

Supplementary Information

Development of D- π -A dye with benzothienopyridine as electron-withdrawing anchoring group for dye-sensitized solar cells

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Experimental Section:

General: Melting points were measured with a Yanaco micro melting point apparatus MP model. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. High-resolution mass spectral data were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. ^1H NMR spectra were recorded on a Varian-400 (400 MHz) FT NMR spectrometer with tetramethylsilane as an internal standard. Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer and fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yield in 1,4-dioxane was determined by using a calibrated integrating sphere system ($\lambda_{\text{ex}} = 408 \text{ nm}$). Cyclic voltammetry (CV) curves were recorded in acetonitrile/ Bu_4NClO_4 (0.1M) 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 highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of **SAT-1** were evaluated from the spectral analyses and the CV data. The HOMO energy level was evaluated from the $E_{1/2}^{\text{ox}}$. The LUMO energy level was estimated from the $E_{1/2}^{\text{ox}}$ and an intersection of absorption and fluorescence spectra (458 nm; 2.71 eV), which correspond to the energy gap between the HOMO and the LUMO.

Synthesis of 4-(2-bromo-4-chlorophenyl)-3-fluoropyridine (1)

To a mixture of 3-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (3.51 g, 15.7 mmol), 2-bromo-4-chloro-1-iodobenzene (5.00 g, 15.7 mmol), $\text{PdCl}_2(\text{dppf})_2$ (0.64 g, 0.785 mmol), and Na_2CO_3 (1.48 g, 14.0 mmol) under an argon atmosphere was added water (8 ml) and DMF (60 ml) and stirred for 48 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract were evaporated under reduced pressure. The residue was

chromatographed on silica gel (dichloromethane–ethyl acetate = 3 : 1 as eluent) to give **1** (1.566 g, yield 35 %) as a light yellow viscous solid; IR (ATR): $\tilde{\nu}$ = 1608, 1463, 1411 cm^{-1} ; ^1H NMR (400 MHz, acetone- d_6) δ = 7.42–7.44 (m, 1H), 7.50 (d, J = 8.3 Hz, 1H), 7.61 (dd, J = 2.1 and 8.3 Hz, 1H), 7.87 (d, J = 2.1 Hz, 1H), 8.55 (dd, J = 1.1 and 4.8 Hz, 1H), 8.64 (d, J = 1.4 Hz, 1H), HRMS (APCI): m/z (%): $[\text{M}+\text{H}^+]$ calcd for $\text{C}_{11}\text{H}_7\text{NBrClF}$, 285.94289; found 285.94354.

Synthesis of 3-((5-chloro-2-(3-fluoropyridin-4-yl)phenyl)thio)-propionic acid ethyl ester (**2**)

A solution of **1** (1.566 g, 5.44 mmol), 3-mercaptopropionic acid ethyl ester (0.804 g, 5.99 mmol), bis[2-(diphenylphosphanyl)phenyl]ether (0.194 g, 0.36 mmol), $\text{Pd}_2(\text{dba})_3$ (0.165 g, 0.18 mmol), and K_2CO_3 (1.83 g, 13.7 mmol) in toluene (30 mL) was stirred for 42 h at 110 °C under an argon atmosphere. The reaction mixture was quenched with an aqueous solution of acetic acid (30 mL) and diluted with ethyl acetate. The two layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate–*n*-hexane = 1 : 2 as eluent) to give **2** (1.556 g, yield 84 %) as a light yellow viscous solid; IR (ATR): $\tilde{\nu}$ = 1731, 1607, 1493, 1461 cm^{-1} ; ^1H NMR (400 MHz, acetone- d_6) δ = 1.18 (t, J = 7.1 Hz, 3H), 2.59 (t, J = 7.0 Hz, 2H), 3.20 (t, J = 7.0 Hz, 2H), 4.05 (q, 2H), 7.34–7.42 (m, 3H), 7.64 (d, J = 2.0 Hz, 1H), 8.50 (dd, J = 1.2 and 4.8 Hz, 1H), 8.57 (d, J = 1.5 Hz, 1H); HRMS (ESI): m/z (%): $[\text{M}+\text{H}^+]$ calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{NCIF}_5$, 340.05688; found 340.05725.

