Significance of $\pi$-bridge contribution in pyrido[3,4-$b$]pyrazine featured D-A-$\pi$-A organic dyes for dye-sensitized solar cells

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Table of Contents

1. Experimental section ...................................................................................................................... S-3

1.1. Regents and materials .................................................................................................................. S-3

1.2. Instruments and characterization ............................................................................................... S-3

1.3. Synthesis ...................................................................................................................................... S-4

1.4. Fabrication of ss-DSSCs and ls-DSSCs ..................................................................................... S-12

1.5 Photovoltaic measurements ......................................................................................................... S-13

1.6. TD-DFT ....................................................................................................................................... S-14

2. Characterization section ................................................................................................................ S-15

3. Characterization of intermediates and compounds SH3 and SH4 ................................................ S-17

4. References ..................................................................................................................................... S-30
1. Experimental Section

1.1. Regents and Materials

All chemicals for device fabrication were purchased from Sigma-Aldrich (Switzerland) and used as received. 2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9’-spirobi fluorene (spiro-MeOTAD) was purchased from Merck KGaA (Germany) and used as received. All chemicals and reagents used in synthesis were purchased from Sigma-Aldrich and TCI and used without further purification. Tetrahydrofuran (THF) was purified by distillation before use. 5,8-dibromo-2,3-diphenylpyrido[3,4-b]pyrazine, (4-(4-(2,2-bis(2',4'-bis-(octyloxy)-[1,1'-biphenyl]-4-yl)vinyl)phenyl)-1,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)boronic acid, tributyl (2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane and (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)tributylstannane were synthesized according to the literatures.1,2,3

1.2. Instruments and Characterization

1H NMR and 13C NMR spectra were obtained via a Brücker AM 400 spectrometer with TMS as the internal standard. High resolution mass spectra were measured on an HITACHI-80 mass spectrometer. The UV-Vis spectroscopy was performed on a Shimdtzu UV-260 UV-Vis spectrometer. Cyclic voltammetry measurement was taken on the dyes using a Versastat II electrochemical workstation (Princeton applied research) and a three-electrode system, in which platinum as the working electrode, Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Ferrocene was used as the external standard and the supporting electrolyte was 0.1 M tetra-n-butyl ammonium hexafluorophosphate in dichloromethane. The scan rate was 100 mV/s.
1.3. Synthesis

The synthetic routes of SH3 and SH4 are depicted in Scheme S1. The synthesis of SH3 and SH4 was similar with the only difference of the π-bridge. It started from Stille coupling reactions of 5,8-dibromo-2,3-diphenylpyrido[3,4-b]pyrazine with tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-y]lstannane and (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)tributylstannane to afford compound 1a and 1b. Afterwards, Vilsmeier-Haack reaction of compounds 1a, 1b, N,N-Dimethylformamide and phosphorus oxychloride provided the intermediates 2a and 2b, respectively. In the next step, Suzuki coupling reactions of compounds 2a, 2b with (4-(4-(2,2-bis(2',4'-bis-(octyloxy)-[1,1'-biphenyl]-4-yl)vinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclo-penta[b]indol-7-yl)boronic acid resulted in aldehydes 3a and 3b, respectively. Finally, the target products SH3 and SH4 were synthesized by Knoevenagel reaction of the aldehydes 3a and 3b with cyanoacetic acid in the presence of acetic acid and ammonium acetate, respectively. All key intermediates and two final sensitizers were fully verified by $^1$H NMR, $^{13}$C NMR and HRMS.
Scheme S1. Synthetic routes of dyes SH3 and SH4.

