Thieno[2,3-*a*]carbazole-based donor- π -acceptor organic dyes for efficient dye-sensitized solar cells

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ABSTRACT

New donor- π -acceptor organic dyes **K-1** and **K-2** containing thieno[2,3-*a*]carbazole as an electron donor were designed and synthesized for dye-sensitized solar cells (DSCs). Photophysical and electrochemical properties of **K**-dyes were investigated. DSCs based on **K**-dyes showed a high conversion efficiency of 6.6–6.7% with a J_{sc} of 12.40–12.49 mA cm⁻² and a V_{oc} of 0.70–0.71 V. The molecular geometry calculation indicated that the existence of thienocarbazole donor in **K**-dyes enhanced the molecular planarity compared to the carbazole analogue dye **MK-3**. As a result, DSCs based on **K**-dyes showed high IPCEs, perhaps due to efficient intramolecular charge transfer and electron injection from excited dye to TiO₂ conduction band.

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1. Introduction

Dye-sensitized solar cells (DSCs) as one of the most promising next-generation photovoltaic technology have attracted significant attention in the past decades due to their versatile, energy-saving, and environmentally friendly nature.¹ At present, the state-of-the-art DSCs based on Ruthenium(II)-polypyridyl complex photosensitizers have an overall power conversion efficiency (η) approaching 12% under standard (Global Air Mass 1.5) illumination.² Metal free organic dyes have attracted considerable attention in recent years due to their higher molar extinction coefficients, structure flexibility and lower cost than Ru complex, even though their conversion efficiencies are lower than Ru complex sensitizers. Therefore, a number of metal free organic sensitizers have been developed to improve the efficiency of solar energy conversion.³ Among them, the donor-(π -linker)-acceptor (D- π -A) conjugated system is the basic structure for designing organic sensitizers, due to the effective photo-induced intramolecular charge transfer characteristics.

Recently, a series of carbazole donor based D- π -A organic dyes has been developed as a promising photosensitizer for efficient DSCs because of the good hole transporting ability of carbazole moiety which results from its strong electron donating property.⁴ During our development of gold-catalyzed cascade cyclization of aniline-tethered arenyl diynes to construct thienocarbazole derivatives⁵ and study of the influence of molecular planarity on DSC performance,⁶ we envisioned that organic dyes based on thieno[2,3-*a*]carbazole as donor unit instead of carbazole may increase the molecular planarity (torsion angle θ) between thieno[2,3-*a*]carbazole and oligothiophene linkage (Figure 1). Generally, the efficiency of DSC is mainly determined by short-circuit photocurrent (J_{sc}) and open-circuit photovoltage (V_{oc}).⁷ J_{sc} is usually correlated with the absorption ability and electron injection efficiency of organic dyes, while one of the important factor of V_{oc} is charge recombination. Taking these points into account, we expected that introduction of thieno[2,3-*a*]carbazole donor moiety would increase the molecular planarity, leading to enhancement of the intramolecular charge transfer due to extension of the π -conjugation system of the molecule.⁸ This intramolecular charge

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transfer between donor and acceptor moieties in the excited dye may enhance the electron injection efficiency from the photosensitizer into conduction band (CB) of the TiO_2 , which is related to higher IPCE and J_{sc} . However, it is also well understood that the dyes with high planarity usually lead to strong dye aggregation on TiO_2 surface, resulting in a decreased V_{oc} .^{7b}

In our continuous effort to enhance DSC performances,⁹ we report herein a novel series of D- π -A sensitizers **K-1** and **K-2** based on thieno[2,3-*a*]carbazole as an electron donor, bithiophene or thienylfuran as a π -linkage, and cyanoacrylic acid as an acceptor for nanocrystalline TiO_2 solar cells (Figure 1). DFT calculation showed that **K**-dyes possess higher molecular planarity than that of the carbazole analogue **MK-3**,^{4a} and DSCs based on **K**-dyes showed sufficiently good efficiency of 6.6~6.7% with J_{sc} of 12.40~12.49 mA cm^{-2} and without significant decrease of V_{oc} (0.70~0.71 V).

