Supporting Information

Molecular design of new organic sensitizers based on thieno[1,4]benzothiazine for dye-sensitized solar cells

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I. Synthetic procedures of TBT-2 and TBT-3

1. Synthetic procedures of TBT-2

Scheme S1. Synthetic route of TBT-2

2-Iodo-4-methylaniline

This compound was prepared according to the reported procedure. To a solution of 4-methylaniline (10.70 g, 100 mmol) in CH₂Cl₂ (50 mL) was added the solution of NaHCO₃ (10.10 g, 120 mmol) in water (100 mL), and then I₂ (25.50 g, 100 mmol) was added. The mixture was stirred at room temperature overnight. Then the mixture was treated with aqueous NaHSO₃ and extracted with CH₂Cl₂ two times. The combined organic layers were washed with water and saturated brine, respectively, dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1, v/v) as the eluent to give the product as a brown solid (22.03 g, 94% yield).

M.p.: 35-37 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.21 (s, 3H), 3.94 (s, 2H), 6.66 (d, J = 8.4 Hz, 1H), 6.95 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.47 (d, J = 1.2 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 20.0, 84.5, 114.8, 129.7, 130.2, 139.2, 144.4 ppm.

4-Amino-3-iodobenzaldehyde (1b)

This compound was prepared according to the reported procedure.²

2-Iodo-4-methylaniline (3.95 g, 17.0 mmol) was added to a stirred 5% aq. HCl. After the solid was absolutely dissolved, DDQ (7.95 g, 35.0 mmol) was slowly added. The mixture was stirred at room temperature for 2 hours and then treated with dilute NaOH (pH = 10) and extracted with CH₂Cl₂ three times. The combined organic layers were washed with water and saturated brine, respectively, dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (8/1, v/v) as the eluent to give the product as a yellow solid (3.43 g, 82% yield). M.p.: 104-106 °C. ¹H NMR (400 MHz, CDCl₃): δ = 4.74 (s, 2H), 6.76 (d, J = 8.4 Hz, 1H), 7.66 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 8.15 (d, J = 2.0 Hz, 1H), 9.67 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 82.7, 113.6, 129.1, 131.5, 142.1, 152.2, 189.1 ppm. HRMS (ESI⁺): calcd for C₇H₇INO [M+H]⁺ 247.9572, found 247.9574.

4-Amino-3-(thiophen-2-ylthio)benzaldehyde (1c)

To a mixture of compound 1b (63 mg, 0.25 mmol), CuI (9.6 mg, 0.05 mmol), L-proline (11.6 mg, 0.10 mmol), and K₃PO₄·7H₂O (127 mg, 0.38 mmol) in H₂O/EtOH (1/1, v/v, 3.0 mL) under an N₂ atmosphere, thiophene-2-thiol (25 μL, 0.26 mmol) was added slowly. The mixture was stirred and heated at 110 °C for 10 hours. After cooling the solution, EtOH was removed under vacuum. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with saturated Na₂CO₃ and water, respectively, dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6/1, v/v) as the eluent to give the product as colorless oil (48 mg, yield 82%). ¹H NMR (400 MHz, CDCl₃): δ = 5.00 (s, 2H), 6.75 (d, J = 8.4 Hz, 1H), 6.96 (dd, J = 5.6 Hz, 3.6 Hz, 1H), 7.17 (dd, J = 3.6 Hz, 1.2 Hz, 1H), 7.31 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.66 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.93 (d, J = 2.0 Hz, 1H), 9.71 (s, 1H) ppm. ¹³C NMR
(100 MHz, CDCl₃): δ = 114.9, 118.5, 127.8, 128.0, 129.3, 132.1, 132.4, 133.1, 138.5, 152.7, 189.9 ppm. HRMS (ESI⁺): calcd for C₁₁H₁₀NOS₂ [M+H]⁺ 236.0204, found 236.0204.