1.3.1. 5-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-8-bromo-2,3-diphenylpyrido[3,4-b]pyrazine (1a):

Under an argon atmosphere, 5,8-dibromo-2,3-diphenylpyrido[3,4-b]pyrazine (484 mg, 1 mmol) and Pd(PPh₃)₂Cl₂ (35 mg, 0.05 mmol) were dissolved in anhydrous toluene (25 mL) and heated to 50 °C. Then a solution of (4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)tributylstannane (1.1 mmol) was injected in toluene slowly. The mixture was heated to 120 °C for 11 h before cooling down to the room temperature. The raw product was extracted using EA (ethyl acetate) and water. The organic layers were combined and dried by anhydrous Na₂SO₄. After evaporating under reduced pressure and the residue was purified by column chromatography with
CH$_2$Cl$_2$/PE (petroleum ether) (1:2 by volume) to give 1a as red solid (666.9 mg, 87.6% yield). m.p.
153.5-154.5 °C; IR (KBr, cm$^{-1}$) v 2957, 2924, 2853, 1460, 1406, 1315, 696.

$^1$H NMR (CDCl$_3$, 400 MHz), δ (TMS, ppm): δ = 8.79 (s, 1H), 8.53 (m, 1H), 7.61 (d, 4H, $J$ = 8 Hz), 7.39-7.29 (m, 6H), 7.18 (d, 1H, $J$ = 4 Hz), 6.91 (d, 1H, $J$ = 4 Hz), 1.93-1.79 (m, 4H), 1.35-1.18 (m, 5H), 0.91-0.77 (m, 14H), 0.71-0.58 (m, 6H), 0.53-0.50 (m, 6H). $^{13}$C NMR (CDCl$_3$, 400 MHz), δ (TMS, ppm): 158.72, 155.92, 152.75, 152.36, 147.21, 143.27, 140.95, 138.73, 136.97, 136.75, 136.01, 133.79, 132.80, 129.23, 129.18, 128.94, 128.56, 127.95, 127.39, 127.36, 126.23, 125.40, 121.36, 114.38, 52.51, 42.26, 34.18, 33.21, 33.07, 30.91, 30.41, 29.17, 28.69, 28.65, 28.36, 27.50, 27.46, 27.14, 26.39, 26.32, 25.77, 21.73, 21.68, 16.30, 13.11, 13.04, 12.94, 12.58, 9.64, 9.58. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{44}$H$_{49}$BrN$_3$S$_2$, 762.2551; found, 762.2526;

1.3.2. 8-bromo-5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2,3-diphenylpyrido[3,4-b]pyrazine (1b): Compound 1b was synthesized in a similar way to compound 1a by 5,8-dibromo-2,3-diphenylpyrido[3,4-b]pyrazine (484 mg, 1 mmol) with tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1.1 mmol). The residue was purified by column chromatography with CH$_2$Cl$_2$/PE (1:1 by volume) to give 1b as yellow solid (418.3 mg, 83.5% yield). m.p. 188.3-189.3 °C; IR (KBr, cm$^{-1}$) v 1541, 1476, 1450, 1368, 1323, 1182, 1070, 970, 698.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz), δ (TMS, ppm): 8.95 (s, 1H), 7.63 (d, 2H, $J$ = 4 Hz), 7.61 (d, 2H, $J$ = 4 Hz), 7.37-7.34 (m, 2H), 7.33-7.28 (m, 4H), 7.19 (s, 1H), 4.40-4.38 (m, 2H), 4.28-4.26 (m, 2H).

$^{13}$C NMR (CDCl$_3$, 400 MHz), δ (TMS, ppm): 156.95, 153.58, 153.06, 148.09, 143.40, 141.90, 141.57, 137.70, 137.59, 134.01, 130.37, 130.27, 130.08, 129.66, 128.46, 128.39, 115.93, 113.25, 107.00, 65.40, 64.23. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{22}$H$_{17}$BrN$_3$O$_2$S, 502.0225; found, 502.0219;
1.3.3. 6-(8-bromo-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (2a):

Under an argon atmosphere, compound 1a (380.6 mg, 0.5 mmol) was dissolved in anhydrous N,N-dimethylformamide (DMF, 25 mL) in an ice bath for 20 min. Phosphorus oxychloride (0.05 mL, 0.55 mmol) was added with anhydrous DMF (5 mL) slowly and stirred at 0 °C for 30 min. Then the mixture was heated to 65 °C for 4 h. After cooling, the mixture was poured into ice water. The precipitates were extracted with CH₂Cl₂ and dried by anhydrous Na₂SO₄. The organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography with CH₂Cl₂/PE (1:1 by volume) to give 2a as red solid (361.1 mg, 91.5% yield). m.p. 198.4-199.4 °C; IR (KBr, cm⁻¹) ν 2957, 2922, 2855, 1658, 1497, 1447, 1396, 1223, 696.