Figure 1. Molecular structures of **K**-dyes and their carbazole analogue **MK-3**.

2. Results and discussion

The synthetic route of organic dyes **K-1** and **K-2** is depicted in Scheme 1. Thieno[2,3-*a*]carbazole unit **2** was synthesized by our gold catalyzed cascade cyclization of aniline-substituted arenyl diyne **1**.⁵ Lithiation and iodination of 2-position of thienyl moiety of **2** followed by Suzuki-Miyaura coupling of the resulting iodide with thiophen-2-ylboronic acid gave intermediate **3** in high yield. Further lithiation of **3** and iodination followed by Suzuki-Miyaura coupling with 5-formylthiophen-2-ylboronic acid or 5-formylfuran-2-ylboronic acid afforded the corresponding aldehydes **4** and **5**, which reacted with cyanoacetic acid under typical Knoevenagel condensation to afford the desired dyes **K-1** and **K-2** in high yields, respectively.

Scheme 1. Synthesis of new **K**-dyes. (a) NaAuCl_4 , Ethanol, 100 °C. (b) $n\text{-BuLi}$, I_2 , THF, -78 °C. (c) thiophen-2-ylboronic acid, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, K_2CO_3 , $\text{DME}/\text{H}_2\text{O}/\text{EtOH}$, reflux. (d) $n\text{-BuLi}$, I_2 , THF, -78 °C. (e) 5-formylthiophen-2-ylboronic acid or 5-formylfuran-2-ylboronic acid, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, K_2CO_3 , $\text{DME}/\text{H}_2\text{O}/\text{EtOH}$, reflux. (f) $\text{NCCH}_2\text{CO}_2\text{H}$, NH_4OAc , $\text{HOAc}/\text{CH}_3\text{CN}$ 100 °C.

The photophysical properties of **K**-dyes in chloroform and on TiO_2 film are summarized in Table 1. As shown in Figure 2a, **K**-

dyes exhibited broad absorption bands in the visible region, which corresponded to the charge transfer transition. The absorption maximum (λ_{max}) of **K-1** dye (476 nm) based on bithiophene bridge was observed at a slightly longer wavelength region compared to **K-2** dye (472 nm) based on thienylfuran bridge due to decreased electronegativity of sulfur atom, and both of them were longer than that of carbazole analogue **MK-3** (443 nm).^{4a} The molar absorption coefficient (ϵ) at λ_{max} was 42000 $\text{M}^{-1} \text{cm}^{-1}$ for **K-1** and 45000 $\text{M}^{-1} \text{cm}^{-1}$ for **K-2**, respectively. The wide range absorption ability and the relatively high ϵ compared with Ru-complexes indicate that **K**-dyes are suitable photosensitizers for DSCs. When adsorbed on transparent thin TiO_2 film, **K-1** and **K-2** showed broad absorption spectra, similar to those in solution, while the absorption peaks were slightly blue-shifted due to the interaction between the carboxylic group and TiO_2 (Figure 2b). Upon dye adsorption on TiO_2 film, the tails of the absorption spectra of **K**-dyes were red-shifted compared to those in solution; the tails of absorption spectra of **K**-dyes extended up to 650 nm, which are desirable for harvesting solar spectrum and lead to a large photocurrent.

Figure 2. Absorption spectra of **K**-dyes in chloroform (a) and (b) on a transparent TiO_2 film.