N-(4-Formyl-2-(thiophen-2-ylthio)phenyl)acetamide (2c)

1c (1.00 g, 4.25 mmol) was diluted in 50 mL CH₂Cl₂ together with Et₃N (1.2 mL, 8.5 mmol). Acetyl chloride (0.6 mL, 8.5 mmol) was added dropwise at room temperature under strong magnetic stirring. The mixture was stirred at room temperature for 4 hours, and then quenched with water and extracted with CH₂Cl₂ two times. The combined organic layers were washed with saturated brine and water, respectively, dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (1.05 g, 89% yield). M.p.: 106-108 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.26 (s, 3H), 7.01 (dd, J = 5.2 Hz, 3.6 Hz, 1H), 7.22 (dd, J = 3.6 Hz, 1.2 Hz, 1H), 7.38 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.83 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H), 8.46 (br. s, 1H), 8.56 (d, J = 8.4 Hz, 1H), 9.87 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 25.2, 120.6, 128.1, 130.6, 131.3, 132.2, 132.4, 133.8, 135.3, 143.4, 168.6, 190.4 ppm. HRMS (ESI⁺): calcd for C₁₃H₁₂NO₂S₂ [M+H]⁺ 278.0309, found 278.0306.

N-(2-(3,5-Dibromothiophen-2-ylthio)-4-formylphenyl)acetamide (3c)

To a stirred solution of 2c (0.83 g, 3.0 mmol) in the mixture of HOAc/CH₂Cl₂ (1/1, v/v, 30 mL), NBS (1.12 g, 6.3 mmol) was added slowly in portions. After this addition, the mixture was stirred at room temperature for 6 hours. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water, saturated Na₂CO₃ and water, respectively, dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (1.07 g, 82% yield). M.p.: 136-138 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.31 (s, 3H), 6.98 (s, 1H), 7.89 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H), 8.56 (br. s, 1H), 8.64 (d, J = 8.8 Hz, 1H),
9.90 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 25.5, 116.6, 117.2, 120.6, 122.3, 130.0, 132.3, 133.0, 133.1, 136.6, 144.1, 168.8, 190.1 ppm. HRMS (ESI$^+$): calcd for C$_{13}$H$_{10}$Br$_2$NO$_2$S$_2$ [M+H]$^+$ 433.8520, found 433.8520.

$N$-(2-(3-Bromo-5-(4-(hexyloxy)phenyl)thiophen-2-ylthio)-4-formylphenyl)acetamide (4c)

A mixture of compound 3c (218 mg, 0.5 mmol), 4-(hexyloxy)phenylboronic acid (133 mg, 0.6 mmol), Pd(PPh$_3$)$_4$ (29 mg, 0.025 mmol) and Na$_2$CO$_3$ (212 mg, 2.0 mmol) were dissolved in THF/H$_2$O (4/1, v/v, 5.0 mL). Then, the mixture was heated at 80 °C for 10 hours under an N$_2$ atmosphere. After cooling, THF was removed under vacuum. The reaction mixture was poured into water and extracted with CH$_2$Cl$_2$ two times. The combined organic layers were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6/1, v/v) as the eluent to give the product as a white solid (174 mg, 65% yield). M.p.: 126-128 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.90 (t, $J$ = 6.8 Hz, 3H), 1.31-1.34 (m, 4H), 1.41-1.48 (m, 2H), 1.74-1.81 (m, 2H), 2.33 (s, 3H), 3.95 (t, $J$ = 6.8 Hz, 2H), 6.87 (d, $J$ = 8.8 Hz, 2H), 7.05 (s, 1H), 7.37 (d, $J$ = 8.8 Hz, 2H), 7.87 (dd, $J$ = 8.8 Hz, 2.0 Hz, 1H), 8.19 (d, $J$ = 1.6 Hz, 1H), 8.64-8.67 (m, 2H), 9.90 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.2, 22.7, 25.5, 25.8, 29.3, 31.7, 68.3, 115.1, 118.4, 120.4, 123.1, 124.9, 125.0, 125.8, 127.1, 132.2, 132.8, 136.7, 144.1, 149.2, 160.0, 168.9, 190.3 ppm. HRMS (ESI$^+$): calcd for C$_{25}$H$_{27}$BrNO$_3$S$_2$ [M+H]$^+$ 532.0616, found 532.0625.

