 3-propyl-1,2-dimethyl imidazolium iodide, 0.03 M iodine, 0.05 M LiI, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tertbutylpyridine in 85:15(v/v) acetonitrile and valeronitrile. The cell performance was measured using 150-W xenon light source, whose power of an AM 1.5 SUN 2000 solar simulator (ABE technology) was calibrated by using KG5 filtered Si reference solar cell. Incident light intensity and active cell area were 100 mW cm⁻² (one sun illumination) and 0.40 cm² (0.5 cm \times 0.8 cm), respectively. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV Measurements).

4.3. Synthesis of dyes

New organic sensitizers **TPTDYE 2** and **TPTDYE 3** were synthesized as outlined in Fig. 2. Compounds **1** and **5** were synthesized from 1-(2,6-diisopropylphenyl)-2,5-di(thiophen-2-yl)pyrrole according the procedures reported.^{52–55} The detailed synthetic procedure and characterization of the intermediates and final sensitizers are given below.

4.3.1. Synthesis of 5-(1-(2,6-diisopropylphenyl)-5-(thiophen-2-yl)pyrrol-2-yl)thiophene-2-carbaldehyde (2). To a stirred solution of compound 1 (0.90 g, 1.91 mmol) in dry diethyl ether (60 mL) was added n-BuLi (2.5 M in hexane, 1.0 mL, 2.5 mmol) drop by drop at 0 °C under argon atmosphere. The solution was stirred for 30 min in the same bath and then N,N-dimethylformamide (DMF, 2.96 mL, 38.2 mmol) was added in one potion. The solution was slowly warmed to room temperature (rt) and stirred for overnight. The solution was poured into 2 N HCl (50 mL), and the aqueous solution was extracted with ethyl acetate (3×50 mL). The combined organic layer was dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified by silica gel column chromatography (hexane/ethyl acetate, 95:5, v/v) to afford compound 2. Yield is 0.40 g (50%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.91 (t, 12H), 2.41-2.50 (m, 2H), 6.48-6.52 (m, 2H), 6.72 (d, 1H), 6.791-6.795(m, 1H), 6.90(d, 1H), 7.03(d, 1H), 7.31 (d, 2H), 7.41(d, 1H), 7.60 (t, 1H), 9.69 (s, 1H); 13 C NMR (75 MHz, CDCl₃) δ (ppm) 23.8, 23.9, 28.6, 110.1, 112.4, 123.0, 124.0, 124.4, 125.3, 127.3, 129.0, 131.3, 132.9, 133.7, 134.4, 137.2, 139.9, 145.4, 148.0, 182.5; HRFAB-MS m/z [M⁺] calcd for C₂₅H₂₅NOS₂ 419.1378, found: 419.1374.

4.3.2. Synthesis of 5-(5-(5-bromothiophen-2-yl)-1-(2,6-diisopropyl phenyl)pyrrol-2-yl)thiophene-2-carbaldehyde (**3**). To a stirred solution of compound **2** (0.20 g, 0.48 mmol) in DMF (10 mL) was added a solution of *N*-bromosuccinimide (NBS) (0.10 g, 0.52 mmol) in DMF (5 mL) drop by drop at 0 °C. The solution was slowly warmed to rt and stirred for overnight. The solvent was completely removed by using

rotary evaporator and then the residue was dissolved in ethyl acetate (50 mL). The organic solution was washed with water and brine and dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified by flash column chromatography (silica gel, hexane) to afford compound **3**. Yield is 0.18 g (75%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.93 (t, 12H), 2.40–2.44 (m, 2H), 6.25 (d, 1H), 6.52 (d, 1H), 6.66 (d, 1H), 6.74(d, 1H), 6.87 (d, 1H), 7.32 (d, 2H), 7.42 (d, 1H), 7.61 (t, 1H), 9.69 (s, 1H); ¹³C NMR (75 MHz. CDCl₃) δ (ppm) 22.9, 23.9, 28.6, 31.8, 110.1, 111.1, 112.4, 123.3, 123.9, 124.9, 125.5, 129.4, 130.1, 131.6, 131.8, 133.2, 136.0, 137.1, 140.1, 144.9, 147.9, 182.5; HRFAB-MS *m*/*z* [M⁺] calcd for C₂₅H₂₄BrNOS₂ 497.0483, found: 497.0485.

4.3.3. Synthesis of 5-(5-(4-(diphenylamino)phenyl)thiophen-2*yl*)-1-(2,6-diisopropylphenyl)pyrrol-2-yl)thiophene-2-carbaldehyde (4). A stirred solution of compound 3 (0.18 g, 0.36 mmol) and 4-(diphenylamino)phenylboronic acid (0.12 g, 0.43 mmol) in toluene (30 mL) was purged well with argon for 45 min and then Pd(PPh₃)₄ (5 mol %) and aqueous 2 M K₂CO₃ solution (7 mL) were added. The reaction mixture was refluxed for 24 h under argon atmosphere. The solvent was completely removed by using a rotary evaporator and the residue was dissolved in ethyl acetate (50 mL). The organic solution was washed with water and brine, and then dried over anhydrous Na₂SO₄. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate=95:5, v/v) to afford compound **4**. Yield is 0.18 g (77%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.91–0.97 (m, 12H), 2.44–2.53 (m, 2H), 6.33 (d, 1H), 6.54 (d, 1H), 6.74 (d, 1H), 6.90-6.93 (m, 2H), 6.99-7.11 (m, 6H), 7.18-7.34 (m, 10H), 7.42 (d, 1H), 7.60 (t, 1H), 9.69 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 22.9, 23.9, 28.6, 29.9, 31.2, 31.8, 110.0, 112.6, 116.5, 122.1, 122.5, 123.0, 123.1, 123.4, 123.8, 124.8, 125.4, 126.4, 127.4, 128.2, 129.1, 129.3, 129.5, 131.4, 132.8, 132.9, 133.7, 137.2, 139.7, 142.7, 145.4, 147.5, 147.6, 147.9, 148.4, 182.5; HRFAB-MS m/z [M⁺] calcd for C₄₃H₃₈N₂OS₂ 662.2426, found: 662.2432.