The ionization potential (IP) of **K**-dyes bound to the nanocrystalline TiO_2 film was measured using the photoemission yield spectrometer (Riken Keiki, AC-3E) (Fig. S1, Table 1). The IP values, which correspond to ground-state oxidation potential ($S^+/0$), were found to be -5.48 eV for **K-1** and **K-2**, which were sufficiently lower than the redox potential of I^-/I_3^- (-5.20 eV),¹⁰ ensuring the favorable thermodynamic ground states for efficient regeneration of the dye through the reaction of the oxidized dye with iodide. The onset of the optical energy gap (E_{0-0}) of **K-1** and **K-2** were 2.04 eV and 2.08 eV, respectively. The excited-state oxidation potential (S^{+*}) of sensitizers **K-1** and **K-2** were -3.44 eV and -3.40 eV, respectively, which lied above the conduction band edge (-4.2 eV)^{1c} of the nanocrystalline TiO_2 , ensuring efficient electron injection into the conduction band edge of TiO_2 from the adsorbed **K**-sensitizers.

Table 1. Photophysical properties and DSCs performance parameters of **K**-dyes.

dye	$\lambda_{\max}^a/\text{nm}$ ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\max}^b/\text{nm}$ on TiO_2 (IP) ^c (eV)	E_{0-0} (eV)	$S^{+/*e,d}$ (eV)	J_{sc} [mA cm^{-2}]	V_{oc} [V]	[ff]	η [%]	
K-1	476 (4.2)	442	-5.48	2.04	-3.44	12.40	0.70	0.759	6.62
K-2	472 (4.5)	437	-5.48	2.08	-3.40	12.49	0.71	0.756	6.73

^a Absorption maxima, measured in chloroform at room temperature.

^b Absorption measured on a transparent 4 μm TiO_2 film.

^c Ionization potential (IP) of adsorbed dyes on the nanocrystalline TiO_2 film was determined by using the photoemission yield spectrometer (Riken Keiki, AC-3E).

^d The excited-state oxidation potential, $S^{+/*}$ levels were calculated from the expression of $S^{+/*} = \text{IP} + E_{0-0}$.

Figure 3. (a) IPCEs of nanocrystalline TiO_2 film sensitized by **K**-dyes. (b) I - V characteristics of **K**-dyes.

Incident photon-to-current conversion efficiencies (IPCEs) for DSCs based on **K**-dyes are plotted in Figure 3a. The IPCEs of **K-1** and **K-2** are consistent with the UV-visible absorption spectra of dyes adsorbed on TiO_2 films. The maximum quantum efficiency of **K**-dyes reached up to 88% in the plateau region, implying that the rigid structures of **K**-dyes should be favorable for efficient electron injection quantum yield, which resulted from high intramolecular charge transfer of the increased molecular planarity. The maximum IPCE value of **K-2** dye was slightly higher than that of **K-1** dye in the range of 350 nm to 550 nm, as the increment of the planarity of the **K-2** (see DFT calculation), while the absorption wavelength of **K-1** was slightly red-shifted than that of **K-2** dye. The solar cell performance for the DSCs is listed in Table 1, and the corresponding I - V curves are shown in Figure 3b. Dye **K-2** with thienylfuran as a π -bridge showed a slightly higher conversion efficiency of 6.73% than that of the bithiophene π -bridge based dye **K-1** (6.62%), being mainly ascribed to the higher J_{sc} and V_{oc} for **K-2** dye (12.49 mA cm^{-2} and 0.71 V) than that of **K-1** dye (12.40 mA cm^{-2} and 0.70 V). It should be noted that η (6.62–6.73%) of **K**-dyes were higher than that of the reference dye **MK-3** (4.7–4.8%)^{4a} with carbazole as

donor unit, although direct comparison between them may be not necessarily pertinent.¹¹ The relatively high V_{oc} of **K**-dyes was ascribed to the *n*-octyl substituent on thienocarbazole moiety and the deoxycholic acid (DCA) co-adsorbent which prevented the serious molecular aggregation on TiO_2 film, decreasing the charge recombination between the TiO_2 and the electrolyte.