¹H NMR (CDCl₃, 400 MHz), δ (TMS, ppm): δ = 9.87 (s, 1H), 6.93 (m, 1H), 8.61 (d, 1H, J = 4 Hz), 7.71-7.67 (m, 4H), 7.61 (d, 1H, J = 4 Hz), 7.50-7.44 (m, 4H), 7.41-7.37 (m, 2H), 2.04-1.97 (m, 4H), 1.29-1.25 (m, 5H), 1.01-0.90 (m, 12H), 0.74-0.71 (m, 5H), 0.63-0.58 (m, 8H). ¹³C NMR (CDCl₃, 400 MHz), δ (TMS, ppm): 182.65, 161.93, 159.16, 157.43, 154.35, 152.56, 148.18, 147.64, 144.24, 144.12, 142.33, 141.98, 137.79, 137.59, 133.79, 130.60, 130.30, 130.21, 129.85, 128.57, 128.49, 126.64, 117.11, 54.05, 43.14, 35.38, 35.34, 34.27, 34.16, 31.48, 30.22, 29.73, 29.47, 28.50, 28.45, 27.50, 27.42, 22.78, 22.73, 14.10, 13.99, 10.69, 10.64. HRMS (ESI) m/z: [M + H]⁺ calcd for C₄₅H₄₀BrN₃O₂, 790.2500; found, 790.2504;

1.3.4. 7-(8-bromo-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (2b):

Compound 2b was synthesized in a similar way to compound 2a by compound 1b (250.5 mg, 0.5
mmol) with phosphorus oxychloride (0.05mL, 0.55 mmol) and anhydrous DMF (20 mL). The residue was purified by column chromatography with CH₂Cl₂/PE (2:1 by volume) to give 2b as yellow solid (229.9 mg, 86.9% yield). m.p. 229.6-230.6 ℃; IR (KBr, cm⁻¹) ν 1647, 1543, 1481, 1447, 1366, 1312, 1233, 1082, 772, 700.

¹H NMR (CDCl₃, 400 MHz), δ (TMS, ppm): 9.98 (s, 1H), 8.98 (s, 1H), 7.63-7.59 (m, 4H), 7.37-7.35 (m, 2H), 7.34-7.30 (m, 4H), 4.41-4.38 (m, 4H). ¹³C NMR (CDCl₃, 400 MHz), δ (TMS, ppm): 180.92, 157.57, 154.42, 151.68, 148.05, 147.95, 145.40, 142.35, 141.56, 137.48, 137.23, 134.39, 130.32, 130.05, 128.58, 128.51, 122.27, 121.42, 118.67, 65.05, 64.94. HRMS (ESI) m/z: [M + H]⁺ calcd for C₇₆H₃₇BrN₃O₃S, 530.0174; found, 530.0175.

1.3.5. 6-(8-(4-(4-(2,2-bis(2',4'-bis((2-ethylhexyl)oxy)-[1,1'-biphenyl]-4-yl)vinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (3a):

