Supplementary Information

Development of D-π-A dyes with pyrazine ring 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. ^{1}H NMR spectra were recorded on a Varian-400 (400 MHz) and Varian-500 (500 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 (λ_{ex} = 402 nm for **OUK-1** and 397 nm for **OUK-2**, respectively). Cyclic voltammetry (CV) curves were recorded in DMF/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 **OUK-1** and **OUK-2** were evaluated from the spectral analyses and the CV data The HOMO energy level was evaluated from the $E_{1/2}^{ox}$. The LUMO energy level was estimated from the $E_{1/2}^{ox}$ and an intersection of absorption and fluorescence spectra (445 nm; 2.79 eV for **OUK-1** and 458 nm; 2.71 eV for **OUK-2**), which correspond to the energy gap between the HOMO and the LUMO. Electrochemical impedance spectroscopy (EIS) for DSSCs in the dark under a forward bias of −0.60 V with a frequency range of 10 mHz to 100 kHz was measured with a AMETEK Versa STAT 3.

Synthesis of 2-(4'-bromo-2-nitro-[1,1'-biphenyl]-4-yl)thiophene (1)

To a mixture of 4,4'-dibromo-2-nitro-1,1'-biphenyl (2.0 g, 5.6 mmol), thiophen-2-ylboronic acid (0.71 g, 5.6 mmol), and $Pd(PPh_3)_4$ (0.06 g, 0.17 mmol) under an argon atmosphere was added aqueous 1M Na_2CO_3 (2 mL) and DMF (20 ml) and stirred for 24 h at 90 ºC. 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–hexane = 3 : 7 as eluent) to give **1** (1.14 g, yield 57 %) as a light yellow solid; m.p. 124–126 °C; IR (ATR): ν = 1509, 1341, 1058 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6, TMS) δ = 7.23 (dd, J = 3.7 and 5.1 Hz, 1H), 7.37 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 8.1 Hz, 1H), 7.64 (dd, J = 1.2 and 5.1 Hz, 1H), 7.68 (d, J = 8.5 Hz, 2H), 7.74 (dd, J = 1.2 and 3.7 Hz, 1H), 8.04 (dd, J = 2.0 and 8.1 Hz, 1H), 8.23 (d, J = 2.0 Hz, 1H); HRMS (APCI): m/z (%):[M+H$^+$] calcd for $C_{16}H_{11}NO_2BrS$, 359.96884; found 359.96826.

Synthesis of 2'-nitro-*N*,*N*-diphenyl-4'-(thiophen-2-yl)-[1,1'-biphenyl]-4-amine (2)

A solution of **1** (0.70 g, 1.9 mmol), diphenylamine (0.66 g, 3.9 mmol), and $Pd(OAc)_2$ (0.021 g, 0.09 mmol), *t*BuONa (0.24 g, 2.5 mmol) and $(tBu)_3P$ (0.042 g, 0.2 mmol) in toluene (30 ml) was stirred for 24 h at 100 ºC under an argon atmosphere. 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–hexane = 3 : 7 as eluent as eluent) to give **2** (0.68 g, yield 77 %) as a yellow solid; mp 173–175 °C; IR (ATR): ν = 1586, 1482, 1352 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) δ = 7.07 (d, J = 8.5 Hz, 2H), 7.10–7.14 (m, 6H), 7.21–7.23 (m, 1H), 7.30 (d, J = 8.5 Hz, 2H), 7.34–7.38 (m, 4H), 7.61–7.64 (m, 2H), 7.71 (d, J = 2.9 Hz, 1H), 8.00 (dd, J = 1.9 and 8.1 Hz, 1H), 8.15 (d, J = 1.9 Hz, 1H) ppm; HRMS (ESI): m/z:(M+H$^+$) calcd for $C_{28}H_{21}N_2O_2S$, 449.13183; found 449.13165.