In order to gain more insights and better understanding into the relationship between electronic structure and molecular geometry of these dyes, the frontier orbitals and the interplanar angle between the donor and acceptor moieties were calculated using density functional theory (DFT) with B3LYP functional and 6-31+G(d) basis set. The optimized geometries of **K**-dyes showed that the HOMOs of **K-1** and **K-2** sensitizers are mainly delocalized on the electron donor moiety, which facilitates the reduction with I^- , and makes dye regeneration more efficient (Figure 4). On the other hand, the LUMOs are delocalized on the π^* cyanuric unit and have significant contributions from the carboxylic group, which facilitates electron injection from the photo-excited sensitizer into the TiO_2 semiconductor. This clearly confirms that this structural motif is an excellent design for efficient charge transfer in DSCs. Moreover, as shown in Figure 5, the torsion angles between thienocarbazole unit and thiophene ring are about 13.6° for **K-1** and 6.9° for **K-2**, respectively, while the torsion angle between carbazole unit and thiophene ring is about 29.6° for **MK-3**. The torsion angles between thienocarbazole and thiophene in **K**-dyes are much smaller than that between carbazole and thiophene in **MK-3** dyes. It should be noted that the calculated bandgaps of **K**-dyes are larger than **MK-3** (2.51 eV and 2.58 eV vs 2.42 eV, Figure S2), but the obtained maximum IPCEs for **K**-dyes are higher than that of **MK-3**, indicating the increased intramolecular charge transfer in the formers, and hence the more efficient electron injection.⁶

Figure 4. Frontier orbitals of **K-1** and **K-2** dyes were calculated at the B3LYP/6-31+G(d) level of theory using the GAUSSIAN 09 program package.

Figure 5. The calculated interplanar angles between the donor and acceptor moieties of **K**-dyes and **MK-3** at the B3LYP/6-31G+(d) level of theory.

3. Conclusion

In conclusion, we synthesized a series of novel **K**-dyes based on thienocarbazole moiety as a donor unit in the D- π -A system for nanocrystalline TiO₂ solar cells. The **K**-dyes showed higher IPCEs compared with their carbazole analogue dye **MK-3** due to their enhanced coplanar geometries, without significant decrease of V_{oc} , which led to the good power conversion efficiencies of 6.62% and 6.73%. The molecular geometry calculation of **K**-dyes and **MK-3** dye indicated that the existence of thienocarbazole as donor enhanced the molecular planarity, which might facilitate the intramolecular charge transfer and electron injection from excited dye to TiO₂ band, leading to high efficiencies. With the aid of molecular modeling, molecular engineering and synthesis in our laboratory are underway to develop a novel and more efficient thienocarbazole dye that have the potential to exhibit significant increase in DSC performance across a wider range of the solar spectrum.

4. Experimental section

4.1. General information

¹H NMR and ¹³C NMR spectra were recorded on JEOL JMT-270/54/SS (JASTEC, 400 MHz) and BRUKER (600 MHz) spectrometers. ¹H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shifts of CDCl₃ at 7.26 ppm and DMSO-*d*₆ at 2.49 ppm, respectively, integration, multiplicities (s = singlet, d = doublet and m = multiple), and coupling constants (Hz). ¹³C NMR spectra reported in ppm (δ) relative to the central line for CDCl₃ at 77 ppm and DMSO-*d*₆ at 39.7 ppm, respectively. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. The ionization potential (IP) of dyes bound to the nanocrystalline TiO₂ film was measured using the photoelectron spectrometer surface analyzer (Riken Keiki, AC-3E). DFT geometry-optimized structure of the lowest-energy conformer of **K**-dyes and **MK-3** dye, HOMO and LUMO energy levels were calculated at the B3LYP/6-31+G(d) level of theory using the GAUSSIAN 09 program package. Column chromatography was carried out employing Silica gel 60N (spherical, neutral, 40–100 μ m, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm pre-coated plate Kieselgel 60 F254 (Merck). All other reagents and solvents commercially available were used without further purification unless otherwise noted. Compound 1 was prepared following the reported procedure.¹²

4.2. Synthesis of **K**-dyes

4.2.1. 10-Octyl-5-phenyl-10H-thieno[2,3-*a*]carbazole (**2**)

