Supporting Information for:

Embedding Electron Donor or Acceptor into Naphtho[2,1-*b*:3,4-*b*']dithiophene Based Organic Sensitizers for Dye-Sensitized Solar Cells

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Contents:

1. Experimental Section. S2
2. Materials and Reagents
3. Synthesis. S2
4. Characterizations. ·····S11
5. DSSC Fabrication and Photovoltaic Measurements
6. Table S1. Photophysical and Electrochemical Properties of the Resulted SensitizersS14
7. Figure S1. Cyclic voltammograms of dye-loaded TiO ₂ films. ······S15
8. Figure S2. Calculated frontier molecular orbitals and experimental energy level diagram of
sensitizers FNE50, FNE51, and FNE52. ······S16
9. Figure S3. J-V curves for the quasi-solid-state DSSCs based on the resulted sensitizers. S17
10. Figure S4. Evolutions of photovoltaic performance parameters for FNE52 based
quasi-solid-state DSSC during one sun soaking

Experimental section.

Materials and reagents.

5,6-Dioctyloxy-naphtho[2,1-*b*:3,4-*b*']dithiophene (**1**) and 5,6-dioctyloxy-2-tri-n-butylstannylnaphtho-[2,1-*b*:3,4-*b*']dithiophene were synthesized according to reported method.^[S1] Organic solvents used in this work were purified using standard process. Other chemicals and reagents were used as received from commercial sources without further purification. Transparent conductive glass (F-doped SnO₂, FTO, 15 Ω , transmittance of 80%, Nippon Sheet Glass Co., Japan) was used as the substrate for the fabrication of TiO₂ thin film electrode.

Synthesis.

Scheme S1. Synthetic routes for FNE50, FNE51 and FNE52.^a



^a Reagents and conditions: (a) POCl₃, DMF, chloroform, reflux, 20 h; (b) NBS, DMF, CHCl₃, rt., 12 h; (c) K₂CO₃, Pd(PPh₃)₄, toluene, H₂O, reflux, 16 h; (d) Pd(PPh₃)₄, DMF, 100 °C, overnight; (e) cyanoacetic acid, piperidine, acetonitrile, reflux, 10 h.

Synthesis of compound 2.

To a cold Vilsmeier reagent, which was prepared with 3 mL of POCl₂ in DMF (3 mL), was added a solution of 5,6-dioctyloxy-naphtho-[2,1-b:3,4-b]dithiophene 1 (437 mg, 0.88 mmol) in dry CHCl₃ (80 mL) at 0 °C. The mixture was stirred at 90 °C for 20 hours, and quenched with 10% aqueous solution of NaOAc (30 mL) at 0 °C. After neutralization with 10% NaOH solution to pH = 7, the mixture was extracted by CH_2Cl_2 for three times. The combined organic layer was washed with H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography $(CH_2Cl_2/petroleum ether (PE) = 1/1)$ on silica gel to obtain aldehyde 2 (346 mg, 78%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃, δ ppm): 10.15 (s, 1H), 8.56 (s, 1H), 7.89 (d, 1H, J = 5.4 Hz), 7.70 (s, 1H), 7.68 (s, 1H), 7.63 (d, 1H, J = 5.4 Hz), 4.20-4.24 (m, 4H), 1.93-1.99 (m, 4H), 1.53-1.60 (m, 4H), 1.32-1.44 (m, 16H), 0.89-0.92 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 183.81, 149.58, 149.54, 140.46, 137.23, 136.11, 133.40, 132.55, 126.72, 123.10, 122.94, 106.78, 106.17, 69.45, 32.11, 30.53, 29.95, 29.70, 29.58, 29.48, 26.38, 22.96, 14.40. HRMS: m/z 525.2493 (C₃₁H₄₁O₃S₂, [M + H]⁺, calc. 525.2497).

Synthesis of compound **3**.