Under an argon atmosphere, a mixture of 2a (157.8 mg, 0.2 mmol) and Pd(PPh₃)₄ (29 mg, 0.025 mmol) in THF (25 mL) was heated to 50 ℃. Then 5 mL 2 M K₂CO₃ aqueous solution was added, followed by injecting a solution of (4-(4-(2,2-bis(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)vinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)boronic acid (269.2 mg, 0.24 mmol) in THF slowly. The mixture was heated to 80 ℃ and refluxed for 8 h before cooling down to the room temperature. The raw product was extracted with CH₂Cl₂. The organic layers were combined and dried by anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure and the residue was purified by chromatography on a silica gel column with CH₂Cl₂/PE (1:1 by volume) to give 3a as red solid (196.6 mg, 55% yield). m.p. 73.1-74.1 ℃; IR (KBr, cm⁻¹) ν 2957, 2924, 2855, 1659, 1599, 1508, 1495, 1462, 1396, 1377, 1298, 1279, 1223, 1180, 1132, 1040, 1024, 696.
$^1$H NMR (CDCl$_3$, 400 MHz), $\delta$ (TMS, ppm): 9.86 (s, 1H), 8.87 (s, 1H), 8.65-8.61 (m, 1H), 7.77-7.73 (m, 3H), 7.65 (d, 2H, $J = 8$ Hz), 7.62-7.59 (m, 2H), 7.56 (d, 2H, $J = 8$ Hz), 7.49-7.45 (m, 5H), 7.38 (d, 3H, $J = 8$ Hz), 7.34-7.28 (m, 6H), 7.18 (d, 1H, $J = 8$ Hz), 7.13 (s, 4H), 7.01 (s, 1H), 6.59-6.55 (m, 4H), 4.83-4.79 (m, 1H), 3.94-3.84 (m, 9H), 2.05-1.94 (m, 8H), 1.72-1.56 (m, 13H), 1.43-1.33 (m, 20H), 1.29-1.23 (m, 24H), 0.97-0.85 (m, 36H). $^{13}$C NMR (CDCl$_3$, 400 MHz), $\delta$ (TMS, ppm): 182.55, 160.08, 158.69, 157.27, 148.23, 147.08, 145.55, 143.67, 141.19, 138.53, 138.35, 137.51, 135.32, 130.95, 130.48, 130.18, 129.91, 129.76, 129.24, 128.49, 128.25, 126.82, 123.31, 118.16, 108.53, 105.18, 100.28, 100.18, 99.99, 70.76, 70.71, 70.56, 70.52, 70.30, 68.90, 53.96, 39.47, 39.34, 35.38, 35.32, 34.20, 34.04, 31.94, 31.45, 30.57, 30.20, 29.71, 29.67, 29.38, 29.13, 29.03, 29.00, 28.48, 27.39, 24.54, 24.11, 23.96, 23.91, 23.09, 23.04, 22.78, 22.74, 22.71, 14.13, 14.07, 13.96, 11.16, 11.10, 10.60. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_{120}$H$_{147}$N$_4$O$_5$S$_2$, 1788.0813; found, 1788.0326.

1.3.6. 7-(8-(4-(4-(2,2-bis(2',4'-bis((2-ethylhexyl)oxy)-[1,1'-biphenyl]-4-yl)vinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine-5-carbaldehyde (3b):

Compound 3b was synthesized in a similar way to compound 3a by compound 2b (105.8 mg, 0.2 mmol) with (4-(4-(2,2-bis(2',4'-bis(octyloxy)-[1,1'-biphenyl]-4-yl)vinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)boronic acid (269.2 mg, 0.24 mmol). The residue was purified by column chromatography with CH$_2$Cl$_2$/PE (2:1 by volume) to give 3b as red solid (229.9 mg, 86.9% yield). m.p. 106.2-107.2 °C; IR (KBr, cm$^{-1}$) v 2955, 2924, 2857, 1651, 1601, 1508, 1491, 1460, 1439, 1379, 1364, 1298, 1269, 1232, 1180, 1132, 1082, 1040, 1024, 696.