A mixture of **1** (2.9 mmol) and NaAuCl₄ (10 mmol%) in dry ethanol was heated at 100 °C in sealed vial overnight. After TLC monitor, the reaction mixture was filtered by Florisil, and the

filtrate was concentrated in vacuum. The crude mixture was purified with silica-gel column chromatography (hexane/CH₂Cl₂ = 5/1) to produce the desired compound **2** in a 81% yield as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.77–7.40 (m, 11H), 7.06 (dd, J = 7.6, 7.6 Hz, 1H), 4.69 (t, J = 7.6 Hz, 2H), 2.10–1.95 (m, 2H), 1.67–1.55 (m, 2H), 1.53–1.25 (m, 8H), 0.95 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.4, 139.9, 139.1, 135.4, 135.1, 129.4, 128.3, 127.3, 125.0, 124.5, 124.4, 123.0, 122.1, 120.5, 118.9, 116.5, 116.4, 108.7, 44.8, 31.9, 30.8, 29.4, 29.3, 27.1, 22.7, 14.2; HRMS (+ESI): m/z : calcd for C₂₈H₂₉NSNa (M+Na⁺), 434.1913; found, 434.1913.

4.2.2. 10-Octyl-5-phenyl-2-(thiophen-2-yl)-10H-thieno[2,3-*a*]carbazole (**3**)

To a THF solution of compound **2** (2.3 mmol) was added the *n*-BuLi (2.5 mmol, 1.63 M in hexane) over 5 min at -78 °C under N₂. The mixture was stirred at -78 °C for 30 minutes, and then I₂ (2.5 mmol) was subsequently added to the mixture and stirred at -78 °C for 5 min. The mixture was slowly warm to room temperature. The reaction was quenched with a saturated Na₂S₂O₃ solution, and the mixture was extracted with diethyl ether. The organic layer was washed with brine and dried over Na₂SO₄. After evaporation of the solvent, the crude mixture was purified with silica-gel column chromatography (hexane/CH₂Cl₂ = 4/1) to give the 2-iodinized product in a quantitative yield. ¹H NMR (400 MHz, CDCl₃) δ 7.69(s, 1H), 7.67–7.38 (m, 9H), 7.07–7.02(m, 1H), 4.52 (t, J = 7.6 Hz, 2H), 2.12–1.92 (m, 2H), 1.60–1.52 (m, 2H), 1.50–1.26 (m, 8H), 0.95 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.9, 139.9, 139.8, 135.1, 134.7, 134.2, 129.3, 128.3, 127.4, 124.9, 124.8, 122.7, 122.2, 119.0, 116.6, 115.1, 108.7, 75.5, 44.6, 31.8, 30.6, 29.3, 29.2, 27.0, 22.7, 14.2; HRMS (+ESI): m/z : calcd for C₂₈H₂₈INSNa (M+Na⁺), 560.0879; found, 560.0879.

A mixture of the above 2-iodinized product (0.37 mmol) and thiophen-2-ylboronic acid (0.555 mmol), PdCl₂(PPh₃)₂ (5 mol%), K₂CO₃ (2.0 equiv.) in DME/ethanol/water was refluxed for overnight. After cooling to room temperature, the reaction mixture was filtered and the filtrate was washed with a saturated NH₄Cl solution. The combined extract was dried over anhydrous Na₂SO₄. After concentration, the solid crude mixture was purified with silica-gel column chromatography (hexane/CH₂Cl₂ = 4/1) to give the compound **3** in a 94% yield as orange solid. ¹H NMR (400 MHz, CDCl₃) δ 7.76–7.27 (m, 12H), 7.20–7.00 (m, 2H), 4.62 (t, J = 7.6 Hz, 2H), 2.15–1.95 (m, 2H), 1.70–1.53 (m, 2H), 1.53–1.25 (m, 8H), 0.95 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 141.2, 140.1, 139.6, 137.2, 135.6, 135.4, 135.0, 129.3, 128.3, 127.8, 127.4, 125.2, 124.7, 124.6, 123.0, 122.1, 121.0, 119.4, 118.9, 116.9, 116.4, 108.7, 44.8, 31.9, 30.7, 29.4, 29.2, 27.1, 22.7, 14.2; HRMS (+ESI): m/z : calcd for C₃₂H₃₁NS₂Na (M+Na⁺), 516.1789; found, 516.1790.