Synthesis of 7-chlorobenzo[4,5]thieno[2,3-*c*]pyridine (BTP-Cl)

A solution of **2** (1.556 g, 4.58 mmol) and potassium *tert*-butoxide (0.771 g, 6.87 mmol) in THF (20 mL) was stirred for 15 h at 50 °C under an argon atmosphere. The reaction mixture was quenched with an aqueous solution of acetic acid (20 mL) and diluted with ethyl acetate. The two layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate–*n*-hexane = 1 : 1 as eluent) to give **BTP-Cl** (0.848 g, yield 84 %) as a white solid; m.p. 104–106 °C; IR (ATR): $\tilde{\nu}$ = 1595, 1440, 1400 cm^{-1} ; ^1H NMR (400 MHz, acetone- d_6) δ = 7.63 (dd, J = 1.9 and 8.5 Hz, 1H), 8.21 (d, J = 1.5 Hz, 1H), 8.27 (dd, J = 1.0 and 5.3 Hz, 1H), 8.48 (d, J = 8.5 Hz, 1H), 8.67 (d, J = 5.4 Hz, 1H), 9.27 (d, J = 1.0 Hz, 1H); HRMS (ESI): m/z (%): $[\text{M}+\text{H}^+]$ calcd for $\text{C}_{11}\text{H}_7\text{NClS}$, 219.99822; found 219.99857.

Synthesis of 4-bromo-*N,N*-bis(4-ethoxyphenyl)aniline (**3**)

A solution of 4-iodophenetole (3.0 g, 12.0 mmol), 4-bromoaniline (1.00 g, 5.8 mmol), CuI (0.1 g, 0.58 mmol), 1,10-phenanthroline (1.00 g, 0.58 mmol), and KOH (2.6 g, 46.4 mmol) in toluene (14 mL) was stirred for 18 h at 125 °C under an argon atmosphere. The reaction mixture was quenched with 1N HCl (14 mL) and diluted with water, and then the solution was extracted with dichloromethane. The dichloromethane extract were evaporated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane–*n*-hexane = 1 : 5 as eluent) to give **3** (1.786 g, yield 75 %) as a purple viscous solid; IR (ATR): $\tilde{\nu}$ = 1584, 1501, 1233 cm⁻¹; ¹H NMR (400 MHz, acetone-*d*₆, TMS) δ = 1.36 (t, *J* = 7.2 Hz, 6H), 4.04 (q, 4H), 6.74 (d, *J* = 9.2 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 4H), 7.05 (d, *J* = 8.8 Hz, 4H), 7.29 (d, *J* = 9.2 Hz, 2H); HRMS (ESI): *m/z* (%):[M+H⁺] calcd for C₂₂H₂₃O₂NBr, 412.09067; found 412.09094.

Synthesis of 4-ethoxy-*N*-(4-ethoxyphenyl)-*N*-(4-(thiophen-2-yl)phenyl)aniline (**4**)

To a mixture of **3** (1.266 g, 3.1 mmol), 2-thiopheneboronic acid (0.392 g, 3.1 mmol), PdCl₂(PPh₃)₂ (0.125 g, 0.15 mmol), and Na₂CO₃ (0.289 g, 2.73 mmol) under an argon atmosphere was added water (3 ml) and DMF (12 ml) and stirred for 15 h at 100 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract were evaporated under reduced pressure. The residue was chromatographed on silica gel (toluene as eluent) to give **4** (2.52 g, yield 63 %) as a yellow viscous solid; IR (ATR): $\tilde{\nu}$ = 1601, 1496, 1232 cm⁻¹; ¹H NMR (400 MHz, acetone-*d*₆) δ = 1.35 (t, *J* = 7.0 Hz, 6H), 4.03 (q, 4H), 6.84 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 4H), 7.03–7.07 (m, 5H), 7.28 (dd, *J* = 1.1 and 3.6 Hz, 1H), 7.32 (dd, *J* = 1.1 and 5.2 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 2H); HRMS (ESI): *m/z* (%):[M+H⁺] calcd for C₂₆H₂₆O₂NS, 416.16788; found 416.16821.