$^1$H NMR (CDCl$_3$, 400 MHz), $\delta$ (TMS, ppm): 10.06 (s, 1H), 9.01 (s, 1H), 7.78-7.73 (m, 3H), 7.66-
7.60 (m, 3H), 7.56 (d, 2H, J = 12 Hz), 7.48 (d, 4H, J = 8 Hz), 7.43-7.41 (m, 3H), 7.38 (d, 2H, J = 8 Hz), 7.36-7.33 (m, 5H), 7.28-7.21 (m, 3H), 7.18-7.13 (m, 4H), 6.59-6.57 (m, 3H), 4.82-4.78 (m, 1H), 4.50 (d, 4H, J = 8 Hz), 3.94-3.84 (m, 8H), 3.80-3.72 (m, 1H), 1.77-1.60 (m, 8H), 1.50-1.23 (m, 36H), 0.95-0.82 (m, 22H). 13C NMR (CDCl3, 400 MHz), δ (TMS, ppm): 180.89, 160.10, 160.05, 157.30, 157.28, 155.65, 152.74, 149.65, 148.12, 147.35, 145.36, 141.73, 141.54, 141.09, 140.82, 140.65, 138.53, 138.26, 137.83, 137.54, 135.37, 133.32, 132.28, 131.03, 130.96, 130.49, 130.31, 130.19, 130.13, 129.92, 129.77, 129.72, 129.26, 128.54, 128.29, 127.73, 126.92, 126.84, 124.97, 123.75, 123.31, 123.22, 120.65, 118.28, 105.20, 100.29, 100.20, 70.74, 70.52, 70.30, 68.93, 65.10, 64.99, 45.45, 39.49, 39.35, 34.85, 34.03, 31.95, 31.47, 30.62, 30.59, 29.73, 29.69, 29.39, 29.15, 29.05, 29.02, 24.54, 24.13, 23.98, 23.92, 23.11, 23.06, 22.72, 14.15, 14.13, 14.10, 11.24, 11.18, 11.12. HRMS (ESI) m/z: [M + H]+ calcd for C101H135N4O7S, 1527.8486; found, 1527.8348;

1.3.7. (E)-3-(6-(8-(4-(4-(2,2-bis(2',4'-bis((2-ethylhexyl)oxy)-[1,1'-biphenyl]-4-yl)vinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2-cyanoacrylic acid (SH3):

Under an argon atmosphere, a mixture of compound 3a (89.4 mg, 0.05mmol), 2-cyanoacetic acid (85 mg, 1 mmol) and ammonium acetate (115 mg, 1.5 mmol) in acetic acid (15 mL) and 5 mL THF was refluxed for 10 h before cooling down. The mixture was poured into 200 mL water and stirred for 30 min. The precipitates were collected by filtration and purified by column chromatography with CH2Cl2/methanol (20:1 by volume) to give SH3 as purple solid (79.4 mg, 85.6% yield). m.p.163.3-164.3 °C; IR (KBr, cm⁻¹) ν 3435, 2957, 2922, 2857, 1603, 1578, 1508, 1491, 1462, 1377, 1298, 1277, 1261, 1182, 1134, 1041, 1024, 696.

1H NMR (CDCl3, 400 MHz), δ (TMS, ppm): 8.70 (s, 1H), 8.41 (s, 1H), 7.66 (s, 4H), 7.56 (d, 4H,
$J = 8 \text{ Hz}$), $7.47$ (d, 2H, $J = 8 \text{ Hz}$), $7.43-7.41$ (m, 5H), $7.37$ (d, 2H, $J = 8 \text{ Hz}$), $7.34-7.31$ (m, 4H), $7.23-7.19$ (m, 2H), $7.12$ (d, 2H, $J = 8 \text{ Hz}$), $7.07$ (d, 3H, $J = 8 \text{ Hz}$), $7.01$ (s, 1H), $6.57-6.54$ (m, 5H), $4.70$ (s, 1H), $3.89-3.83$ (m, 8H), $3.77-3.74$ (m, 1H), $2.05-1.82$ (m, 12H), $1.76-1.65$ (m, 9H), $1.54-1.40$ (m, 20H), $1.36-1.24$ (m, 36H), $0.95-0.84$ (m, 24H). $^{13}$C NMR (CDCl$_3$, 400 MHz), $\delta$ (TMS, ppm): $160.04$, $157.27$, $141.45$, $140.94$, $140.57$, $138.46$, $137.57$, $135.41$, $130.98$, $130.49$, $129.96$, $129.93$, $129.75$, $129.33$, $129.26$, $127.05$, $126.85$, $126.80$, $123.28$, $123.20$, $118.74$, $105.17$, $100.28$, $100.18$, $100.00$, $70.71$, $70.51$, $70.29$, $39.47$, $39.33$, $31.46$, $30.67$, $30.59$, $30.57$, $30.21$, $29.73$, $29.65$, $29.39$, $29.35$, $29.14$, $29.03$, $29.00$, $24.11$, $23.96$, $23.90$, $23.11$, $23.05$, $22.72$, $14.15$, $14.12$, $14.09$, $11.22$, $11.17$, $11.11$. HRMS (MALDI) m/z: [M + H]$^+$ calcd for C$_{123}$H$_{148}$N$_5$O$_6$S$_2$, 1855.0871; found, 1855.0901;

