Electronic Supplementary Information

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

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General information

$^1$H NMR and $^{13}$C NMR spectra were recorded on JEOL JMT-270/54/SS (JASTEC, 400 MHz) and (JASTEC (700 MHz) spectrometers. $^1$H NMR spectra are reported as follows: chemical shift in ppm ($\delta$) relative to the chemical shifts of CDCl$_3$ at 7.26 ppm and DMSO-$d_6$ at 2.49 ppm, respectively. $^{13}$C NMR spectra reported in ppm ($\delta$) relative to the central line for CDCl$_3$ 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 TiO$_2$ film was measured using the photoelectron spectrometer surface analyser (Riken Keiki, AC-3E). Optimized ground state geometry of the lowest-energy conformer of K-dyes were calculated using the hybrid DFT energy functional B3LYP and the basis set of DGDZVP (density Gauss double-$\zeta$ with polarization functions). Column chromatography was carried out employing Silica gel 60N (spherical, neutral, 40~100 µm, KANTO Chemical Co.). All other reagents and solvents commercially available were used without further purification unless otherwise noted. Intermediates 2a and 2b were prepared according to the reported method.[1,2]


Fabrication of the DSCs

A double-layer TiO$_2$ photoelectrode (10 + 5) µm in thickness with a 10 µm thick nanoporous layer and a 5 µm 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 x 10$^{-4}$ 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 °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), 0.05 M I$_2$, 0.1M LiI and 0.5 M 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 µm thick) and sealed by heating the polymer frame. Photocurrent density-voltage (I-V) of sealed solar cells was measured under AM 1.5 G simulated solar light at a light intensity of 100 mW cm$^{-2}$ with a metal
mask of 0.25 cm². The photovoltaic parameters, i.e. short circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and power conversion efficiency ($\eta$) 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 analyser under atmosphere with a 0.2 mL min⁻¹ N₂ flow. The adsorption amounts of dyes on the surface of TiO₂ films that were prepared under the same conditions with those fabricated into cells. TiO₂ films sensitized with K-dyes were immersed into 0.1 M NaOH solution for desorption of the dyes. The amounts of desorbed dyes were evaluated by their corresponding absorbance spectra.

**Electrochemical impedance spectroscopy (EIS) and intensity modulated photo-voltage spectroscopy (IMVS) measurements**

The IMVS spectra were measured with a potentiostat (Solartron 1287) equipped with a frequency response analyser (Solartron 1255B) at an open-circuit condition, based on a monochromatic illumination (420 nm) controlled by Lab-view system, to obtain the photovoltaic response induced by the modulated light. The modulated light was driven with a 10% AC perturbation current superimposed on a DC current in a frequency range from 0.1 to $10^6$ Hz. The charge extraction method (CEM) was performed with the same monochromatic light source. The solar cell was illuminated at an open-circuit condition for 5s to attain a steady state and then the light source was switched off when the device simultaneously switched to a short-circuit condition to extract the charges generated at that light intensity. The electrochemical impedance spectra were measured with an impedance analyser (Solartron Analytical, 1255B) connected with a potentiostat (Solartron Analytical, 1287) under illumination using a solar simulator (WXS-155S-10: Wacom Denso Co. Japan). EIS spectra were recorded over a frequency range of $10^{-2}$ to $10^6$ Hz at 298 K. The applied bias voltage and AC amplitude were set at the $V_{oc}$ of the DSCs. The electrical impedance spectra were characterized using Z-View software (Solartron Analytical).

**Ionization Potentials (IP) of K-dyes**
Fig S1 Ionization potentials of K-dyes.

**Electrochemical cyclic voltammetry (CV) measurement of K-dyes**

Potential values are versus Ag/AgCl reference electrode; 0.1 M TBAPF₆ as a supporting electrolyte in dichloromethane; redox potential of ferrocene is 0.37 V (vs Ag/AgCl) and we take the energy level of Fc/Fc⁺ as -4.8 eV. The HOMO energy levels of K-dyes were calculated from the onset of the first oxidation potential ($E_{1ox}$) according to the equation, HOMO = (-4.43 + $E_{1ox}$) (eV);

**K-3**: $E_{1ox}$: 1.24 eV; HOMO: 5.67 eV  
**K-4**: $E_{1ox}$: 1.16 eV; HOMO: 5.59 eV  
**K-5**: $E_{1ox}$: 1.12 eV; HOMO: 5.55 eV
Fig. S2 Cyclic voltammograms of K-dyes.