2-(4-(Hexyloxy)phenyl)-4H-benzo[b]thieno[3,2-e][1,4]thiazine-7-carbaldehyde (5c)

A mixture of compound 4c (134 mg, 0.25 mmol), CuI (9.6 mg, 0.05 mmol), $N$,$N$-dimethylglycine hydrochloride (7.0 mg, 0.05 mmol) and K$_3$PO$_4$ (108 mg, 0.5 mmol) were dissolved in DMF (4.0 mL) under an N$_2$ atmosphere and heated at 135 °C for 20 hours. After cooling the solution, H$_2$O (2.0 mL) was added and the mixture was heated again to 80 °C for 4 hours. The reaction mixture was cooled to ambient temperature, diluted with 10 mL of water, and then filtered through a
filtration funnel to get a yellow solid. The solid was used as the substrate without further purification. HRMS (ESI⁺): calcd for C_{23}H_{24}NO_{2}S_{2} [M+H]⁺ 410.1248, found 410.1241.

**4-Hexyl-2-(4-(hexyloxy)phenyl)-4H-benzo[b]thieno[3,2-e][1,4]thiazine-7-carbaldehyde (6c)**

A mixture of compound 5c (206 mg, 0.5 mmol) and K₂CO₃ (690 mg, 5.0 mmol) were dissolved in DMF (8.0 mL) under an N₂ atmosphere and heated to 80 °C. After 30 min, n-C₆H₁₃Br (175 μL, 1.3 mmol) was added. The mixture was kept at 80 °C for 12 h under an N₂ atmosphere. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water and dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1, v/v) as the eluent to give the product as yellow oil (211 mg, 85% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.91 (m, 6H), 1.34-1.35 (m, 8H), 1.46 (m, 4H), 1.78-1.80 (m, 4H), 3.75 (t, J = 7.2 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 6.74-6.75 (m, 2H), 6.89 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.44 (s, 1H), 7.57 (d, J = 8.4 Hz, 1H), 9.72 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 14.2, 22.8, 25.8, 26.6, 26.9, 29.3, 31.6, 31.7, 48.8, 68.3, 106.2, 113.0, 113.1, 115.1, 121.7, 126.5, 126.6, 128.6, 130.9, 131.1, 142.7, 143.2, 150.2, 159.2, 189.6 ppm. HRMS (ESI⁺): calcd for C_{29}H_{36}NO_{2}S_{2} [M+H]⁺ 494.2187, found 494.2182.

**((E))-2-Cyano-3-(4-hexyl-2-(4-(hexyloxy)phenyl)-4H-benzo[b]thieno[3,2-e][1,4]thiazin-7-yl) acrylic acid (TBT-2)**

This material was prepared according to the reported method with some modification.³ A mixture of compound 6c (740 mg, 1.5 mmol) and cyanoacetic acid (631 mg, 7.5 mmol) in acetic acid (120 mL) was refluxed in the presence of ammonium acetate (1.27 g, 16.5 mmol) overnight under an N₂ atmosphere. Then, water was added and extracted with CH₂Cl₂. Next, the solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc/HOAc (100/50/1, v/v/v) to give the product.
as a dark purple solid (489 mg, 58% yield). M.p.: 228-230 °C. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 0.83-0.88\) (m, 6H), 1.25-1.30 (m, 8H), 1.38-1.43 (m, 4H), 1.63-1.71 (m, 4H), 3.85 (t, \(J = 7.2\) Hz, 2H), 3.96 (t, \(J = 6.4\) Hz, 2H), 6.93-6.95 (m, 2H), 7.02 (d, \(J = 9.2\) Hz, 1H), 7.25 (s, 1H), 7.50 (d, \(J = 8.8\) Hz, 2H), 7.66 (d, \(J = 2.0\) Hz, 1H), 7.87 (dd, \(J = 8.8\) Hz, \(J = 2.0\) Hz, 1H), 8.08 (s, 1H), 13.67 (br. s, 1H) ppm. \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta = 13.86, 13.91, 22.08, 22.13, 25.2, 25.6, 26.3, 28.6, 30.9, 31.0, 47.5, 67.6, 98.6, 103.6, 114.0, 114.2, 114.9, 116.9, 119.4, 125.2, 125.6, 126.1, 129.5, 132.3, 141.8, 142.4, 148.0, 152.1, 158.6, 163.9 ppm. HRMS (ESI\(^+\)): calcd for C\(_{32}\)H\(_{37}\)N\(_2\)O\(_3\)S\(_2\) [M+H]\(^+\) 561.2246, found 561.2239. Anal. calcd for C\(_{32}\)H\(_{36}\)N\(_2\)O\(_3\)S\(_2\) (%): C, 68.54; H, 6.47; N, 5.00; S, 11.43. found: C, 68.30; H, 6.48; N, 5.50; S, 10.69.