Synthesis

of

4-ethoxy-*N*-(4-ethoxyphenyl)-*N*-(4-(5-(trimethylstannyl)thiophen-2-yl)phenyl)aniline (**5**)

To a THF solution (100 mL) of **4** (0.669 g, 1.6 mmol) under an argon atmosphere was added 1.6M hexane solution of *n*BuLi (2 ml) at –78 °C. After stirring for 1 h, Me₃SnCl (0.32 g, 1.6 mmol) was added and the solution was stirred at –78 °C for 2h. After then, the solution was stirred at room temperature for 10 h. The reaction was quenched with water, and then the solution was extracted with dichloromethane. The dichloromethane extract was evaporated and the residue was chromatographed on silica gel (toluene as eluent) to give **5** (1.01 g, yield 73%) as a yellow viscous solid; IR (ATR): $\tilde{\nu}$ = 1601, 1502, 1233 cm⁻¹; ¹H NMR (400 MHz, acetone-*d*₆) δ = 0.37 (s, 9H), 1.36 (t, *J* = 7.2 Hz, 6H), 4.03 (q, 4H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 4H), 7.06 (d, *J* = 9.0 Hz, 4H), 7.17 (d, *J* = 3.4 Hz, 1H), 7.38 (d, *J* = 3.4 Hz,

1H), 7.47 (d, $J = 8.9$ Hz, 2H); HRMS (ESI): m/z (%): $[M+H^+]$ calcd for $C_{29}H_{34}O_2N_2SSn$, 580.13267; found 580.13239.

Synthesis of 4-(5-(benzo[4,5]thieno[2,3-*c*]pyridin-7-yl)thiophen-2-yl)-*N,N*-bis(4-ethoxyphenyl)aniline (SAT-1)

A solution of **BTP-Cl** (0.420 g, 2.01 mmol), **5** (1.285 g, 2.22 mmol), Pd-PEPPSI-*i*Pr (0.055 g, 0.08 mmol), CsF (0.61 g, 4.04 mmol) in 1,4-dioxane (10 mL) was stirred for 20 h at 60 °C under an argon atmosphere. The reaction mixture was diluted with water, and then the solution was extracted with dichloromethane. The dichloromethane extract were evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate as eluent) to give a crude solid, which was then subjected to reprecipitation from dichloromethane–hexane to give **SAT-1** (0.407 g, yield 34 %) as an orange solid; m.p.221–224 °C; IR (ATR): $\tilde{\nu} = 1594, 1502, 1227$ cm^{-1} ; 1H NMR (400 MHz, acetone- d_6) $\delta = 1.36$ (t, $J = 7.2$ Hz, 6H), 4.05 (q, 4H), 6.88 (d, $J = 8.8$ Hz, 2H), 6.93 (d, $J = 9.0$ Hz, 4H), 7.09 (d, $J = 9.0$ Hz, 4H), 7.39 (d, $J = 3.9$ Hz, 1H), 7.55 (d, $J = 8.8$ Hz, 2H), 7.67 (d, $J = 3.9$ Hz, 1H), 7.92 (dd, $J = 1.6$ and 8.3 Hz, 1H), 8.25 (dd, $J = 0.9$ and 5.3 Hz, 1H), 8.41 (d, $J = 1.2$ Hz, 1H), 8.48 (d, $J = 8.3$ Hz, 1H), 8.64 (d, $J = 5.3$ Hz, 1H), 9.24 (d, $J = 0.9$ Hz, 1H); HRMS (ESI): m/z (%): $[M+H^+]$ calcd for $C_{37}H_{31}N_2O_2S_2$, 599.18215; found 599.18182. Anal. calcd for $C_{37}H_{30}N_2O_2S_2$: C 74.22, H 5.05, N 4.68; found C 74.04, H 5.13, N 4.67.