DFT calculation of K-dyes

HOMO

LUMO

structure

K-3

K-4

K-5

Fig. S3 The DFT calculation of the frontier orbitals and the optimized ground state structures of K-dyes.
Synthesis of K-dyes and analytic data

A mixture of 4a (2.9 mmol) and NaAuCl₄ (5 mol%) 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 1a in a 92% yield as a yellow oil. 1a: 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, 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.

10-Octyl-5-phenyl-2-(thiophen-2-yl)-10H-thieno[2,3-a]carbazole (1a)

10-(3,5-Di-tert-butyl-4-methoxyphenyl)-5-phenyl-10H-thieno[2,3-a]carbazole (1b)

1b' (R = H) was prepared in 61% yield under the same conditions with 1a by using 4b a starting substrate. To the mixture of 1b' (202 mg, 0.675 mmol), 5-bromo-1,3-di-tert-butyl-2-methoxybenzene (182 mg, 1.08 mmol), CuI (13 mg, 0.0675 mmol), N,N-dimethylethylene diamine (DMEDA, 30 μL, 0.27 mmol), and K₃PO₄ (286 mg, 1.35 mmol) was added toluene (3 mL) at room temperature under argon. The reaction mixture was then heated to 120 °C for 24 h. After removal of the solvent, the residue was directly transferred into silica gel chromatography using hexane/ethyl acetate (10:1) as eluent, yielding the corresponding product 1b (297 mg, 85%) as a yellow solid. 1b: ¹H NMR (400 MHz, CDCl₃) δ 7.77-7.72 (m, 2H), 7.63-7.51 (m, 4H), 7.50-7.45 (m, 4H), 7.40-7.30 (m, 3H), 7.10-7.05 (m, 1H), 3.92 (s, 3H), 1.53 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 145.1, 141.5, 141.3, 139.3, 136.0, 134.9, 130.9, 129.4,
128.3, 127.7, 127.3, 125.9, 124.7, 124.2, 122.9, 121.9, 121.2, 119.4, 116.7, 116.2, 109.9, 64.8, 36.1, 32.0;
HRMS (ESI): m/z: calcd for C_{35}H_{35}ONS (M+H^+), 518.2512; found, 518.2511.

10-Ethyl-5-phenyl-10H-thieno[2,3-a]carbazole (1c)
1c was prepared in a 91% yield under the same conditions with 1a by using 4c as a starting substrate. 1c: ^1^H NMR (400 MHz, CDCl$_3$) δ 8.10-8.03 (m, 2H), 7.95-7.80 (m, 5H), 7.78-7.68 (m, 3H), 7.64 (d, J = 5.6 Hz, 1H), 7.47-7.40 (m, 1H), 4.90 (q, J = 7.6 Hz, 2H), 1.80 (t, J = 7.2 Hz, 3H);

Synthesis of K-3

5''-(10-Octyl-5-phenyl-10H-thieno[2,3-a]carbazol-2-yl)-[2,2':5',2''-terthiophene]-5-carbaldehyde (3a)

Under an argon atmosphere, 1.6 M of n-BuLi (0.52 mL, 0.84 mmol) in hexane was added to 1a (288 mg, 0.7 mmol) in dry THF (10 mL) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C before 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxabororane (195 mg, 1.05 mmol) was added. After stirring for 12 h at room temperature, the reaction was quenched with a saturated NH$_4$Cl aqueous solution and was extracted with Et$_2$O for 3 times. The organic layer was combined and dried with Na$_2$SO$_4$. After concentration, the residue was purified by silica gel chromatography using hexane/EtOAc (10:1) as eluents, giving the corresponding aldehyde 3a (318 mg, 80% from 2a) as a red solid. 3a: ^1^H NMR (400
K-3 dye

To a solution of 3a (103 mg, 0.15 mmol) and cyanoacetic acid (38 mg, 0.45 mmol) in chloroform (1.5 mL) and acetonitrile (1.5 mL) was added piperidine (104 μL, 1.05 mmol). The reaction mixture then refluxed for 20 h. After removal of the solvent, the residue was purified by silica gel column chromatography using CHCl₃:EtOH (10:1 v/v) as eluents, giving K-3 as a dark red solid (85%, 96 mg).