2. Synthetic procedures of TBT-3

4-Amino-3-(thiophen-3-ylthio)benzaldehyde (2b)

To a mixture of compound 1b (4.94 g, 20.0 mmol), CuI (384 mg, 2.0 mmol), L-proline (464 mg, 4.0 mmol), and K\(_2\)PO\(_4\)·7H\(_2\)O (10.14 g, 30.0 mmol) in H\(_2\)O/EtOH (1/1, v/v, 100 mL) under an N\(_2\) atmosphere, thiophene-3-thiol (2.49 g, 21.0 mmol) was added slowly. The mixture was vigorously stirred and heated at 110 °C for 10 hours. After cooling the solution, EtOH was removed under vacuum. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with saturated Na\(_2\)CO\(_3\) and water, respectively, dried over anhydrous Na\(_2\)SO\(_4\). After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6/1, v/v) as the eluent to give the product as a yellow solid (3.62g, 77% yield). M.p.: 80-82 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 4.98\) (s, 2H), 6.79 (d, \(J = 8.4\) Hz, 1H), 6.88 (dd, \(J = 4.8\) Hz, 0.8 Hz, 1H), 6.99 (d, \(J = 1.6\) Hz, 1H), 7.31 (dd, \(J = 4.8\) Hz, 2.8 Hz, 1H), 7.71 (dd, \(J = 8.4\) Hz, 1.6 Hz, 1H), 7.95 (d, \(J = 1.6\) Hz, 1H), 9.72 (s, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 114.8, 116.3, 122.3, 127.0, 127.9, 128.3, 130.4, 132.2, 139.7, 153.3, 189.9 ppm. HRMS (ESI\(^+\)): calcd for C\(_{11}\)H\(_{10}\)NOS\(_2\) [M+H]\(^+\) 236.0204, found 236.0205.

N-(4-Formyl-2-(thiophen-3-ylthio)phenyl)acetamide (3b)
2b (3.53 g, 15 mmol) was diluted in 100 mL CH₂Cl₂ together with Et₃N (4.2 mL, 30 mmol). Acetyl chloride (2.2 mL, 30 mmol) was added dropwise at room temperature under strong magnetic stirring. The mixture was stirred at room temperature for 4 hours, then quenched with water and extracted with CH₂Cl₂ two times. The combined organic layers were washed with saturated brine and water, respectively, dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (3.22 g, 78% yield). M.p.: 118-120 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.18 (s, 3H), 6.86 (dd, J = 4.8 Hz, 1.2 Hz, 1H), 7.10 (dd, J = 3.2 Hz, 1.6 Hz, 1H), 7.35 (dd, J = 4.8 Hz, 2.8 Hz, 1H), 7.86 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.05 (d, J = 1.6 Hz, 1H), 8.44 (br. s, 1H), 8.61 (d, J = 8.4 Hz, 1H), 9.87 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 25.1, 120.4, 122.7, 124.3, 127.8, 128.5, 128.9, 132.26, 132.29, 136.3, 144.0, 168.7, 190.4 ppm. HRMS (ESI⁺): calcd for C₁₃H₁₂NO₂S₂ [M+H]+ 278.0309, found 278.0300.