Synthesis of 4-(2-bromophenyl)-3-fluoropyridine (6)

To a mixture of 3-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-pyridine (1.0 g, 4.48 mmol), 1-bromo-2-iodobenzene (1.268 g, 4.48 mmol), $PdCl_2(dppf)_2$ (0.183 g, 0.224 mmol), and Na_2CO_3 (0.183 g, 3.99 mmol) under an argon atmosphere was added water (1 ml) and DMF (10 ml) and stirred for 12 h at 90 °C. After concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The dichloromethane extract were evaporated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane–ethyl acetate = 3 : 1 as eluent) to give **6** (0.583 g, yield 52 %) as a light yellow viscous solid; IR (ATR): $\tilde{\nu} = 1609, 1463, 1408$ cm^{-1} ; 1H NMR (400 MHz, acetone- d_6 , TMS) $\delta = 7.40$ – 7.47 (m, 3H), 7.53– 7.57 (m, 1H), 7.80 (d, $J = 8.4$ Hz, 1H), 8.54 (dd, $J = 1.2$ and 4.8 Hz, H), 8.61 (d, $J = 1.2$ Hz, H); HRMS (ESI): m/z (%): $[M+H^+]$ calcd for $C_{11}H_8NBrF$, 251.98187; found 251.98209.

Synthesis of 3-((2-(3-fluoropyridin-4-yl)phenylthio)-propionic acid ethyl ester (7)

A solution of **6** (0.583 g, 2.31 mmol), 3-mercaptopropionic acid ethyl ester (0.341 g, 2.54

mmol), bis[2-(diphenylphosphanyl)phenyl]ether (0.124 g, 0.231 mmol), Pd₂(dba)₃ (0.105 g, 0.115 mmol), and K₂CO₃ (0.799 g, 5.80 mmol) in toluene (15 mL) was stirred for 48 h at 110 °C under an argon atmosphere. The reaction mixture was quenched with an aqueous solution of acetic acid (15 mL) and diluted with ethyl acetate. The two layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate–*n*-hexane = 1 : 2 as eluent) to give **7** (0.365 g, yield 52 %) as a light yellow viscous solid; IR (ATR): $\tilde{\nu}$ = 1729, 1607, 1460 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆, TMS) δ = 1.17 (t, *J* = 7.2 Hz, 3H), 2.53 (t, *J* = 7.2 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 4.04 (q, 2H), 7.32–7.42 (m, 3H), 7.49–7.53 (m, 1H), 7.65 (dd, *J* = 1.2 and 8.0 Hz, 1H), 8.50 (dd, *J* = 1.2 and 4.8 Hz, 1H), 8.56 (d, *J* = 1.6 Hz, 1H); HRMS (ESI): *m/z* (%):[M+H⁺] calcd for C₁₁H₈NBrF, 306.09585; found 306.09583.