**K-3**: ¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 1H), 7.66-7.22 (m, 15H), 7.13 (d, J = 8.0 Hz, 1H), 6.88 (dd, J = 7.6, 7.6 Hz, 1H), 4.42 (broad, 3H), 1.78-1.75 (m, 2H), 1.41-1.20 (m, 10H), 0.81 (t, J = 6.8 Hz, 3H); ¹³C NMR is not shown due to low solubility; HRMS (ESI): m/z: calcd for C₄₄H₃₅O₂N₂S₄ (M-H⁺), 751.1586; found, 751.1585.

**Synthesis of K-4 dye**

![Diagram of synthetic process]

5″-(10-(3,5-Di-tert-butyl-4-methoxyphenyl)-5-phenyl-10H-thieno[2,3-a]carbazol-2-yl)-[2,2′:5′,2″-terthiophene]-5-carbaldehyde (3b)

3b was prepared in 81% yield as a red solid by using the similar procedure of 3a from 1b. 3b: ¹H NMR (400 MHz, CDCl₃) δ 9.75 (s, 1H), 7.79-7.68 (m, 2H), 7.63-7.55 (m, 3H), 7.52 (d, J = 0.8 Hz, 1H), 7.50-7.45 (m, 4H), 7.44 (s, 1H), 7.42-7.33 (m, 2H), 7.15 (d, J = 3.6 Hz, 1H), 7.11-7.05 (m, 2H), 7.04 (d, J = 4.0 Hz, 1H), 6.99 (d, J = 4.0 Hz, 1H), 6.96 (d, J = 3.6 Hz, 1H), 3.96 (s, 1H), 1.57 (s, 18H); ¹³C NMR (100
MHz, CDCl$_3$) δ 182.0, 160.3, 146.2, 145.1, 141.6, 141.3, 141.0, 139.7, 138.3, 137.3, 137.0, 135.9, 135.5, 135.4, 134.4, 130.7, 129.3, 128.3, 127.5, 127.4, 126.7, 125.0, 124.9, 124.7, 124.4, 123.8, 122.9, 121.9, 120.5, 120.1, 119.6, 116.9, 116.7, 109.9, 64.9, 36.1, 32.0; HRMS (ESI): m/z: calcd for C$_{48}$H$_{41}$O$_2$NS$_4$ (M$^+$), 791.2014; found, 791.2014.

**K-4 dye**

K-4 dye was synthesized in 86% yield using the similar procedure of K-3 from 3b. K-4: red solid; $^1$H NMR (400 MHz, DMSO-$d_6$/CDCl$_3$) δ 8.22 (s, 1H), 7.86 (d, $J = 4.0$ Hz, 1H), 7.73 (s, 1H), 7.63-7.45 (m, 8H), 7.42 (s, 2H), 7.35-7.20 (m, 5H), 7.14 (d, $J = 3.6$ Hz, 1H), 6.99 (t, $J = 8.0$ Hz, 1H), 3.88 (s, 3H), 1.47 (s, 18H); $^{13}$C NMR (100 MHz, DMSO-$d_6$/CDCl$_3$) δ 163.3, 160.0, 144.8, 141.1, 140.4, 140.0, 139.6, 137.3, 136.2, 135.2, 135.1, 134.9, 134.4, 134.1, 130.0, 128.9, 128.4, 127.6, 127.1, 125.9, 125.5, 125.4, 125.3, 124.9, 122.3, 121.2, 120.9, 119.6, 119.3, 116.7, 116.6, 116.3, 109.7, 64.7, 39.1, 31.6; HRMS (ESI): m/z: calcd for C$_{51}$H$_{41}$O$_3$N$_2$S$_4$ (M-H$^+$), 857.2005; found, 857.2004.

