Supplementary Informations

Preparation of donor-acceptor type organic dyes bearing various electron-withdrawing groups for dye-sensitized solar cell application

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General
All chemicals and reagents were used as received from chemical companies without further purification. Anhydrous solvents were degassed by Ar bubbling for 20 min. before use. \( p-(N,N\text{-diphenylamino})\text{phenylmethyl triphenylphosphonium bromide} \) was synthesized according to the reported method. Column chromatography was performed using Wakogel-C300 as a stationary phase. UV-Vis-NIR spectra were measured in acetonitrile solution using UV-3600 UV-VIS-NIR Spectrophotometer (SHIMADZU). Photoluminescence spectra were measured using a F-7000 Fluorescent spectrometer (HITACHI High Technologies Corporation). Work functions of the dyes adsorbed onto TiO\(_2\) film was measured using with AC-3E Photoemission yield spectrometer (RIKEN KEIKI). The \(^1\)H- and \(^13\)C-NMR measurements were performed by a DRX-600 spectrometer (Bruker BioSpin). Incident photon-to-current conversion efficiency spectra were measured by a CEP-200BX spectrometer (Bunko Keiki). The \( I-V \) curves were obtained by a WXS-90S-L2 Super solar simulator (WACOM). Photovoltaic parameters are obtained by the measurements on two different cells of each dye.

Preparation
2-Bromo-5-\( p-(N,N\text{-diphenylamino})\text{stylyl} \)thiophene (1)
A suspension of \( p-(N,N\text{-diphenylamino})\text{phenylmethyl triphenylphosphonium bromide} \) (5.0 g, 9.975 mmol) in anhydrous-THF (50 mL) was cooled to \(-78 \text{ °C}\) under Ar atmosphere. To the suspension, 2.0 M lithium diisopropylamide \( n\text{-pentane solution} \) (6.0 mL, 11.969 mmol) was slowly added and the mixture was stirred at the temperature for 1 hours. Then, a solution of 5-bromothiophene-2-carbaldehyde (1.2 mL, 9.975 mmol) in anhydrous-THF (10 mL) was slowly added and stirred for further 1 h keeping the temperature. Then, the reaction mixture was warmed up to room temperature and stirred for overnight. The reaction mixture was quenched by brine, and extracted with CH\(_2\)Cl\(_2\). The organic layer was dried over anhydrous MgSO\(_4\), and the solvent was evaporated under reduced pressure.
The residue was purified by silica-gel column chromatography with mixture of CH$_2$Cl$_2$/n-hexane (1:2 v/v) as an eluent to give 1 (3.4 g, 92%) as a bright yellow solid. $^1$H-NMR (600 MHz, CD$_2$Cl$_2$): $\delta$ 7.31-7.33 (d, 2H), 7.28-7.25 (t, 4H), 7.09-7.08 (d, 4H), 7.06-7.05 (t, 2H), 7.03 (s, 1H), 7.00-6.99 (d, 2H), 6.96-6.95 (d, 1H), 6.79-6.77 (m, 2H); $^{13}$C-NMR (150 MHz, CD$_2$Cl$_2$): 148.10, 147.84, 145.44, 131.02, 130.78, 129.72, 128.75, 127.58, 126.15, 125.09, 123.66, 123.52, 119.71, 110.69; Anal. calcd for C$_{24}$H$_{18}$BrN$_2$: C, 66.67; H, 4.20; N, 3.24. Found: C, 66.77; H, 4.25; N, 3.21.