A solution *N*-bromosuccinimide (134 mg, 0.75 mmol) of 8 mL dry, nitrogen-flushed dimethylformamide was added dropwise to a cold, stirred solution of compound **2** (332 mg, 0.63 mmol) in CHCl₃ (40 mL). The reaction mixture was stirred at room temperature for 12 hours, and quenched with water (10 mL). The mixture was extracted by CH_2Cl_2 for three

times. The combined organic layer was washed with H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/PE = 1/1) on silica gel to obtain compound **3** (258 mg, 68%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃, δ ppm): 10.12 (s, 1H), 8.46 (s, 1H), 7.80 (s, 1H), 7.61 (s, 1H), 7.47 (s, 1H), 4.16-4.21 (m, 4H), 1.93-1.97 (m, 4H), 1.52-1.64 (m, 4H), 1.31-1.42 (m, 16H), 0.88-0.92 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 183.74, 149.92, 149.74, 140.80, 137.01, 133.46, 132.37, 125.93, 123.28, 121.93, 115.44, 106.40, 106.00, 69.46, 69.43, 32.08, 29.94, 29.91, 29.66, 29.61, 29.55, 29.51, 29.44, 29.41, 26.33, 22.94, 14.38. HRMS: *m/z* 603.1609 (C₃₁H₄₀BrO₃S₂, [M + H]⁺, calc. 603.1602).

Synthesis of compound 9a.

A mixture of compound **3** (118 mg, 0.20 mmol), compound **4** (110 mg, 0.26 mmol), Pd(PPh₃)₄ (80 mg, 0.08 mmol), K₂CO₃ (2.76 g, 0.6 mmol), toulene (30 mL) and H₂O (10 mL) was refluxed for 16 hours under N₂. After cooling, water was added and the reaction mixture was extracted three times with CH₂Cl₂. The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/PE = 1/1) on silica gel to yield the product as a orange solid, **9a** (134 mg, 81%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 10.12 (s, 1H), 8.51 (s, 1H), 7.88 (s, 1H), 7.66 (s, 1H), 7.64 (s, 1H), 7.59 (d, 2H, *J* = 8.4 Hz), 7.12 (d, 4H, *J* = 8.8 Hz), 6.98 (d, 2H, *J* = 8.4 Hz), 6.88 (d, 4H, *J* = 8.8 Hz), 4.21 (t, 4H, *J* = 6.6 Hz), 3.83 (s, 6H), 1.92-1.99 (m, 4H), 1.54-1.61 (m, 4H), 1.32-1.46 (m, 16H), 0.88-0.92 (m, 6H);

¹³C NMR (100 MHz, CDCl₃, δ ppm): 183.60, 156.51, 149.52, 149.43, 149.39, 145.66, 140.45, 139.95, 138.33, 135.92, 132.90, 132.56, 128.23, 127.34, 127.22, 125.51, 123.27, 122.61, 120.04, 118.81, 116.42, 115.04, 114.91, 106.73, 106.17, 69.42, 55.74, 32.12, 29.73, 29.59, 29.53, 26.39, 25.07, 22.96, 14.39. HRMS: *m/z* 828.3750 (C₅₁H₅₈NO₅S₂, [M + H]⁺, calc. 828.3756).

Synthesis of sensitizer FNE50.

A mixture of aldehyde **9a** (105 mg, 0.13 mmol) with cyanoacetic acid (33 mg, 0.39 mmol) in chloroform (20 mL) was refluxed in the presence of piperidine (0.2 mL) for 10 hours under N₂. After cooling, the mixture was diluted with CH₂Cl₂, and washed with water and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/methanol = 10/1) on silica gel to yield the product as a brown powder, **FNE50** (85 mg, 76%). ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 8.73 (s, 1H), 8.44 (s, 1H), 8.35 (s, 1H), 7.96 (s, 1H), 7.88 (s, 1H), 7.71 (d, 2H, *J* = 8.4 Hz), 7.11 (d, 4H, *J* = 8.8 Hz), 6.96 (d, 4H, *J* = 8.8 Hz), 6.86 (d, 2H, *J* = 8.4 Hz), 4.20-4.24 (m, 4H), 3.78 (s, 6H), 1.80-1.87 (m, 4H), 1.50-1.57 (m, 4H), 1.29-1.42 (m, 16H), 0.85-0.88 (m, 6H); ¹³C NMR (100 MHz, THF-d₈, δ ppm): 156.74, 149.57, 149.28, 148.99, 145.47, 144.40, 140.47, 137.87, 134.31, 133.60, 132.68, 127.98, 127.27, 127.03, 126.87, 126.03, 122.65, 122.26, 119.75, 117.89, 116.84, 114.78, 106.23, 73.42, 58.01, 54.88, 47.10, 32.23, 32.20, 29.90, 29.77, 29.72, 29.02, 26.62, 26.53, 22.92, 13.85, 13.82. HRMS: *m*/z 895.3818 (C₅₄H₅₉N₂O₆S₂, [M + H]⁺, calc. 895.3815).