Synthesis of *N*,*N*-diphenyl-7-(thiophen-2-yl)-9*H*-carbazol-2-amine (3)

To a mixture of **2** (3.0 g, 6.7 mmol) and PPh_3 (4.4 g, 16.7 mmol) under an argon atmosphere was added *o*-dichloromethane (60 ml) and stirred for 40 h at 160 ºC. 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 (ethyl acetate–hexane = 1 : 5 as eluent as eluent) to give **3** (2.3 g, yield 83 %) as a white solid; m.p. 255–257 °C; IR (ATR): ν = 1584, 1486, 1457 cm^{-1}; ^1H NMR (500 MHz, acetone-d_6, TMS) δ = 6.94 (dd, J = 1.9 and 8.4 Hz, 1H), 7.02–7.06 (m, 2H), 7.10–7.12 (m, 4H), 7.14 (dd, J = 3.6 and 5.1 Hz, 1H), 7.15 (d, J = 1.9 Hz, 1H), 7.28–7.31 (m, 4H), 7.43 (dd, J = 1.1 and 5.1 Hz, 1H), 7.49 (dd, J = 1.1 and 3.6 Hz, 1H), 7.53 (dd, J = 1.6 and 8.1 Hz, 1H), 7.75 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H), 10.22 (-NH, s, 1H); HRMS (APCI): m/z (%):[M+H$^+$] calcd for $C_{28}H_{21}N_2S$, 417.14254; found 417.14200.

Synthesis of 9-butyl-*N*,*N*-diphenyl-7-(thiophen-2-yl)-9*H*-carbazol-2-amine (4)

A solution of **3** (1.0 g, 2.4 mmol) in DMF (25 ml) was treated with sodium hydride (0.2 g, 8.3 mmol) and stirred for 30 min at room temperature. 1-iodobutane (3 ml, 7.0 mmol) was added dropwise and the solution was stirred at room temperature for 2 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 (dichloromethane as eluent) to give **4** (0.8 g, yield 70%) as a white solid; m.p. 148–149 °C; IR (ATR): ν = 1586, 1485, 1455 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d$_6$, TMS) δ = 0.87 (t, *J* = 7.0 Hz, 3H), 1.29–1.34 (m, 2H), 1.76–1.82 (m, 2H), 4.35 (t, *J* = 7.0 Hz, 3H), 6.93 (dd, *J* = 1.9 and 8.4 Hz, 1H), 7.03–7.06 (m, 2H), 7.11–7.14 (m, 4H), 7.15 (dd, *J* = 3.6 and 5.1 Hz, 1H), 7.23 (d, *J* = 1.9 Hz, 1H), 7.29–7.33 (m, 4H), 7.45 (dd, *J* = 1.2 and 5.1 Hz, 1H), 7.52 (dd, *J* = 1.5 and 8.1 Hz, 1H), 7.56 (dd, *J* = 1.2 and 3.6 Hz, 1H), 7.81 (d, *J* = 1.5 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.1 Hz, 1H); HRMS (ESI): *m*/*z* (%):[M+H$^+$] calcd for $C_{32}H_{29}N_2S$, 473.20460; found 473.20389.

Synthesis of 9-butyl-*N*,*N*-diphenyl-7-(5-(trimethylstannyl)thiophen-2-yl)-9*H*-carbazol-2-amine (5)