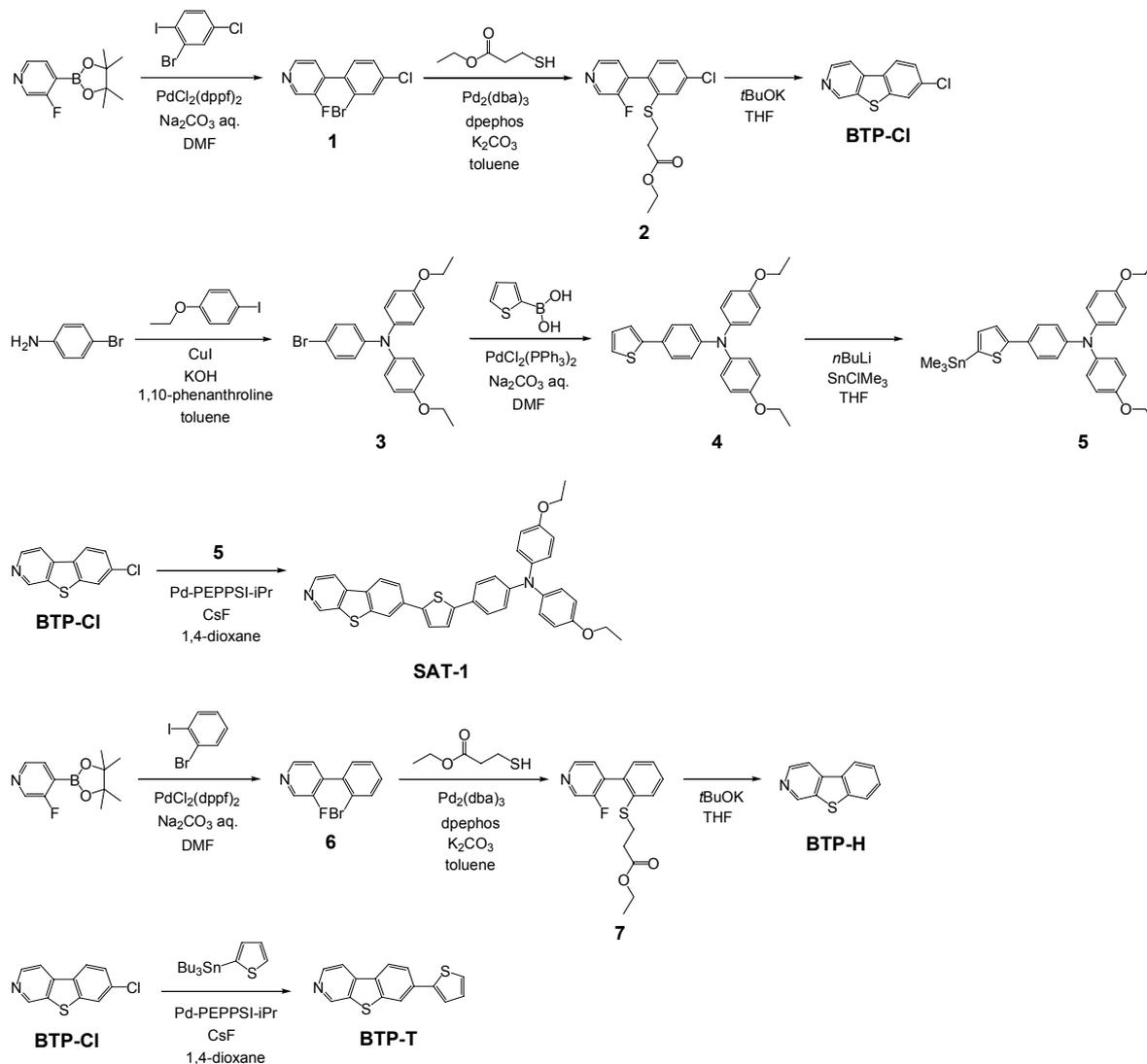
Synthesis of benzo[4,5]thieno[2,3-*c*]pyridine (BTP-H)

A solution of **7** (0.365 g, 1.20 mmol) and potassium *tert*-butoxide (0.201 g, 1.79 mmol) in THF (6 mL) was stirred for 18 h at 50 °C under an argon atmosphere. The reaction mixture was quenched with an aqueous solution of acetic acid (20 mL) and diluted with ethyl acetate. The two layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were evaporated under reduced pressure. The residue was chromatographed on silica gel (dichloromethane–ethyl acetate = 3 : 1 as eluent) to give **BTP-H** (0.134 g, yield 60 %) as a white solid; m.p.103–105 °C; IR (ATR): $\tilde{\nu}$ = 1593, 1541, 1397 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆, TMS) δ = 7.59–7.63 (m, 1H), 7.67–7.71 (m, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.27 (dd, *J* = 1.2 and 5.2 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.65 (d, *J* = 5.2 Hz, 1H), 8.25 (d, *J* = 1.2 Hz, 1H); HRMS (ESI): *m/z* (%):[M+H⁺] calcd for C₁₁H₈NS, 186.03720; found 186.03700.