4.2.3. 5'-(10-Octyl-5-phenyl-10H-thieno[2,3-*a*]carbazol-2-yl)-[2,2'-bithiophene]-5-carbaldehyde (**4**)

To a THF solution of compounds **3** (0.80 mmol), the *n*-BuLi (1.0 mmol, 1.63 M in hexane) was added over 5 min at $-78\text{ }^{\circ}\text{C}$ under N_2 . The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 minutes, and I_2 (1.1 mmol) was subsequently added to the mixture and stirred at $-78\text{ }^{\circ}\text{C}$ for 5 min. The mixture was allowed to slowly warm to room temperature. The reaction was then quenched with an aqueous $\text{Na}_2\text{S}_2\text{O}_3$ saturated solution, and the mixture was extracted into diethyl ether. The organic layer was washed with brine and dried over Na_2SO_4 . After evaporation of solvent, the crude mixture was purified with silica-gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2 = 4/1$) to give the corresponding iodide as yellow solid in 100% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.70-7.58 (m, 2H), 7.58-7.47 (m, 3H), 7.50 (s, 1H), 7.47-7.30 (m, 3H), 7.44 (s, 1H), 7.23 (d, $J = 3.6\text{ Hz}$, 1H), 7.06-6.97 (m, 2H), 4.59 (t, $J = 7.6\text{ Hz}$, 2H), 2.05-1.90 (m, 2H), 1.60-1.50 (m, 2H), 1.49-1.20 (m, 8H), 0.90 (t, $J = 6.8\text{ Hz}$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 141.1, 140.1, 139.4, 137.7, 135.6, 134.9, 134.3, 129.3, 128.3, 127.5, 125.9, 124.8, 123.0, 122.1, 121.5, 119.4, 119.0, 117.2, 116.4, 108.8, 73.0, 44.9, 31.9, 30.7, 29.4, 29.2, 27.1, 22.7, 14.2; HRMS (+EI): m/z : calcd for $\text{C}_{32}\text{H}_{30}\text{NS}_2\text{I}(\text{M}^+)$, 619.0864; found, 619.0864.

A mixture of above iodide (0.287 mmol) and 5-formylthiophen-2-ylboronic acid, $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mmol%), K_2CO_3 (2.0 equiv.) in DME/ethanol/water was refluxed for overnight. After cooling to room temperature, the mixture was filtered and the filtrate was washed with an aqueous NH_4Cl saturated solution. The combined organic layer was dried over anhydrous Na_2SO_4 . After concentration of solvent, the solid crude was purified with silica-gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2 = 1/1$) to give the compound **4** as an orange solid in 60% yield. ^1H NMR (400 MHz, CDCl_3) δ 9.85 (s, 1H), 7.70-7.60 (m, 4H), 7.58-7.47 (m, 3H), 7.46-7.36 (m, 3H), 7.36-7.22 (m, 4H), 7.00 (dd, $J = 7.6, 7.6\text{ Hz}$, 1H), 4.62 (t, $J = 8.0\text{ Hz}$, 2H), 2.05-1.93 (m, 2H), 1.65-1.50 (m, 2H), 1.47-1.22 (m, 8H), 0.89 (t, $J = 6.8\text{ Hz}$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.2, 146.4, 141.7, 141.0, 140.2, 139.5, 138.9, 137.2, 135.8, 135.3, 134.9, 134.5, 129.3, 128.4, 127.5, 126.8, 125.5, 124.9, 124.1, 123.0, 122.2, 121.9, 119.7, 119.1, 117.4, 116.5, 108.8, 44.9, 31.9, 30.8, 29.4, 29.3, 27.1, 22.7, 14.2; HRMS (+ESI): m/z : calcd for $\text{C}_{37}\text{H}_{33}\text{NOS}_3\text{Na}(\text{M}+\text{Na}^+)$, 626.1615; found, 626.1617.