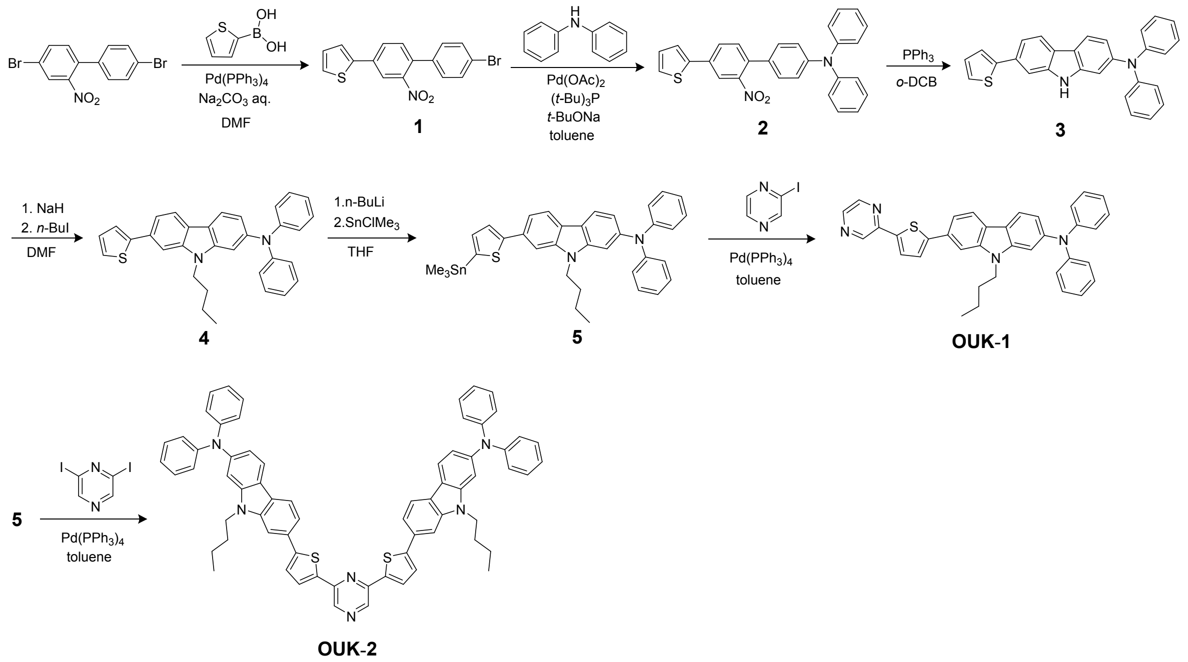
To a THF solution (100 mL) of **4** (0.38 g, 0.8 mmol) under an argon atmosphere was added 1.6M hexane solution of *n*BuLi (0.8 ml) at –78 °C. After stirring for 1 h, Me_3SnCl (0.26 g, 1.3 mmol) was added and the solution was stirred at –78 °C for 1h. After then, the solution was stirred at room temperature for 10 h. The reaction was quenched with water, and then the solution was extracted with ethyl acetate. The ethyl acetate extract were evaporated under reduced pressure. The resulting residue was subjected to reprecipitation from dichloromethane–hexane to give **5** (0.31 g, yield 61 %) as a green powder; ^{1}H NMR (400 MHz, acetone-d$_6$, TMS) δ = 0.41 (s, 9H), 0.87 (t, *J* = 7.4 Hz, 3H), 1.28–1.34 (m, 2H), 1.76–1.81 (m, 2H), 4.34 (t, *J* = 7.0 Hz, 3H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.03–7.06 (m, 2H), 7.11–7.14 (m, 4H), 7.22 (s, 1H), 7.25 (d, *J* = 3.4 Hz, 1H), 7.26–7.33 (m, 4H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.64 (dd, *J* = 3.4 Hz, 1H), 7.80 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H); HRMS (ESI): *m*/*z* (%):[M$^{+\bullet}$] calcd for $C_{35}H_{36}N_2SSn$, 636.16157; found 636.16260.

Synthesis of 9-butyl-*N*,*N*-diphenyl-7-(5-(pyrazin-2-yl)thiophen-2-yl)-9*H*-carbazol-2-amine (OUK-1)

A solution of **5** (0.3 g, 0.47 mmol), 2-iodopyrazine 47 μl, 0.47 mmol), and $Pd(PPh_3)_4$ (0.005 g, 0.0043 mmol) in toluene (2.5 mL) was stirred for 24 h at 100 ºC 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 (dichloromethane as eluent) to give **OUK-1** (0.18 g, yield 69%) as a yellow solid; m.p. 132–134 °C; IR (ATR): ν = 1593, 1489, 1461 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d$_6$, TMS) δ = 0.88 (t, J = 7.3 Hz, 3H), 1.30–1.36 (m, 2H), 1.78–1.83 (m, 2H), 4.39 (t, J = 7.0 Hz, 3H), 6.94 (dd, J = 1.8 and 8.4 Hz, 1H), 7.04–7.07 (m, 2H), 7.12–7.14 (m, 4H), 7.24 (d, J = 1.8 Hz, 1H), 7.30–7.33 (m, 4H), 7.62 (dd, J = 1.5 and 8.1 Hz, 1H), 7.67 (d, J = 3.9 Hz, 1H), 7.92 (d, J = 1.5 Hz, 1H), 7.96 (d, J = 3.9 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H), 8.47 (d, J = 2.5 Hz, 1H), 8.56 (dd, J = 1.6 and 2.5 Hz, 1H), 9.18 (d, J = 1.6 Hz, 1H); HRMS (ESI): *m*/*z* (%):[M+H$^+$] calcd for $C_{36}H_{31}N_4S$, 551.22639; found 551.22589, Anal. calcd for $C_{36}H_{30}N_4S$: C 78.51, H 5.49, N 10.17; found C 78.13, H 8.14, N 9.96.