N-(2-(2-Bromothiophen-3-ylthio)-4-formylphenyl)acetamide (4b)

To a stirred solution of 3b (1.11 g, 4.0 mmol) in the mixture of HOAc-CH₂Cl₂ (1/1, v/v, 40 mL), NBS (785 mg, 4.4 mmol) was added slowly in portions. After this addition, the mixture was stirred for 6 hours. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water, saturated Na₂CO₃ and water respectively, dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was crystallized by petroleum ether/EtOH to give the product as a white solid (1.07 g, 75% yield). M.p.: 132-134 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.23 (s, 3H), 6.62 (d, J = 6.0 Hz, 1H), 7.23 (d, J = 6.0 Hz, 1H), 7.87 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 8.13 (s, 1H), 8.46 (br. s, 1H), 8.63 (d, J = 8.8 Hz, 1H), 9.89 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 25.3, 113.8, 120.3, 122.0, 127.6, 129.6, 130.5, 132.2, 132.8, 136.7, 144.4, 168.8, 190.3 ppm. HRMS (ESI⁺): calcd for C₁₃H₁₁BrNO₂S₂ [M+H]+ 355.9415, found 355.9416.

9-Acetyl-9H-benzo[b]thieno[2,3-e][1,4]thiazine-6-carbaldehyde (5b)

A mixture of compound 4b (45 mg, 0.125 mmol), CuI (4.8 mg, 0.025 mmol),
N,N-dimethylglycine hydrochloride (3.6 mg, 0.025 mmol) and K₃PO₄ (108 mg, 0.5 mmol) were dissolved in dioxane (4.0 mL) under an N₂ atmosphere and heated at 105 °C for 20 hours. After cooling, water was added and extracted with CH₂Cl₂ two times. The combined organic layers were washed with water and dried over anhydrous Na₂SO₄. Next, the solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (22 mg, 64% yield). M.p.: 138-140 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.41 (s, 3H), 6.82 (d, J = 5.6 Hz, 1H), 7.21 (d, J = 6.0 Hz, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.79 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.86 (d, J = 1.6 Hz, 1H), 9.96 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 23.5, 123.4, 124.0, 127.2, 128.3, 129.2, 134.0, 134.7, 135.7, 143.6, 169.3, 190.4 ppm. HRMS (ESI⁺): calcd for C₁₃H₁₀NO₂S₂ [M+H]⁺ 276.0153, found 276.0158.

9-Acetyl-2-bromo-9H-benzo[b]thieno[2,3-e][1,4]thiazine-6-carbaldehyde (6b)

To a stirred solution of 5b (138 mg, 0.5 mmol) in the mixture of HOAc-CH₂Cl₂ (1:1, v/v, 10.0 mL), NBS (98 mg, 0.55 mmol) was added slowly in portions. After this addition the mixture was stirred at room temperature for 6 hours. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water, saturated Na₂CO₃ and water, respectively, dried over anhydrous Na₂SO₄. After removal of the solvent under vacuum, the residue was crystalized by ether/EtOH to give the product as a white solid (135 mg, 76% yield). M.p.: 148-150 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 3H), 6.82 (s, 1H), 7.44 (d, J = 5.6 Hz, 1H), 7.80 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.85 (d, J = 1.6 Hz, 1H), 9.97 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 23.3, 110.6, 125.5, 126.6, 128.5, 129.3, 133.4, 134.9, 135.0, 143.0, 169.0, 190.2 ppm. HRMS (ESI⁺): calcd for C₁₃H₉BrNO₂S₂ [M+H]⁺ 353.9258, found 353.9259.

9-Acetyl-2-(4-hexyloxyphenyl)-9H-benzo[b]thieno[2,3-e][1,4]thiazine-6-carbaldehyde (7b)