4.2.4. Synthesis of **K-1** dye

A mixture of aldehyde **4** (0.14 mmol), 2-cyanoacetic acid (0.448 mmol), and ammonium acetate (0.08 mmol) in acetonitrile/acetic acid was heated at $100\text{ }^{\circ}\text{C}$ in sealed vial for overnight. After evaporation of the solvent, the crude solid was purified by silica-gel column chromatography (CHCl_3 followed by $\text{CHCl}_3/\text{EtOH} = 10/1$) to give **K-1** as a red solid in 86% yield. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.08 (s, 1H), 7.91 (s, 1H), 7.70-7.63 (m, 2H), 7.60-7.48 (m, 8H), 7.50 (s, 1H), 7.37 (dd, $J = 8.0, 8.0\text{ Hz}$, 1H), 7.14 (d, $J = 8.0\text{ Hz}$, 1H), 6.96 (dd, $J = 8.0, 8.0\text{ Hz}$, 1H), 4.61 (t, $J = 7.6\text{ Hz}$, 2H), 1.89-1.75 (m, 2H), 1.49-1.40 (m, 2H), 1.38-1.12 (m, 8H), 0.81 (t, $J = 6.4\text{ Hz}$, 3H); ^{13}C NMR (100 MHz, $\text{THF}-d_8/\text{DMSO}-d_6$) δ 167.1, 143.0, 142.5, 141.1, 140.2, 139.7, 137.4, 136.1, 135.9, 135.4, 134.8, 134.6, 129.2, 128.3, 127.4, 126.4, 125.9, 124.7, 124.5, 122.7, 121.7, 121.6, 119.2, 118.8, 118.3, 116.9, 116.4, 109.2, 106.3, 44.2, 31.8, 30.6, 29.3, 29.2, 26.8, 22.6, 13.8; HRMS (+ESI): m/z : calcd for $\text{C}_{40}\text{H}_{34}\text{N}_2\text{O}_2\text{S}_3\text{Na}(\text{M}+\text{Na}^+)$, 693.1675; found, 693.1675.

4.2.5. 5-(5-(10-Octyl-5-phenyl-10H-thieno[2,3-a]carbazol-2-yl)thiophen-2-yl)furan-2-carbaldehyde (**5**)

A mixture of above iodide (0.263 mmol), the procedure is shown in the synthesis of **4**, 5-formylfuran-2-ylboronic acid, $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mol%), and K_2CO_3 (2.0 equiv.) in dry DME/Ethanol/water was refluxed for overnight. After cooling to

room temperature, the mixture was filtered, and the filtrate was washed with an aqueous NH_4Cl saturated solution. The combined organic layer was dried over anhydrous Na_2SO_4 . After concentration of solvent, the solid crude was purified with silica-gel column chromatography (hexane/ $\text{CH}_2\text{Cl}_2 = 1/1$) to give the compound **5** as an orange solid in 56% yield. ^1H NMR (400 MHz, CDCl_3) δ 9.63 (s, 1H), 7.65-7.26 (m, 13H), 7.00 (dd, $J = 7.2, 7.2\text{ Hz}$, 1H), 6.70 (d, 3.6 Hz, 1H), 4.63 (t, $J = 8.0\text{ Hz}$, 2H), 2.05-1.93 (m, 2H), 1.65-1.50 (m, 2H), 1.49-1.22 (m, 8H), 0.89 (t, $J = 6.4\text{ Hz}$, 3H); ^{13}C NMR (100 MHz, CDCl_3) two aromatic peaks are not shown due to superimposition; δ 176.6, 154.1, 151.5, 141.0, 140.2, 139.5, 139.4, 135.8, 134.9, 134.5, 130.7, 129.3, 128.4, 127.5, 126.9, 125.4, 124.9, 122.9, 122.2, 122.0, 119.1, 117.4, 116.5, 108.8, 107.8, 44.9, 31.9, 30.8, 29.5, 29.3, 27.1, 22.7, 14.2; HRMS (+EI): m/z : calcd for $\text{C}_{37}\text{H}_{33}\text{O}_2\text{NS}_2(\text{M}^+)$, 587.1953; found, 587.1953.