1.3.8. (E)-3-[(7-(8-(4-(4-(2,2-bis(2',4'-bis((2-ethylhexyl)oxy)-[1,1'-biphenyl]-4-yl)vinyl)phenyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)-2,3-diphenylpyrido[3,4-b]pyrazin-5-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-cyanoacrylic acid (SH4):

SH4 was synthesized in a similar way to SH3 by compound 3b (76.3 mg, 0.05 mmol) with 2-cyanoacetic acid (85 mg, 1 mmol) and ammonium acetate (115 mg, 1.5 mmol) in acetic acid (15 mL) and 5 mL THF. The residue was purified by column chromatography with CH$_2$Cl$_2$/methanol (10:1 by volume) to give SH4 as black solid (66.3 mg, 83.2%yield). m.p. 215.4-216.4 $^\circ$C; IR (KBr, cm$^{-1}$) v 3430, 2957, 2926, 2859, 1601, 1580, 1510, 1493, 1468, 1371, 1310, 1298, 1273, 1261, 1180, 1132, 1070, 1040, 1024, 698.

$^1$H NMR (CD$_2$Cl$_2$, 400 MHz), $\delta$ (TMS, ppm): 8.62 (s, 1H), 8.32 (s, 1H), 7.73 (s, 2H), 7.48 (d, 4H, $J = 8 \text{ Hz}$), 7.37 (d, 2H, $J = 8 \text{ Hz}$), 7.27-7.24 (m, 5H), 7.21 (d, 3H, $J = 4 \text{ Hz}$), 7.19-7.13 (m, 6H), 7.01 (s, 4H), 6.92 (s, 1H), 6.49-6.43 (m, 5H), 4.61 (s, 1H), 4.34 (s, 4H), 3.80-3.73 (m, 8H), 3.60 (s, 1H),
1.75-1.54 (m, 9H), 1.44-1.32 (m, 12H), 1.29-1.17 (m, 26H), 0.86-0.76 (m, 24H). $^{13}$C NMR (CDCl$_3$, 400 MHz), $\delta$ (TMS, ppm): 160.10, 160.04, 157.30, 157.28, 141.54, 140.95, 140.66, 138.53, 138.21, 137.53, 135.47, 133.34, 131.03, 130.98, 130.62, 130.50, 130.33, 130.30, 129.93, 129.78, 129.26, 128.99, 128.29, 126.93, 126.85, 123.30, 123.22, 118.35, 105.18, 100.28, 100.18, 70.72, 70.56, 70.51, 70.29, 39.47, 39.33, 30.69, 30.58, 29.73, 29.35, 29.14, 29.01, 24.12, 23.96, 23.91, 23.11, 23.05, 22.72, 14.15, 14.13, 14.10, 11.24, 11.22, 11.18, 11.11. HRMS (MALDI) m/z: [M + H]$^+$ calcd for C$_{104}$H$_{116}$N$_5$O$_8$S, 1594.8545; found, 1594.8536;