A mixture of compound 6b (213 mg, 0.6 mmol), 4-(hexyloxy)phenylboronic acid (167 mg, 0.75 mmol), Pd(PPh₃)₄ (35 mg, 0.03 mmol) and Na₂CO₃ (255 mg, 2.4 mmol)
were dissolved in THF/H$_2$O (4/1, v/v, 10.0 mL). Then, the mixture was heated at 85 °C for 10 hours under an N$_2$ atmosphere. After cooling, the solvent was removed under vacuum. The reaction mixture was diluted with water and extracted with CH$_2$Cl$_2$ two times. The combined organic layers were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6/1, v/v) as the eluent to give the product as a white solid (249 mg, 92% yield). M.p.: 74-76 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.91 (t, $J$ = 7.2 Hz, 3H), 1.32-1.35 (m, 4H), 1.42-1.50 (m, 2H), 1.75-1.82 (m, 2H), 2.45 (s, 3H), 3.97 (t, $J$ = 6.4 Hz, 2H), 6.89-6.91 (m, 3H), 7.42-7.44 (m, 2H), 7.56 (d, $J$ = 6.8 Hz, 1H), 7.80 (dd, $J$ = 8.4 Hz, 2.0 Hz, 1H), 7.88 (d, $J$ = 1.6 Hz, 1H), 9.97 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.2, 22.7, 23.6, 25.8, 29.3, 31.7, 68.3, 115.1, 117.9, 125.8, 127.1, 127.3, 128.3, 129.3, 133.5, 133.9, 134.7, 143.0, 143.6, 159.6, 169.4, 190.4 ppm. HRMS (ESI$^+$): calcd for C$_{25}$H$_{26}$NO$_3$S$_2$ [M+H]$^+$ 452.1354, found 452.1360.

**9-Hexyl-2-(4-(hexyloxy)phenyl)-9H-benzo[b]thieno[2,3-e][1,4]thiazine-6-carbaldehyde (8b)**

A mixture of compound 7b (720 mg, 1.6 mmol) and K$_2$CO$_3$ (2.21 g, 16 mmol) were dissolved in DMF/H$_2$O (v/v, 4/1, 15.0 mL) under an N$_2$ atmosphere and heated to 85 °C overnight. After cooling, the solvent was removed under vacuum. Then, the residue was dissolved in anhydrous DMF under an N$_2$ atmosphere and followed by the addition of n-C$_6$H$_{13}$Br (560 $\mu$L, 4.0 mmol). The mixture was kept at 85 °C for 12 hours under an N$_2$ atmosphere. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1, v/v) as the eluent to give the product as an orange red solid (640 mg, 81% yield). M.p.: 68-70 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 0.91 (t, $J$ = 6.8 Hz, 6H), 1.34-1.36 (m, 8H), 1.46-1.47 (m, 4H), 1.76-1.89 (m, 4H), 3.71 (t, $J$ = 6.8 Hz, 2H), 3.96 (t, $J$ = 6.8 Hz, 2H), 6.57 (s, 1H), 6.69 (d, $J$ = 8.4 Hz, 1H), 6.87 (d, $J$ = 8.4 Hz, 1H), 7.48-7.52 (m, 3H), 7.80 (d, $J$ = 8.4 Hz, 1H), 7.88 (d, $J$ = 1.6 Hz, 1H), 9.97 (s, 1H) ppm.
Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 1.6 Hz, 1H), 7.52 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 9.72 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 14.1, 14.2, 22.7, 22.8, 25.9, 26.5, 26.7, 29.3, 31.5, 31.7, 51.1, 68.3, 108.6, 112.9, 115.0, 118.9, 122.4, 126.2, 126.4, 128.5, 130.7, 131.5, 135.0, 140.6, 148.9, 158.8, 189.7 ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{36}$NO$_2$S$_2$ [M+H]$^+$ 494.2187, found 494.2180.

(E)-2-Cyano-3-(9-hexyl-2-(4-(hexyloxy)phenyl)-9H-benzo[b]thieno[2,3-e][1,4]thiazin-6-yl)acrylic acid (TBT-3)