4.2.6. Synthesis of **K-2** dye

A mixture of aldehyde **5** (0.14 mmol), 2-cyanoacetic acid (0.448 mmol), and ammonium acetate (0.08 mmol) in acetonitrile/acetic acid was heated at $100\text{ }^{\circ}\text{C}$ in sealed vial for overnight. After evaporation of the solvent, the crude solid was purified by silica-gel column chromatography (CHCl_3 followed by $\text{CHCl}_3/\text{EtOH} = 10/1$) to give compounds **K-2** as a dark red solid in 95% yield. ^1H NMR (400 MHz, $\text{THF}-d_8$) δ 7.91 (s, 1H), 7.71 (s, 1H), 7.60-7.20 (m, 12H), 6.90-6.80 (m, 2H), 4.63 (t, $J = 7.6\text{ Hz}$, 2H), 1.99-1.84 (m, 2H), 1.55-1.48 (m, 2H), 1.47-1.22 (m, 8H), 0.83 (t, $J = 6.4\text{ Hz}$, 3H); ^{13}C NMR (100 MHz, $\text{THF}-d_8$) one aromatic peak is not shown due to superimposition δ 163.1, 153.8, 148.1, 141.4, 140.4, 139.8, 139.2, 136.8, 135.8, 134.8, 134.6, 130.9, 129.2, 128.2, 127.3, 125.8, 124.8, 124.1, 122.9, 122.1, 121.9, 119.6, 118.9, 117.4, 116.5, 115.4, 109.2, 108.9, 98.1, 44.6, 32.0, 30.8, 29.5, 29.3, 27.0, 22.7, 13.6; HRMS (+ESI): m/z : calcd for $\text{C}_{40}\text{H}_{33}\text{O}_3\text{N}_2\text{S}_2(\text{M}-\text{H}^+)$, 653.1938; found, 653.1937.

4.3. Fabrication of dye sensitized solar cells

A double-layer TiO_2 photoelectrode ($10 + 5\text{ }\mu\text{m}$ in thickness with a $10\text{ }\mu\text{m}$ thick nanoporous layer and a $5\text{ }\mu\text{m}$ thick scattering layer (area: 0.25 cm^2) was prepared by screen printing on conducting glass substrate. A dye solution of K-dyes with $3 \times 10^{-4}\text{ M}$ concentration in acetonitrile/*tert*-butyl alcohol (1/1, v/v) was used to up take the dye on to the TiO_2 film. Deoxycholic acid (DCA) (20 mM) as a co-adsorbent was added into the dye solution to prevent aggregation of the dye molecules. The TiO_2 films were immersed into the dye solution and then kept at $25\text{ }^{\circ}\text{C}$ for 30 h. Photovoltaic measurements were performed in a sandwich type solar cell in conjunction with an electrolyte consisting of a solution of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05M I_2 , 0.1M LiI and 0.5M *tert*-butylpyridine (TBP) in acetonitrile (AN). The dye-deposited TiO_2 film and a platinum-coated conducting glass were separated by a Surlyn spacer ($40\text{ }\mu\text{m}$ thick) and sealed by heating the polymer frame. Potocurrent density-voltage (I - V) of sealed solar cells was measured under AM 1.5G simulated solar light at a light intensity of 100 mW cm^{-2} with a metal mask of 0.25 cm^2 . The photovoltaic parameters, *i.e.* short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (η) were estimated from I - V characteristics under illumination. The photoemission yield curves were measured with a Riken Keiki Co. Ltd. model AC-3E photoelectron spectrometer surface analyzer under atmosphere with a $0.2\text{ ml min}^{-1}\text{ N}_2$ flow.

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