Synthesis of 7-(thiophen-2-yl)benzo[4,5]thieno[2,3-*c*]pyridine (BTP-T)

A solution of **BTB-Cl** (0.10 g, 0.46 mmol), tributyl(thiophen-2-yl)stannane (0.187 g, 0.50 mmol), Pd-PEPSI-*i*Pr (0.012 g, 0.02 mmol), CsF (0.138 g, 0.91 mmol) in 1,4-dioxane (2 mL) was stirred for 17 h at 60 °C under an argon atmosphere. The reaction mixture was diluted with water, and then the solution was extracted with dichloromethane. The dichloromethane extract were evaporated under reduced pressure. The residue was chromatographed on silica gel (ethyl acetate–*n*-hexane = 1 : 1 as eluent) to give a crude solid, which was then subjected to reprecipitation from dichloromethane–hexane to give **BTP-T** (0.02 g, yield 17 %) as a light yellow solid; m.p.218–221 °C; IR (ATR): $\tilde{\nu}$ = 1595, 1448, 1405 cm⁻¹; ¹H NMR (400 MHz, acetone-d₆, TMS) δ = 7.21 (dd, *J* = 3.6 and 5.2 Hz, 1H), 7.58 (dd, *J*

= 1.2 and 5.2 Hz, 1H), 7.70 (dd, $J = 0.8$ and 3.6 Hz, 1H), 7.92 (dd, $J = 1.6$ and 8.4 Hz, 1H), 8.26 (d, $J = 0.8$ and 5.2 Hz, 1H), 8.42 (d, $J = 1.6$ Hz, 1H), 8.49 (d, $J = 8.4$ Hz, 1H), 8.64 (d, $J = 5.6$ Hz, 1H), 9.25 (d, $J = 0.8$ Hz, 1H); HRMS (ESI): m/z (%): $[M+H^+]$ calcd for $C_{15}H_{10}NS_2$, 268.02492; found 268.02493.



Scheme S1. Synthesis of compounds SAT-1, BTP-H, and BTP-CI and BTP-T.

Computational Methods: The semi-empirical calculation was carried out with the WinMOPAC Ver. 3.9 package (Fujitsu, Chiba, Japan). Geometry calculation in the ground state was made using the AM1 method. The geometry was completely optimized (keyword PRECISE) by the eigenvector following routine (keyword EF). Experimental absorption spectrum of the compound was compared with its absorption data by the semi-empirical method INDO/S (intermediate neglect of differential overlap/spectroscopic). INDO/S calculation was performed using single excitation full SCF/CI (self-consistent field/configuration interaction), which included the configuration with one electron excited from any occupied orbital to any unoccupied orbital, where 225 configurations were considered [keyword CI (15 15)].

Preparation of the Dye-Sensitized Solar Cells Based on Dye SAT-1: The TiO₂ 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 TiO₂ electrode (0.5×0.5 cm² in photoactive area) was immersed into a 1m M dye solution (with or without CDCA) in THF for a number of hours enough to adsorb the photosensitizer. The DSSCs were fabricated by using the TiO₂ electrode 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 dye-coated film was immersed in a mixed solvent of THF–DMSO–NaOH aq 1 M (5 : 4 : 1), which was used to determine the amount of dye molecules adsorbed onto the film by measuring the absorbance. The quantification of dye was made based on the λ_{max} (410 nm) and the molar extinction coefficient of dye in the above solution. Absorption spectra of the dyes adsorbed on TiO₂ nanoparticles were recorded on the dyes-adsorbed TiO₂ film (thickness of 3 μm) in the transmission mode with a calibrated integrating sphere system.