To a stirred solution of 8b (59 mg, 0.12 mmol) and cyanoacetic acid (32 mg, 0.36 mmol) in CHCl$_3$ (10.0 mL) was added piperidine (80 $\mu$L, 0.84 mmol). The resulting mixture was refluxed for 20 hours under an N$_2$ atmosphere, then cooled to room temperature and acidified with 2 M hydrochloric acid aqueous solution. The solution was extracted with CHCl$_3$. Then the organic phase was washed with water and dried over anhydrous Na$_2$SO$_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc/HOAc (100:50:1, v/v/v) to give the product as a blue solid (44 mg, 65% yield). M.p.: 214-216 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 0.84-0.88 (m, 6H), 1.23-1.30 (m, 8H), 1.36-1.41 (m, 4H), 1.65-1.76 (m, 4H), 3.75 (t, $J$ = 6.8 Hz, 2H), 3.95 (t, $J$ = 6.4 Hz, 2H), 6.90-6.92 (m, 3H), 7.01 (d, $J$ = 8.8 Hz, 1H), 7.41 (d, $J$ = 8.4 Hz, 2H), 7.62 (d, $J$ = 1.6 Hz, 1H), 7.82 (d, $J$ = 9.6 Hz, 1H), 8.06 (s, 1H) ppm. Clear $^{13}$C NMR spectrum was not obtained even after overnight collection of data due to the poor solubility of the compound. HRMS (ESI$^+$): calcd for C$_{32}$H$_{37}$N$_2$O$_3$S$_2$ [M+H]$^+$ 561.2246, found 561.2244. Anal. calcd for C$_{32}$H$_{36}$N$_2$O$_3$S$_2$ (%): C, 68.54; H, 6.47; N, 5.00; S, 11.43. found: C, 67.90; H, 6.40; N, 5.55; S, 11.18.

II. Electrochemical properties

The electrochemical properties were recorded by cyclic voltammetry (CV) in CH$_2$Cl$_2$ using 0.1 M tetrabutylammonium hexa-fluorophosphate as supporting electrolyte, Pt as the counter electrode, Ag/AgNO$_3$ as a reference electrode, ferrocene/ferricenium (Fc/Fc$^+$) redox couple as an internal standard at 0.63 V (vs NHE).$^6$ The ground oxidation potential ($E_{ox}$) corresponding to the highest occupied
molecular orbital (HOMO) and the zero–zero band gaps \((E_{0-0})\) estimated from the onset of the UV-vis absorption spectra. The excited-state oxidation potential \((E_{\text{ox}}^*)\) corresponding to the lowest unoccupied molecular orbital (LUMO), calculated from \(E_{\text{ox}}^*-E_{0-0}\).

![CV curves of three thieno[1,4]-benzothiazine-based dyes.](image)

**Figure S1.** CV curves of three thieno[1,4]-benzothiazine-based dyes.

### III. Photophysical and photovoltaic parameters

1) \(J-V\) curves of TBT-1–3 and PT-C₆ based DSSCs with CDCA

The TiO₂ photoanode was dipped into the solution containing 0.5 mM dye sensitizers in THF with 2.5 mM chenodeoxycholic acid (CDCA) as co-adsorbent for 36 h.

![J–V curves of TBT-1–3 and PT-C₆-based DSSCs with CDCA](image)

**Figure S2.** \(J-V\) curves of TBT-1–3 and PT-C₆-based DSSCs with CDCA

2) The absorption spectra of the dyes desorbed from the TiO₂ photoanodes
Dye adsorption amounts on TiO₂ photoanodes were obtained by using 0.1 M NaOH aqueous-THF (1:1) mixture solutions to desorb the dye on photoanode for 10 min and measuring their UV-vis spectra. The TBT-1–3 and PT-C₆ standard sample were prepared into 1×10⁻⁵ M by using 0.1 M NaOH aqueous-THF (1:1) mixture solutions as solvent.

![Absorption spectra of the dyes desorbed from the TiO₂ photoanodes](image1)

**Figure S3.** The absorption spectra of the dyes desorbed from the TiO₂ photoanodes (ss = standard sample, ds = desorbed sample)

3) **LHE of TBT-1–3 and PT-C₆**

The light harvesting efficiency (LHE) was calculated from the absorption spectra of dyes loaded on 7 μm TiO₂ films through the relation of \( LHE = 1 - 10^{-\alpha} \), where \( \alpha \) is the intensity of light absorption on the nanoporous TiO₂ film.

![LHE of TBT-1–3 and PT-C₆](image2)

**Figure S4.** LHE of TBT-1–3 and PT-C₆
IV. References


V. Copies of $^1$H, and $^{13}$C NMR spectra