**Synthesis of K-5**

3,4',4''-Trihexyl-5''-ido-[2,2':5',2''-terthiophene]-5-carbaldehyde (2b)[2]

2b: $^1$H NMR (400 MHz, CDCl$_3$) δ 9.76 (s, 1H), 7.52 (s, 1H), 7.06 (s, 1H), 6.78 (s, 1H), 2.76 (t, $J = 8.0$ Hz, 2H), 2.68 (t, $J = 8.0$ Hz, 2H), 2.52 (t, $J = 8.0$ Hz, 2H), 1.75-1.55 (m, 6H), 1.50-1.30 (m, 18H), 0.90 (t, $J = 6.0$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 181.8, 147.4, 140.5, 140.0, 139.9, 139.8, 139.5, 138.6, 132.5, 132.1, 129.8, 126.3, 74.6, 32.1, 31.5, 31.5, 30.3, 30.0, 29.8, 29.3, 29.1, 29.0, 28.8, 22.5, 14.0, 14.0; HRMS (ESI): m/z: calcd for C$_{31}$H$_{43}$IOS$_3$ (M$^+$), 654.1515; found, 654.1515.

5''-(10-Ethyl-5-phenyl-10H-thieno[2,3-a]carbazol-2-yl)-3,4',4''-triethxyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (3c)
3c was prepared in 80% yield under the similar procedure with the 3a and 3b using 2b as an aldehyde source instead of 2a from 1c. 3c: 1H NMR (400 MHz, CDCl₃) δ 9.82 (s, 1H), 7.72-7.65 (m, 2H), 7.62-7.47 (m, 8H), 7.46-7.38 (m, 2H), 7.16 (s, 1H), 7.10 (s, 1H), 7.05 (dd, J = 7.2, 7.2 Hz, 1H), 4.76 (q, J = 7.2 Hz, 2H), 2.94 (dd, J = 7.6, 7.6 Hz, 2H), 2.86 (dd, J = 7.2, 7.2 Hz, 2H), 2.84 (dd, J = 7.2, 7.2 Hz, 2H), 1.85-1.68 (m, 6H), 1.63 (t, J = 7.2 Hz, 3H), 1.55-1.35 (m, 18H), 1.00-0.93 (m, 9H); 13C NMR (100 MHz, CDCl₃) δ 182.2, 141.1, 141.0, 140.9, 140.2, 140.1, 139.9, 139.6, 139.2, 138.8, 135.5, 134.6, 134.3, 134.1, 132.6, 132.5, 130.8, 130.3, 129.2, 129.0, 128.2, 127.4, 124.7, 123.3, 123.1, 122.1, 120.2, 119.0, 116.8, 116.3, 108.4, 39.4, 31.6, 31.6, 31.6, 30.7, 30.4, 30.2, 29.5, 29.4, 29.3, 29.2, 29.1, 22.6, 22.6, 22.6, 15.7, 14.1, 14.1; HRMS (ESI): m/z: calcd for C₅₃H₉₉O₄NS₄ (M+H⁺), 854.3552; found, 854.3551.

K-5 dye

K-5 dye was synthesized in 83% yield under the similar procedure with K-3 and K-4 dyes from 3c. K-5: red solid; 1H NMR (400 MHz, DMSO-d₆/CDCl₃) δ 8.00 (s, 1H), 7.67 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.60-7.50 (m, 7H), 7.36 (t, J = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.14 (s, 1H), 6.94 (dd, J = 7.6, 7.6 Hz, 1H), 4.70 (q, J = 7.6 Hz, 2H), 2.87-2.72 (m, 6H), 1.75-1.50 (m, 6H), 1.50-1.20 (m, 21H), 0.90-0.82 (m, 9H); 13C NMR (100 MHz, DMSO-d₆/CDCl₃) δ 163.8, 143.7, 141.0, 140.5, 140.3, 139.9, 139.3, 139.3, 137.8, 135.0, 134.0, 133.6, 133.4, 133.3, 132.1, 131.4, 130.2, 130.0, 129.1, 128.8, 128.3, 127.6, 127.5, 124.8, 123.2, 122.3, 121.5, 121.2, 119.4, 118.9, 117.4, 117.0, 116.2, 116.2, 109.1, 56.0, 30.9, 30.9, 29.9, 29.7, 29.4, 28.8, 28.6, 28.5, 28.4, 28.4, 21.9, 18.3, 15.3, 13.7; HRMS (ESI): m/z: calcd for C₅₆H₉₉O₃N₂S₄ (M-H+), 919.3464; found, 919.3464.
NMR spectra