Synthesis of compound **5**.

A mixture of 4-bromo-*N*,*N*-bis(4-methoxyphenyl)aniline (1.56 g, 4.07 mmol), excess tributyl(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)stannane, Pd(PPh₃)₄ (100 mg, 0.10 mmol), and DMF (40 mL) was heated at 100 °C overnight under N₂ atmosphere. After cooling, water was added and the reaction mixture was extracted three times with CH₂Cl₂. The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/PE = 1/2) on silica gel to yield the product as a green solid (1.36 g, 75%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.50 (d, 2H, *J* = 7.8 Hz), 7.05 (d, 4H, *J* = 8.0 Hz), 6.92 (d, 2H, *J* = 7.8 Hz), 6.82 (d, 4H, *J* = 8.0 Hz), 4.22-4.28 (m, 4H), 3.80 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 155.99, 147.50, 141.08, 126.96, 126.65, 125.67, 120.99, 114.87, 96.48, 64.94, 64.72, 55.72. HRMS: *m*/z 446.1418 (C₂₆H₂₄NO₄S, [M + H]⁺, calc. 446.1426).

Under nitrogen atmosphere and at -78 \mathbb{C} , *n*-BuLi (1.8 mL, 1.6 M in hexane) was added dropwise to a dry tetrahydrofuran (THF, 30 mL) solution containing the above green compound (1.17 g, 2.62 mmol). After the reaction solution was stirred for 1 hour at -78 \mathbb{C} , 0.85 mL (3.14 mmol) of tri-n-butylchlorostannane was added slowly. The solution was brought back to room temperature, and after being stirred for another 8 hours, the reaction was quenched with saturated aqueous ammonium chloride solution. The solution was extracted with CH₂Cl₂, and the extract was washed with brine and dried over magnesium sulfate. Compound **5** was obtained as a brown liquid after removal of the solvent for the next reaction without further purification.

Synthesis of compound 9b.

A mixture of compound 3 (116 mg, 0.19 mmol), compound 5 (1.59 g), $Pd(PPh_3)_4$ (50 mg, 0.05 mmol), and DMF (20 mL) was heated at 100 $\,$ C overnight under N_2 atmosphere. After cooling, water was added and the reaction mixture was extracted three times with CH₂Cl₂. The combined organic layer was washed with H₂O and brine, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/PE = 1/1) on silica gel to yield the product as a red solid **9b** (116) mg, 63%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 9.95 (s, 1H), 8.24 (s, 1H), 7.55 (d, 2H, J = 8.4 Hz), 7.45 (s, 1H), 7.39 (s, 1H), 7.29 (s, 1H), 7.09 (d, 4H, J = 8.8 Hz), 6.94 (d, 2H, J = 8.4 Hz), 6.85 (d, 4H, J = 8.8 Hz), 4.36-4.43 (m, 4H), 4.11-4.15 (m, 4H), 3.81 (s, 6H), 1.91-1.98 (m, 4H), 1.56-1.68 (m, 4H), 1.29-1.43 (m, 16H), 0.89-0.94 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 183.58, 156.23, 149.36, 149.24, 147.90, 140.76, 139.68, 137.40, 137.11, 135.77, 132.87, 128.18, 127.00, 126.94, 124.64, 123.17, 122.29, 120.44, 117.16, 115.90, 114.95, 108.66, 106.70, 106.05, 69.36, 65.27, 64.82, 55.74, 32.15, 29.83, 29.78, 29.64, 29.62, 28.19, 27.09, 26.44, 22.99, 17.73, 14.43, 13.89. HRMS: m/z 968.3683 (C₅₇H₆₂NO₇S₃, $[M + H]^+$, calc. 968.3688).

Synthesis of sensitizer FNE51.