Synthesis of 7,7'-(pyrazine-2,6-diylbis(thiophene-5,2-diyl))bis(9-butyl-*N*,*N*-diphenyl-9H-carbazol-2-amine) (OUK-2)

A solution of **5** (0.32 g, 0.5 mmol), 2,6-diiodopyrazine (0.08 g, 0.24 mmol), and Pd(PPh$_3$)$_4$ (0.006 g, 0.0052 mmol) in toluene (4 mL) was stirred for 24 h at 110 ºC 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 (dichloromethane–hexane = 1 : 1 as eluent as eluent) to give **OUK-2** (0.17 g, yield 67%) as a yellow solid; m.p. 179–182 °C; IR (ATR): ν = 1593, 1490, 1447 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d$_6$, TMS) δ = 0.90 (t, J = 7.3 Hz, 6H), 1.31–1.37 (m, 4H), 1.80–1.84 (m, 4H), 4.40 (t, J = 7.0 Hz, 6H), 6.95 (dd, J = 1.8 and 8.4 Hz, 2H), 7.04–7.07 (m, 4H), 7.13–7.15 (m, 8H), 7.24 (d, J = 1.8 Hz, 2H), 7.30–7.34 (m, 8H), 7.66 (dd, J = 1.5 and 8.1 Hz, 2H), 7.71 (d, J = 3.9 Hz, 2H), 7.96 (d, J = 1.5 Hz, 2H), 8.01 (d, J = 3.9 Hz, 2H), 8.07 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 8.1 Hz, 2H), 9.01 (s, 2H); HRMS (ESI): *m*/*z* (%):[M+H$^+$] calcd for $C_{68}H_{57}N_6S_2$, 1021.40806; found 1021.40607, Anal. calcd for $C_{68}H_{56}N_6S_2$: C 79.97, H 5.53, N 8.23; found C 79.61, H 5.01, N 8.12.



Scheme S1. Synthesis of compounds **OUK-1** and **OUK-2**.