1.4. Fabrication of ss-DSSCs and ls-DSSCs

For solid-state devices, a 1.3 μm-thick mesoporous TiO$_2$ transparent layer was deposited by spin-coating diluted TiO$_2$ paste (Dyesol 30NRD: ethanol = 5:6, by weight ratio) on a TiO$_2$ compact layer on top of laser-etched clean fluorine-doped tin-oxide (FTO) glass substrates. After dried at 100 °C, the substrates were sintered gradually up to 450 °C for 30 min. For liquid-state devices, 10 μm mesoporous TiO$_2$ transparent layers (Dyesol 18NRT) and a 5μm TiO$_2$ scattering layer were screen printed onto the FTO substrates. The substrates were sintered gradually up to 500 °C for 15 min. After cooling down to 80 °C, the photoanodes were placed in 0.2 mM dye solutions for 1.5 h with the solid-state devices and 18h for liquid state devices. The compositions of SH3/SH4 solution were 0.2 mM SH3/SH4, 5 mM chenodeoxycholic acid (CDCA) in a mixture solvent of chloroform and ethanol (3:7, volume ratio). The HTM layers were deposited by spin-coating at 2000 rpm for 30 s. The HTM solution consisted of 110 mM spiro-MeOTAD, 22 mM lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), 88 mM 4-tertbutylpyridine (TBP) and 3.3 mM tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl) imide) (FK209)
in chlorobenzene. Finally 80 nm of gold was thermally evaporated on top of the device. For traditional DSSC devices, the iodide electrolyte used here was composed of 0.03 M I\(_2\), 0.05 M LiI, 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.1 M guanidinium thiocyanate, 0.5 M TBP in mixed solvent of acetonitrile:valeronitrile (85:15, v/v). After combined the platinized counter electrode and dye-sensitized photoanode, the iodide electrolyte was injected into the cell through drilled holes in the counter electrode. Then the cell was sealed with hot-melting polymer and cover glass.

1.5. Photovoltaic Measurements

The current-voltage (I-V) measurement was performed using a 450 W xenon light (Oriel) with Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH) and AM1.5G standard and a Keithley model 2400 digital source meter to record the generated photocurrents. The light intensity was automatically calibrated via a standard silicon photodiode with an IR-cutoff filter (KG3, Schott). Each cell was measured with a black metal mask on top and the active area is 0.16 cm\(^2\) for both solid-state and liquid-state DSSCs. The voltage scan rate was 10 mVs\(^{-1}\). Incident photon-to-electron conversion efficiency (IPCE) spectra were recorded with a setup consist of a 300 W xenon lamp (ILC Technology), a Gemini-180 double monochromator (Jobin Yvon Ltd.) and a Keithley 2400 digital source meter under constant white light bias of 0.1 Sun provided by a white LED array. The chop frequency is at approximately 2 Hz.

1.6. TD-DFT

The molecular structures were optimised in vacuum, using the software Avogadro\(^4\) to enter the
starting geometry. Then the structure was optimised in dichloromethane, using the optimised structure from vacuum. All calculations were carried out using the Gaussian 09 program with the hybrid B3LYP functional and the standard 6-31G(d) basis set. In the calculations, the long alkyl chains were replaced by methyl groups to reduce computational costs without affecting the nature of frontier molecular orbitals. Time-dependent DFT calculations (TD-DFT) were performed using Gaussian 09 program with a dichloromethane polarisable continuum model (PCM), using the range-separated CAM-B3LYP functional and the triple-zeta TZVP basis set. The 20 lowest singlet electronic transitions were calculated and processed with the GaussSum software package.
2. Characterization section.

**Figure S1.** The oxidative cyclic voltammetry plots of **SH3** and **SH4**.

**Figure S2.** The lifetime of luminescence of **SH3** on TiO$_2$ film and on Al$_2$O$_3$ film.
Figure S3. The lifetime of luminescence of SH4 on TiO$_2$ film and on Al$_2$O$_3$ film.
Table S1. The time coefficients and relative magnitude of PL decay trace in Figure S1 and S2.