We examined the durability of the DSSC based on SAT-1 to light soaking. As the result, it was demonstrated the DSSC based on the dye SAT-1 shows a good light-soaking stability under simulated solar light: there is little change in the J_{sc} , V_{oc} , ff , and η values during 24 h of light soaking under a simulated solar light (AM 1.5, 100 mW cm⁻²).

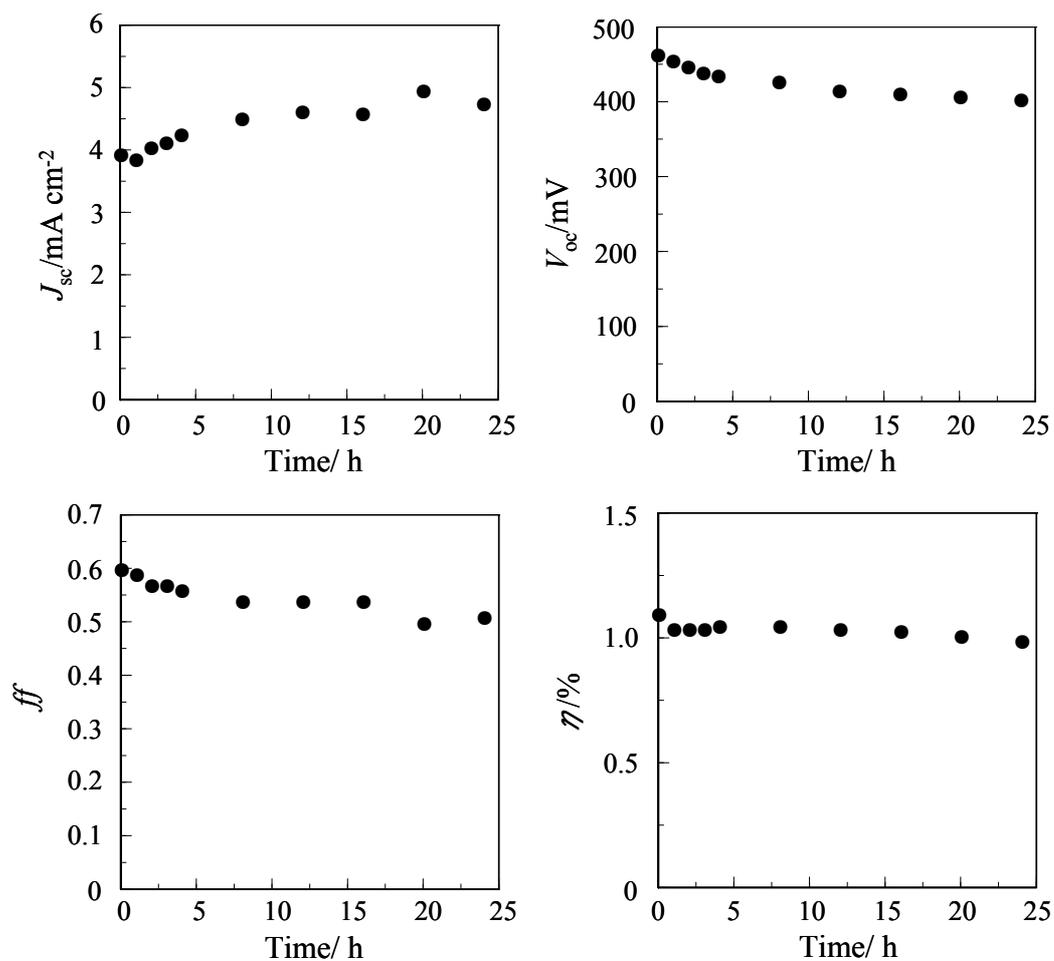


Fig. S2 Photovoltaic parameters (J_{sc} , V_{oc} , ff , and η) with SAT-1 during light soaking (AM 1.5, 100 mW cm⁻²).