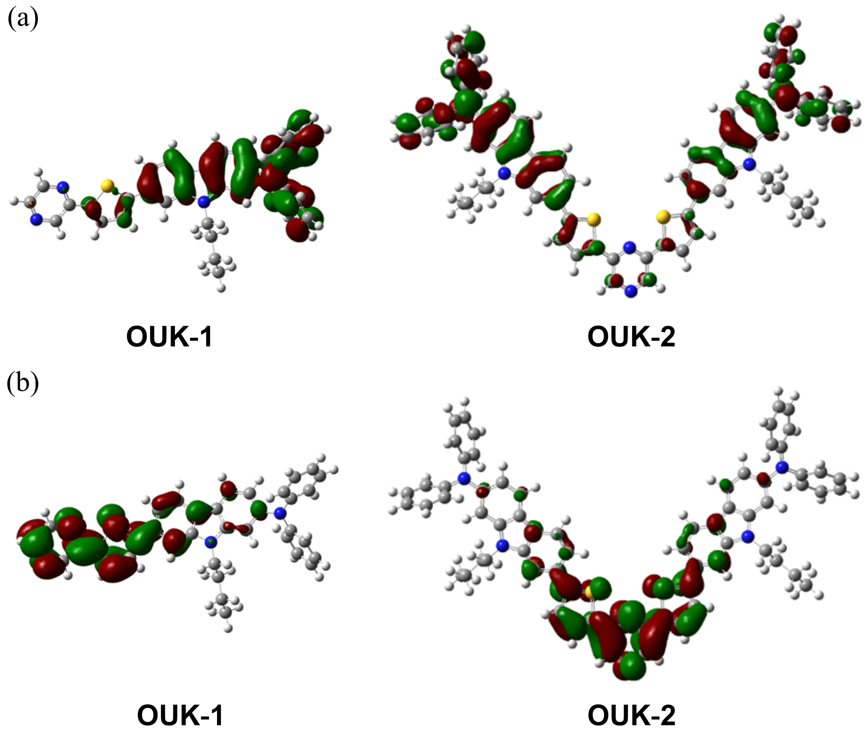


Fig. S1 (a) HOMO and (b) LUMO of **OUK-1** and **OUK-2** by the density functional theory (DFT) calculations at B3LYP/6-31G(d,p) level.

Cyclic voltammetry (CV) curves of **OUK-1** (0.1 mM) and **OUK-2** (0.1 mM) were recorded at a scan rate of 10 mV s^{-1} in DMF/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.

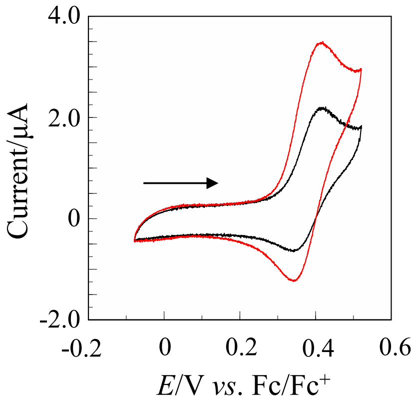


Fig. S2 Cyclic voltammograms of (a) **OUK-1** (0.1 mM) (black) and (b) **OUK-2** (0.1 mM) (red) in DMF containing 0.1 M Bu_4NClO_4 at a scan rate of 10 mV s^{-1}. The arrow denotes the direction of the potential scan.

Table S1 Electrochemical properties of **OUK-1** and **OUK-2**.

Dye	E_{pa}/V[a]	E_{pc}/V[b]	ΔE_p/V	$E_{1/2}^{ox}$/V
OUK-1	0.42	0.35	0.07	0.39
OUK-2	0.42	0.35	0.07	0.39

[a, b] E_{pa} and E_{pc} are the anodic and cathodic peak potentials *vs*. Fc/Fc^+.

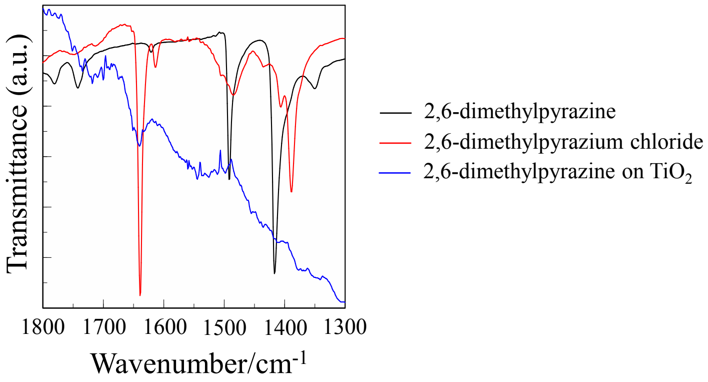


Fig. S3 FTIR spectra of 2,6-dimethylpyrazine (black line), 2,6-dimethylpyrazium chloride (red line) and 2,6-dimethylpyrazine adsorbed on TiO_2 nanoparticles (blue line).

Preparation of the Dye-Sensitized Solar Cells Based on Dyes OUK-1 and OUK-2: The TiO_2 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 ºC. The 9 μm thick TiO_2 electrode (0.5×0.5 cm^2 in photoactive area) was immersed into 0.1 mM or 1 mM dye solution in THF for 15 hours enough to adsorb the photosensitizer. The DSSCs were fabricated by using the TiO_2 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} (405 nm for **OUK-1** and 395 nm for **OUK-2**) and the molar extinction coefficient of dye in the above solution. Absorption spectra of the dyes adsorbed on TiO_2 nanoparticles were recorded on the dyes-adsorbed TiO_2 film (thickness of 9 μm) in the transmission mode with a calibrated integrating sphere system.