5´-{4´(N,N-diphenylamino)styryl}-2,2´-bithiophene-5-carbaldehyde (2)
To a suspension of 1 (2.0 g, 5.428 mmol), 2-bromothiophene-5-boronic acid (1.02 g, 6.513 mmol) and K$_2$CO$_3$ (3.0 g) in a mixture of anhydrous-toluene (30 mL) and anhydrous-MeOH (20 mL), a solution of [Pd(dba)$_2$] (156 mg, 0.271 mmol) and XantPhos (156 mg, 0.271 mmol) in anhydrous-toluene (6 mL) and anhydrous-MeOH (4 mL) was added. The mixture was warmed up to 85 °C and refluxed for overnight. To the reaction mixture, brine was added and extracted with CH$_2$Cl$_2$. The organic layer was dried over anhydrous MgSO$_4$, and the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography with CH$_2$Cl$_2$/n-hexane (1:1 v/v) as eluent to give 2 (1.47 g, 59%) as an vivid orange solid. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ 9.85 (s, 1H), 7.67 (d, 1H), 7.35-7.33 (d, 2H), 7.29-7.26 (m, 5H), 7.23 (d, 1H), 7.12-7.11 (d, 4H), 7.07-7.06 (d, 1H), 7.05-7.03 (m, 4H), 6.98-6.97 (d, 1H), 6.92-6.89 (d, 1H); $^{13}$C-NMR (150 MHz, CD$_2$Cl$_2$): 182.73, 148.30, 147.77, 147.23, 145.68, 141.95, 137.86, 134.26, 130.69, 129.83, 129.74, 127.77, 127.25, 127.23, 125.19, 124.46, 123.78, 123.33, 119.58; Anal. calcd for C$_{29}$H$_{21}$NOS$_2$: C, 75.13; H, 4.56; N, 2.83. Found: C, 75.20; H, 4.63; N, 2.83.

$p$-Nitrophenylacetic acid tert-butyldimethylsilyl ester (5a)
A mixture of $p$-nitrophenyl acetic acid (1.0 g, 5.510 mmol), pyridine (0.9 mL, 11.042 mmol), tert-butyldimethylsilyl chloride (1.66 mg, 11.042 mmol) and N,N-dimethylaminopyridine (34 mg, 0.276 mmol) in THF (30 mL) was stirred at 0 °C for overnight. The suspension was extracted with diethylether and water, and then, the organic layer was dried over anhydrous MgSO$_4$. The solvent was removed under reduced pressure. The residual clear oil was
purified by silica-gel column chromatography with ethyl acetate/n-hexane (1:4, v/v) as eluent to give 3a (1.2 g, 73 %) as a pale yellow crystal. $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ 8.13-8.11 (d, 1H), 7.60-7.58 (t, 1H), 7.47-7.45 (t, 1H), 7.36-7.35 (d, 1H), 4.02 (s, 2H), 0.85 (s, 9H), 0.26 (s, 6H); $^{13}$C-NMR (150 MHz, CD$_2$Cl$_2$): 170.59, 142.72, 130.84, 123.90, 43.12, 25.55, 17.87, $-$4.80; Anal. calcd for C$_{14}$H$_{21}$NO$_4$Si: C, 56.92; H, 7.17; N, 4.74. Found: C, 56.86; H, 7.16; N, 4.74.

$\alpha$-Nitrophenylacetic acid tert-butyldimethylsilyl ester (3b)

3b was obtained by similar method with 3a using $\alpha$-nitrophenylacetic acid instead of $p$-nitrophenylacetic acid as a pale yellow solid (74 %). $^1$H-NMR (600 MHz, CD$_2$Cl$_2$): $\delta$ 8.09-8.07 (d, 1H), 7.62-7.60 (t, 1H), 7.48-7.46 (t, 1H), 7.37-7.36 (d, 1H), 4.00 (s, 1H), 0.84 (s, 9H), 0.24 (s, 6H); $^{13}$C-NMR (150 MHz, CD$_2$Cl$_2$): 170.25, 149.23, 133.92, 133.74, 131.04, 128.81, 125.42, 41.73, 25.51, $-$3.47; Anal. calcd for C$_{14}$H$_{21}$NO$_4$Si: C, 56.92; H, 7.17; N, 4.74. Found: C, 57.03; H, 7.24; N, 4.69.

3,3,3-Trifluoropropanoic acid tert-butyldimethylsilyl ester (3c)

3c was obtained by similar method with 3a using 3,3,3-trifluoropropanoic acid instead of $p$-nitrophenylacetic acid as colorless needles (78 %). (This compound sublimes even at room temperature under atmospheric pressure.) $^1$H-NMR (600 MHz, CD$_2$Cl$_2$): $\delta$ 3.23-3.17 (q, 2H), 0.94 (s, 9H), 0.30 (s, 6H); $^{13}$C-NMR (150 MHz, CD$_2$Cl$_2$): 164.43, 126.89-121.41, 41.62-41.02, 25.45, 17.83, $-$3.46; MS spectrum and elemental analysis could not be performed because of sample sublimation.