FNE51 was obtained as brown powder in similar way as **FNE50** (84 mg, yield 78%): ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 8.57 (s, 1H), 8.28 (s, 1H), 8.11 (s, 1H), 7.84 (s, 1H), 7.79 (s, 1H), 7.53 (d, 2H, *J* = 8.4 Hz), 7.05 (d, 4H, *J* = 8.8 Hz), 6.93 (d, 4H, *J* = 8.8 Hz), 6.83 (d, 2H, *J* = 8.4 Hz), 4.52 (br, 2H), 4.42 (br, 2H), 3.77 (s, 6H), 1.80-1.86 (m, 4H), 1.50-1.56 (m, 4H), 1.25-1.42(m, 16H), 0.85-0.89 (m, 6H); ¹³C NMR (100 MHz, THF-d₈, δ ppm): 156.49, 152.39, 140.78, 137.95, 135.00, 131.32, 126.62, 125.86, 124.37, 122.95, 120.63, 119.41, 119.25, 118.78, 114.69, 109.95, 100.24, 67.20, 67.06, 54.83, 50.62, 46.13, 42.84, 40.09, 39.88, 37.64, 36.41, 35.42, 34.10, 32.19, 32.10, 30.97, 29.88, 29.71, 29.54, 28.35, 27.23, 26.56, 25.66, 25.07, 24.94, 24.87, 24.74, 24.67, 24.54, 24.34, 24.14, 23.14, 22.89, 22.79, 21.19, 19.05, 18.59, 18.47, 13.80, 13.67, 11.47. HRMS: *m*/*z* 1035.3729 (C₆₀H₆₃N₂O₈S₃, [M + H]⁺, calc. 1035.3747).

Synthesis of compound **6**.

A 250 mL three-necked round-bottomed flask equipped with a dropping funnel and stir bar was charged with *N*-bis(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)phenyl)aniline (206 mg, 0.48 mmol), 4,7-dibromobenzothiadiazole (603 mg, 2.05 mmol), Pd(PPh₃)₄ (120 mg, 0.12 mmol), K₂CO₃ (2.76 g, 0.02 mol), water (10 mL), toluene (10 mL) and THF (30 mL). Then the mixture was refluxed for 18 hours, cooled, and extracted with CH₂Cl₂ for two times. The combined organic solution was washed with brine, dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, CH₂Cl₂/PE = 1:1). Orange solid was obtained with a yield of 81% (202 mg). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.87 (d, 2H, J = 7.6 Hz), 7.74 (d, 2H, J = 8.8 Hz), 7.50 (d, 2H, J = 7.6 Hz), 7.13 (d, 4H, J = 8.8 Hz), 7.03 (d, 2H, J = 8.8 Hz), 6.86 (d, 4H, J = 8.8 Hz), 3.81 (s, 6H); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 156.49, 149.51, 140.53, 134.00, 132.63, 129.97, 128.02, 127.38, 127.14, 119.67, 115.01, 111.87, 55.74. HRMS: m/z 518.0559 (C₂₆H₂₁BrN₃O₂S, [M + H]⁺, calc. 518.0538).

Synthesis of compound 8.

Under a nitrogen atmosphere, a mixture of compound **6** (194 mg, 0.37 mmol), compound **7** (588 mg, 0.74 mmol) and Pd(PPh₃)₄ (80 mg, 0.08 mmol) in DMF (15 mL) was stirred and heated at 90 °C for 16 hours. After removal of the solvent, the residue was purified by flash column chromatography (silica gel, CH₂Cl₂/PE = 1:1). Red solid compound **8** was obtained with a yield of 74% (256 mg). ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.86 (s, 1H), 7.95 (d, 2H, J = 7.6 Hz), 7.79-7.85 (m, 3H), 7.75 (s, 1H), 7.63 (d, 1H, J = 7.6 Hz), 7.60 (s, 1H), 7.45 (d, 1H, J = 5.2 Hz), 7.15 (d, 4H, J = 8.8 Hz), 7.06 (d, 2H, J = 8.4 Hz), 6.88 (d, 4H, J = 8.8 Hz), 4.27 (t, 2H, J = 6.6 Hz), 4.16 (t, 2H, J = 6.6 Hz), 3.82 (s, 6H); 1.93-2.00 (m, 4H), 1.53-1.65 (m, 4H), 1.32-1.43 (m, 16H), 0.89-0.92 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 156.42, 154.18, 153.04, 149.24, 149.09, 140.67, 137.28, 134.80, 134.59, 132.99, 130.90, 130.15, 130.00, 128.79, 127.33, 126.84, 126.67, 125.28, 124.17, 123.05, 122.89, 122.81, 119.82, 115.00, 109.71, 107.14, 106.80, 69.59, 69.38, 55.76, 32.14, 29.79, 29.75, 29.64, 29.61, 29.56, 26.48, 26.41, 22.98, 14.42. HRMS: m/z 934.3742 (C₅₆H₆₀N₃O₄S₃, [M + H]⁺, calc. 934.3746).