4.3.4. Synthesis of (E)-3-(5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-1-(2,6-diisopropylphenyl)pyrrol-2-yl)thiophen-2-yl)-2cyanoacrylic acid (TPTDYE 2). To a stirred solution of compound 4 (0.18 g, 0.28 mmol) in a mixture of chloroform and acetonitrile (30 mL, 1:1, v/v) was added piperidine (0.14 mL, 1.40 mmol) and cyanoacetic acid (0.12 g, 1.40 mmol) at rt under argon atmosphere. The solution was refluxed for 24 h and then cooled to room temperature. The solvent was concentrated by using a rotary evaporator and the residue was dissolved into 10 mL of methylene chloride (CH₂Cl₂) and the resulting mixture was poured into 100 mL water. To the stirred mixture was added 2 N HCl until the reaction mixture became acidic. The aqueous layer was extracted with CH₂Cl₂ and the organic layer was washed with water and brine, and then dried over anhydrous Na₂SO₄, filtered, and evaporated on a rotary evaporator to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2 /methanol=90:10, v/v) to afford **TPTDYE 2**. Yield is 0.16 g (80%). ¹H NMR (300 MHz, DMSO d_6): δ (ppm) 0.86–0.89 (m, 12H), 2.43–2.45 (m, 2H), 6.26–6.27 (m, 1H), 6.66 (d, 2H), 6.86 (d, 2H), 6.99-7.06 (m, 8H), 7.22-7.26 (m, 8H), 7.52 (d, 2H), 8.09 (s, 1H); IR (KBr, cm⁻¹): 3438, 3061, 3031, 2960, 2926, 2866, 2215,1627, 1593, 1492; HRFAB-MS *m*/*z* [M⁺] calcd for C₄₆H₃₉N₃O₂S₂ 729.2484, found: 729.2486.

4.3.5. Synthesis of 4-(5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-1-(2,6-diisopropylphenyl)pyrrol-2-yl)thiophen-2-yl)-2fluorobenzaldehyde (6). A stirred solution of compound 5 (0.46 g, 0.84 mmol) and 4-(diphenylamino)phenylboronic acid (0.24 g, 0.84 mmol) in toluene (40 mL) was purged well with argon for 45 min and then Pd(PPh₃)₄ (2 mol %) and aqueous 2 M K₂CO₃ solution (7 mL) were added. The whole mixture was refluxed under argon atmosphere for 16 h. Under reflux condition, 3-fluoro-4formylphenylboronic acid (0.34 g, 2.00 mmol) was added to the reaction mixture. The reaction mixture was refluxed again for additional 16 h. Then, the reaction mixture was allowed to cool to room temperature and the solvent was completely removed by using a rotary evaporator. The residue was dissolved in ethyl acetate (50 mL) and washed with water and brine, and then dried over anhydrous Na₂SO₄. The solvent was concentrated and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate=90:10, v/v) to afford compound **6**. Yield is 0.25 g (40%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.95–0.98 (m, 12H), 2.51–2.56 (m, 2H), 6.30 (d, 1H), 6.72-6.77 (m, 2H), 6.91 (d, 1H), 6.99-7.16 (m, 10H), 7.20–7.35 (m, 10H), 7.60 (t, 1H), 7.79 (t, 1H), 10.27 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 23.9, 28.6, 109.6, 110.6, 112.0, 112.3, 121.2, 122.5, 122.9, 123.3, 123.9, 124.1, 124.4, 124.5, 124.7, 125.1, 126.4, 128.4, 128.8, 129.4, 129.5, 131.0, 131.5, 132.4, 132.6, 133.4, 134.2, 138.0, 142.0, 142.6, 147.3, 147.7, 148.1, 186.5; HRFAB-MS m/z [M⁺] calcd for C₄₉H₄₁FN₂OS₂ 756.2644, found: 756.2646.

4.3.6. Synthesis of (E)-3-(4-(5-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-1-(2,6-diisopropylphenyl)pyrrol-2-yl)thiophen-2-yl)-2fluorophenyl)-2-cyanoacrylic acid (TPTDYE 3). TPTDYE 3 was synthesized by using the synthetic procedure similar to that for TPTDYE 2. Compound 6 (0.25 g, 0.34 mmol) was subjected to Knoevenagel condensation with cyanoacetic acid in the presence of piperidine to afford **TPTDYE 3**. Yield is 0.22 g (80%). ¹H NMR (300 MHz, DMSO-d₆) δ (ppm) 0.95-0.98 (m, 12H), 2.49-2.58 (m, 2H), 6.34 (d, 1H), 6.67-6.75 (m, 2H), 6.91 (d, 2H), 7.01-7.09 (m, 10H), 7.21–7.34 (m, 10H), 7.57–7.60 (m, 1H), 8.02 (s, 1H); IR (KBr, cm⁻¹): 3440, 3061, 3030, 2961, 2927, 2868, 2217,1610, 1592, 1489; HRFAB-MS m/z [M⁺] calcd for C₅₂H₄₂FN₃O₂S₂ 823.2702, found: 823.2703.

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