(E)-2-($p$-nitrophenyl)-3-[5´-{4´-($N,N$-diphenylamino)stylyl}]-2,2´-bithiophen-5-yl]acrylic acid ($p$-$\text{NO}_2\text{Ph}$)

A solution of 2 (50 mg, 0.108 mmol), 3a (48 mg, 0.162 mmol), and piperidine (2 µL, 0.022 mmol) in CH$_3$CN (20 mL) was stirred at 85 °C for 96 h. Then, to the solution, tetra-$n$-butylammonium fluoride trihydrate (51 mg, 0.162 mmol) and trifluoroacetic acid (0.1 mL) was added and stirred at 85 °C overnight. After cooling to room temperature, to the solution, diluted hydrochloric acid was added. The solution was extracted with CH$_2$Cl$_2$ and
the organic layer was dried over anhydrous MgSO₄. The solvent was removed by rotary-evaporator, and the residue was purified by the silica-gel column chromatography with CH₂Cl₂/ AcOH (100:1, v/v) as eluent to give **p-NO₂Ph** (26 mg, 38%) as dark red solid. ¹H-NMR (600 MHz, DMSO-**d₆**): δ 8.36-8.34 (d, 2H), 8.05 (s, 1H), 7.60-7.59 (d, 2H), 7.47-7.44 (m, 3H), 7.34-7.31 (t, 4H), 7.26-7.22 (m, 2H), 7.23-7.22 (d, 1H), 7.09-7.06 (m, 3H), 7.04-7.03 (d, 4H), 6.93-6.92 (d, 2H), 6.88-6.86 (d, 1H) (Proton of CO₂H could not be observed); ¹³C-NMR (150 MHz, DMSO-**d₆**): 172.46, 167.61, 147.97, 147.47, 147.29, 143.76, 143.48, 141.97, 137.17, 136.41, 133.94, 133.76, 132.11, 130.88, 130.09, 128.89, 128.10, 127.98, 126.60, 124.83, 124.47, 124.28, 123.93, 123.03, 120.14; Anal. calcd for C₃₇H₂₆N₂O₄S₂: C, 70.91; H, 4.18; N, 4.47. Found: C, 70.80; H, 4.51; N, 3.97.

**(E)**-2-(o-nitrophenyl)-3-[5’-{4-(N,N-diphenylamino)styryl]-2,2’-bithiophen-5-yl]acrylic acid (**o-NO₂Ph**)

A solution of **2** (50 mg, 0.108 mmol), **3b** (48 mg, 0.162 mmol), and piperidine (2 µL, 0.022 mmol) in CH₃CN (20 mL) was stirred at 85 °C for 96 h. Then, to the solution, tetra-n-butylammonium fluoride trihydrate (51 mg, 0.162 mmol) and trifluoroacetic acid (0.1 mL) was added and stirred at 85 °C for 96 h. After cooling to room temperature, to the solution, dilute hydrochloric acid was added. The solution was extracted with CH₂Cl₂ and the organic layer was dried over anhydrous MgSO₄. The solvent was removed by rotary-evaporator, and the residue was purified by the silica-gel column chromatography with CH₂Cl₂/ AcOH (100:1, v/v) as eluent to give **o-NO₂Ph** (6 mg, 9%) as dark red solid. ¹H-NMR (600 MHz, CD₂Cl₂-**d₅**): δ 8.30-8.29 (d, 1H), 7.99 (s, 1H), 7.89-7.86 (t, 1H), 7.82-7.79 (t, 1H), 7.56-7.54 (d, 1H), 7.51-7.50 (d, 1H), 7.47 (s, 1H), 7.46-7.45 (d, 2H), 7.34-7.31 (t, 4H), 7.28 (d, 1H), 7.26-7.23 (d, 1H), 7.10-7.06 (m, 3H), 7.05-7.03 (d, 4H), 6.92-6.91 (d, 2H), 6.89-6.86 (d, 1H) (Proton of CO₂H could not be observed); ¹³C-NMR (150 MHz, CD₂Cl₂-**d₅**): 167.07, 148.72, 147.47, 147.29, 143.68, 141.54, 140.27, 136.63, 135.29, 133.94, 133.57, 131.15, 131.01, 130.89, 130.10, 128.86, 128.32, 128.16, 128.10, 128.01, 126.33, 125.58, 124.83, 124.38, 123.94, 123.03, 120.15.