Synthesis of compound **9c**.

To a cold Vilsmeier reagent, which was prepared with 2 mL of POCl₃ in DMF (2 mL), was added a solution of compound 8 (238 mg, 0.25 mmol) in dry CHCl₃ (50 mL) at 0 °C. The mixture was stirred at 90 °C for 20 hours, and guenched with 10% aqueous solution of NaOAc (30 mL) at 0 °C. After neutralization with 10% NaOH solution to pH 7, the mixture was extracted by CH₂Cl₂ for three times. The combined organic layer was washed with H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude product was purified by column chromatography (CH₂Cl₂/PE = 2/1) on silica gel to obtain aldehyde compound **9c** (156 mg, 65%) as a purple solid. ¹H NMR (400 MHz, CDCl₃, δ ppm): 10.07 (s, 1H), 8.77 (s, 1H), 8.38 (s, 1H), 7.95 (d, 1H, J = 7.6 Hz), 7.84 (d, 2H, J = 8.4 Hz), 7.63-7.66 (m, 2H), 7.54 (s, 1H), 7.16 (d, 4H, J = 8.8 Hz), 7.04 (d, 2H, J = 8.4 Hz), 6.89 (d, 4H, J = 8.8 Hz), 4.25 (t, 2H, J = 6.6 Hz), 4.17 (t, 2H, J = 6.6 Hz), 3.83 (s, 6H); 1.95-2.03 (m, 4H), 1.53-1.63 (m, 4H), 1.30-1.48 (m, 16H), 0.90-0.92 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, δ ppm): 183.44, 156.49, 153.73, 152.54, 149.38, 149.30, 140.51, 140.32, 139.93, 137.55, 135.26, 133.41, 133.16, 132.19, 129.94, 129.55, 128.27, 127.41, 126.63, 126.23, 124.05, 122.91, 122.59, 122.02, 119.53, 115.02, 106.70, 105.76, 69.44, 69.24, 55.74, 32.16, 30.53, 29.94, 29.86, 29.80, 29.67, 29.63, 29.58, 26.52, 26.43, 23.00, 14.44. HRMS: m/z 962.3690 $(C_{57}H_{60}N_3O_5S_3, [M + H]^+, calc. 962.3695).$

Synthesis of sensitizer FNE52.

S10

FNE52 was obtained as brown powder in similar way as **FNE50** (105 mg, yield 73%). ¹H NMR (400 MHz, THF-d₈, δ ppm): 9.03 (s, 1H), 8.70 (s, 1H), 8.55 (s, 1H), 8.29 (d, 1H, J = 7.6 Hz), 7.97 (d, 2H, J = 8.4 Hz), 7.92 (s, 1H), 7.84 (d, 1H, J = 7.6 Hz), 7.80 (s, 1H), 7.12 (d, 4H, J = 8.8 Hz), 7.01 (d, 2H, J = 8.4 Hz), 6.89 (d, 4H, J = 8.8 Hz), 4.19-4.29 (m, 4H), 3.78 (s, 6H); 1.87-1.96 (m, 4H), 1.56-1.62 (m, 4H), 1.28-1.35 (m, 16H), 0.89-0.93 (m, 6H); ¹³C NMR (100 MHz, THF-d₈, δ ppm): 156.83, 155.85, 153.29, 149.98, 148.95, 147.30, 141.91, 140.55, 139.02, 137.31, 135.26, 133.95, 132.95, 130.02, 129.21, 128.03, 127.61, 127.14, 120.00, 119.30, 118.50, 114.79, 68.45, 67.06, 54.85, 33.49, 32.09, 29.86, 29.33, 26.47, 25.07, 24.93, 24.87, 24.74, 24.66, 24.54, 24.34, 24.14, 22.85, 13.72. HRMS: m/z 1029.3744 (C₆₀H₆₁N₄O₆S₃, [M + H]⁺, calc. 1029.3753).

Characterizations.

UV-vis absorption spectra of dye solutions were recorded with a Shimadzu Model 3100 UV-vis spectrophotometer. Cyclic voltammetry (CV) measurements were performed with an Autolab analyzer using a typical three-electrode electrochemical cell in a solution of tetrabutylammonium hexafluorophosphate (0.1M) in acetonitrile at room temperature under argon. The scan rate was 50 mV/ s. Dye adsorbed TiO₂ on conductive glass was used as the working electrode, a Pt wire was used as counter electrode, and an Ag/Ag⁺ electrode as reference electrode. The potential of the reference electrode was calibrated by ferrocene, and all potentials mentioned in this work are against normal hydrogen electrode (NHE). The film thickness was measured by a surface profiler (VeecoDektak150, USA). The geometrical and

electronic properties of the resulted sensitizers are calculated by density functional methods using the Gaussian 03 program package at the B3LYP/6-31G(d) level.