<table>
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<th>TiO₂</th>
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<th>TiO₂</th>
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<td>0.48</td>
<td>1.84</td>
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<td>3</td>
<td>35</td>
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<tr>
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<td>2.03</td>
<td>72</td>
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The signal was fitted by two exponential as $I_{PL} = A_1 \exp \left(-t/\tau_1\right) + A_2 \exp \left(-t/\tau_2\right)$. $\tau_i$ refers to time constant of exponential component. $A_i$ denotes the fractional amplitude of each exponential. We estimated the electron injection efficiencies of various dyes using Equation $\eta_{inj} = 1 - \frac{<\tau_{TiO2}>}{<\tau_{Al2O3}>}$. The values of $<\tau_{av}>$ were determined with $<\tau_{av}> = A_1\tau_1 + A_2\tau_2$.

3. Characterization of intermediates and compounds SH3 and SH4.
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM     DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
31 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used
C: 0-44  H: 0-200  N: 0-3  S: 0-2  Br: 0-1

JL-HUA
ECUST institute of Fine Chem

HL-SZJ-503 129 (0.892) Cm (128:130)

Minimum: 300.0  50.0  -1.5
Maximum: 100.0

Mass    Calcd. Mass    m/z     PPM     DBE    i-FIT    i-FIT (Norm)    Formula
762.2526  762.2551  -3.5  -3.3  21.5  78.9  0.0  C44 H49 N3 Br
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
105 formula(e) evaluated with 2 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0.26 H: 0.200 N: 0.3 O: 0.3 S: 0.1 Br: 0.1

ECUST Institute of Fine Chem
JL-HUA
HL-52J-50173 (5.53) Cm (71.74)

Minimum: 300.0 50.0 -1.5
Maximum: 500.0 50.0 100.0

Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
502.0219 502.0225  -0.6  -1.2  18.5  110.0  0.0  C25 H17 N3 O2 S Br
Elemental Composition Report

Single Mass Analysis
Tolerance = 30.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
393 formula(e) evaluated with 35 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0.54   H: 0.50   N: 1.3   O: 0.6   S: 0.2   Br: 0.1

HL-SZ1-114 81 (2.586) Cm (81.64)

ECUST institute of Fine Chem

Minimum:
Mass  Calcd. Mass  mDa  FPK  DBE  i-FIT  i-FIT (Norm)  Formula
790.2504  790.2500  0.4  0.5  22.5  64.7  0.0  C45 H49 N3 O S2 Br
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron ions
75 formula(s) evaluated with 1 results within limits (up to 5 closest results for each mass)
Elements Used:
C: 0.26  H: 0.200  N: 0.3  O: 0.3  S: 0.1  Br: 0.1

Minimum: 530.0175  Maximum: 530.0174

Mass  Calc. Mass  m/z  FPM  DBE  i-FIT  i-FIT (Norm)  Formula
530.0175  530.0174  0.1  0.2  19.5  43.5  0.0  O26 H17 N3 O3 S  Br
Elemental Composition Report

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
41 formula(e) evaluated with 1 results within limits (up to 1 closest results for each isotope)
Elements Used:
C: 0-120  H: 0-150  N: 0-4  O: 0-5  S: 0-2

HL-52J-603 236 (1.54) Cm (236.241)

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<th>mDa</th>
<th>PPM</th>
<th>DBE</th>
<th>i-FIT</th>
<th>i-FIT (Norm)</th>
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# Elemental Composition Report

## Single Mass Analysis

Tolerance = 50.0 PPM  /  DBE: min = -1.5, max = 100.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions  
41 formula(s) evaluated with 1 results within limits (up to 1 closest results for each mass) 
Elements Used: 
C: 0-101  H: 0-115  N: 0-4  O: 0-7  S: 0-1  

HL-52J-60L 291 (1.887) Cm (208.293)

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4. References