**(Z)**-2-trifluoromethyl-3-[5’-{4-(N,N-diphenylamino)styryl]-2,2’-bithiophen-5-yl]acrylic acid (**z-NO₂Ph**)

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yl]acrylic acid (CF₃)

A solution of 2 (50 mg, 0.108 mmol), 3c (39 mg, 0.162 mmol), and piperidine (2 µL, 0.022 mmol) in CH₃CN (20 mL) was stirred at 85 °C for 96 h. Then, to the solution, tetra-n-butylammonium fluoride trihydrate (51 mg, 0.162 mmol) and trifluoroacetic acid (0.1 mL) was added and stirred at 85 °C overnight. After cooling to room temperature, to the solution, diluted hydrochloric acid was added. The solution was extracted with CH₂Cl₂ and the organic layer was dried over anhydrous MgSO₄. The solvent was removed by rotary-evaporator, and the residue was purified by the silica-gel column chromatography with CH₂Cl₂/AcOH (100:1, v/v) as eluent to give 5d (19 mg, 30 %) as dark red solid. ¹H-NMR (600 MHz, DMSO-d₆): δ 7.90 (s, 1H), 7.81-7.80 (d, 1H), 7.50-7.49 (d, 2H), 7.46-7.44 (dd, 2H), 7.34-7.32 (t, 4H), 7.30 (s, 1H), 7.19-7.18 (d, 1H), 7.10-7.07 (t, 2H), 7.06-7.04 (d, 4H), 6.99-6.96 (d, 1H), 6.94-6.93 (d, 2H) (Proton of CO₂H could not be observed); ¹³C-NMR (150 MHz, DMSO-d₆): 163.89, 147.00, 146.71, 145.69, 143.96, 142.17, 133.47, 132.69, 130.27, 129.53, 128.74, 127.61, 126.66, 124.28, 123.50, 123.39, 122.46, 119.58 (Three peaks could not be observed due to the coupling between fluorine atoms); Anal. calcd for C₃₂H₂₂F₃NO₂S₂: C, 67.00; H, 3.87; N, 2.44. Found: C, 66.73; H, 3.97; N, 2.36.
Cell Fabrication

The DSC devices were fabricated as follows. A 22 µm main transparent layer with \textit{ca.} 20 nm sized titania particles and a 6 µm scattering layer with \textit{ca.} 400 nm sized titania particles were screen printed on the fluorine-doped tin oxide (FTO) conducting glass substrate. Coating of the titania film was carried out by immersing in $3 \times 10^{-4}$ M acetonitrile/tert-butyl alcohol (1/1, \(v/v\)) solution of sensitizers for 45 h. Deoxycholic acid (20 mM) was added into the dye solution as a coadsorbant to prevent aggregation of the dye molecules. The dye adsorbed titania film was clipped with a platinized FTO glass used as counter electrode. Finally, the sandwich-type solar cell could be obtained after the injection of an electrolyte consisting of 0.6 mM 1-methyl-3-propylimidazolium iodide, 0.1 mM LiI, 0.2 mM tert-butylpyridine and 0.05 mM I\(_2\) in acetonitrile.
DFT Calculation

Geometry optimization and Molecular orbital distributions of three dyes were performed using B3LYP functional and 6-31G (d,p) basis set implemented in the Gaussian 09 program package.²

Figure S1. HOMO and LUMO distributions of three dyes. HOMO (a) and LUMO (b) of $p$-NO₂Ph, HOMO (c) and LUMO (d) of $o$-NO₂Ph, and HOMO (e) and LUMO (f) of CF₃, respectively.
Figure S2. Side views of the optimized structures of $\sigma$-NO$_2$Ph (left) and $p$-NO$_2$Ph (right) parallel to $\pi$-plane of the bithiophene units and torsion angles between $\pi$-conjugate planes of EWGs and C=C bond.

Figure S3. $J$-$V$ curves of the DSC with three dyes.
Table S1. Photovoltaic parameters of DSCs based on the new dyes.

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<th>Entry</th>
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<th>$J_{SC}$ / mA cm$^{-2}$</th>
<th>$V_{OC}$ / V</th>
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<td>0.685</td>
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Measurements were performed under AM 1.5 irradiation on the DSC devices with 0.25 cm$^2$ active surface area defined by a metal mask. $J_{SC}$, short circuit current; $V_{OC}$, open circuit voltage; FF, fill factor; $\eta$, conversion efficiency.

References