DSSC Fabrication and Photovoltaic Measurements.

TiO₂ films (12 µm) composed of 6 µm nanoparticle (20 nm) layer in direct contact with the FTO substrate and 6 μ m light scattering particle (80% 20 nm TiO₂ + 20% 100 nm TiO₂) layer were fabricated with a screen printing method and used in this study. The films were sintered at 500 $\,^{\circ}$ C for 1 hour to achieve good necking of neighboring TiO₂ particles. The sintered films were then treated with 0.05 M TiCl₄ aqueous solution at 70 °C for 30 min followed by calcinations at 450 °C for 30 min. When TiO₂ electrodes were cooled down at 120 °C, the electrodes were dipped in dye solutions (0.3 mM dye + 10 mM DCA) for 16 hours at room temperature. The Pt-coated FTO as a counter electrode and the dye-loaded film were separated by a hot-melt Surlyn film (30 µm) and sealed together by pressing them under heat. The liquid electrolyte was a solution of 0.05 M I₂, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI) and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile. The quasi-solid-state gel electrolyte was prepared by mixing 5 wt% poly(vinylidenefluoride-co-hexafluoropropylene) with a redox solution containing 0.05 M I₂, 0.1 M LiI, 0.5 M TBP and 0.6 M DMPImI in 3-methoxypropionitrile under heating at 100 °C until all solids were dissolved. After introducing the electrolyte or the hot gel solution into the internal space of the cell from the two holes predrilled on the back of the counter electrode, the holes were sealed with a Surlyn film covered with a thin glass slide under heat. The

working performance of the DSSC was tested by recording the current density-voltage (J-V) curves with a Keithley 2400 source meter (Oriel) under illumination of simulated AM1.5G solar light coming from a solar simulator (Oriel-94043A equipped with a Xe lamp and an AM1.5G filter). The light intensity was calibrated using a standard Si solar cell (Newport 91150). A black mask with aperture area of 0.2304 cm² was used during measurement to avoid stray light. The electron lifetimes were measured with intensity modulated photovoltage spectroscopy (IMVS),^[S2] whereas electron densities at open-circuit were measured using charge extraction technique.^[S3] IMVS analysis and charge extraction were carried out on an electrochemical workstation (Zahner XPOT, Germany), which includes a white light emitting diode and corresponding control system. The intensity-modulated spectra were measured at room temperature with light intensity ranging from 20 to 120 W m⁻², in modulation frequency ranging from 0.1 Hz to 10 kHz, and with modulation amplitude less than 5% of the light intensity. Three identical devices were tested in each case with standard deviation less than 5%. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with an Oriel-74125 system (Oriel Instruments). The intensity of monochromatic light was measured with a Si detector (Oriel-71640).

Dye	$\lambda_{ m max}$ nm ^a	ϵ $M^{-1} cm^{-1}$	$\lambda_{ m max}$ on TiO ₂ nm	HOMO V ^b	<i>E</i> ₀₋₀ eV	LUMO V
FNE50	471	2.91×10^4	460	0.873	2.11	-1.24
FNE51	495	3.56×10^{4}	494	0.786	1.95	-1.16
FNE52	526	4.03×10^{4}	526	0.915	1.91	-1.00

Table S1. Photophysical and Electrochemical Properties of the Resulted Sensitizers.

^[a] Absorption peaks (λ_{max}) and molar extinction coefficients (ε) were measured in THF solutions (~ 10⁻⁵ M).

^b The potentials (vs. NHE) were calibrated with ferrocene



Figure S1. Cyclic voltammograms of dye-loaded TiO₂ films.

Figure S2. Calculated frontier molecular orbitals and experimental energy level diagram of sensitizers **FNE50**, **FNE51**, and **FNE52**.





Figure S3. J-V curves for the quasi-solid-state DSSCs based on the resulted sensitizers.

Figure S4. Evolutions of photovoltaic performance parameters for FNE52 based quasi-solid-state DSSC during one sun soaking.



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