Electronic supplementary information

Synthesis
2-acetyl-5-bromothiophene, N,N-dimethylaminobenzaldehyde, 5-Formyl-2-thienylboronic Acid, Dichlorobis(triphenylphosphine)palladium(II), cyanoacetic acid were purchased commercially without further purification. 4-(6-methylbenzothiazol-2-yl)phenylhydrazone was synthesized by Nippon Chemical Works. Solvents and other chemicals were used as received.

General procedure 1 for the preparation of 3a–c
To a stirred solution of 2-acetyl-5-bromothiophene (1 mmol) and respective benzaldehyde (1 mmol) in EtOH (3 ml) was added 15 % NaOH aq (0.2 ml). The solution was stirred overnight and added small amount of water. The resulting precipitate was filtered and washed with water then EtOH. The crude solid was purified by recrystallization from EtOH or column chromatography on silica gel.

General procedure 2 for the preparation of 4a–c
To a stirred solution of 3 (1 mmol) and 4-(6-methylbenzothiazol-2-yl)phenylhydrazone (1 mmol) in EtOH (6.5 ml) were added a few drops of 37 % HCl. The solution was refluxed overnight. The reaction mixture was cooled to room temperature and extracted with water/EtOAc. The organic layer was dried over MgSO₄ and evaporated. The crude solid was purified by recrystallization from EtOH/THF or column chromatography on silica gel.

General procedure 3 for the preparation of 5a–c
4 (1 mmol), 5-Formyl-2-thienylboronic Acid (1.5 mmol), Cs₂CO₃ (2.5 mmol) and PdCl₂(PPh₃)₂ (0.01 mmol) were dissolved in THF (6 ml)/EtOH (3 ml) and refluxed overnight. After the reaction completed, the mixture was cooled to room temperature and extracted with water/EtOAc. The organic layer was dried over MgSO₄ and concentrated by evaporation. The crude product was purified by recrystallization or column chromatography on silica gel.

General procedure 4 for the preparation of the pyrazoline photosensitizers (6a–c)
5 (1 mmol), cyanoacetic acid (3 mmol), piperidine (3.3 mmol) were dissolved in CH₃CN and refluxed for . After the reaction completed, the mixture was cooled to room temperature and diluted with EtOAc, and then washed with HCl aq and water. The organic layer was dried over MgSO₄ and concentrated by evaporation. The crude product was purified by recrystallization.

Synthesis of compound 3a
Compound 3a was synthesized according the general procedure 1 and obtained as a yellow solid.
Yield 49 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.05 (s, 6 H), 6.68 (d, $J$ = 8.9 Hz, 2 H), 7.11 (d, $J$ = 15.3 Hz, 1 H), 7.12 (d, $J$ = 4.0 Hz, 1 H), 7.53 (d, $J$ = 8.9 Hz, 2 H), 7.55 (d, $J$ = 4.0 Hz, 1 H), 7.81 (d, $J$ = 15.3 Hz, 1 H).$^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 40.1, 117.8, 115.0, 121.5, 122.2, 130.6, 130.8, 131.2, 145.5, 147.9, 152.2, 180.9. Elemental analysis calcd for C$_{15}$H$_{14}$BrNOS (336.25): C 53.58, H 4.20, N 4.17, S 9.54; found: C 53.20, H 4.16, N 4.41, S 9.58.

Synthesis of compound 3b

Compound 3b was synthesized according the general procedure 1 and obtained as a yellow solid. Yield 81 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.89 (t, $J$ = 7.0 Hz, 3 H), 1.35 (m, 4 H), 1.47 (m, 2 H), 1.80 (m, 2 H), 4.00 (t, $J$ = 6.6 Hz 3 H), 6.92 (d, $J$ = 8.8 Hz, 2 H), 7.14 (d, $J$ = 4.0 Hz, 1 H), 7.19 (d, $J$ = 15.5 Hz, 1 H), 7.58 (d, $J$ = 4.0 Hz, 1 H), 7.58 (d, $J$ = 8.7 Hz, 1 H), 7.81 (d, $J$ = 15.4 Hz, 1 H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 14.0, 22.6, 25.7, 29.1, 31.6, 68.2, 115.0, 117.9, 122.3, 127.0, 130.4, 131.3, 131.4, 144.6, 147.4, 161.6, 180.9. Elemental analysis calcd for C$_{19}$H$_{21}$BrO$_2$S (393.34): C 58.02, H 5.38, S 8.15; found: C 57.9, H 5.40, S 7.29.

Synthesis of compound 3c

Compound 3c was synthesized by 2 steps. First, carboxyl functionalized chalcone was obtained according to the general procedure 1 using terephthaldehydic acid (Yield 68 %). Then esterification using EtBr with K$_2$CO$_3$ was carried out to afford 3c as a white solid. Yield 88 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.41 (t, $J$ = 7.1 Hz, 3 H), 4.40 (q, $J$ = 7.1 Hz, 6 H), 7.16 (d, $J$ = 4.0 Hz, 1 H), 7.33 (d, $J$ = 15.6 Hz, 1 H), 7.43 (m, 3 H), 7.60 (d, $J$ = 4.0 Hz, 1 H), 7.64 (m, 2 H), 7.85 (d, $J$ = 15.6 Hz, 1 H), 8.08 (d, $J$ = 8.3 Hz, 2 H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 14.3, 61.3, 122.4, 123.4, 128.3, 130.1, 131.5, 132.1, 138.6, 143.1, 146.8, 165.9, 180.5. Elemental analysis calcd for C$_{16}$H$_{13}$BrO$_3$S (365.24): C 52.61, H 3.59, S 8.78; found: C 52.24, H 3.58, S 8.91.

Synthesis of compound 3d

Compound 3d was synthesized according the general procedure 1 and obtained as a yellow solid. Yield 39 %. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (d, $J$ = 4.0 Hz, 1 H), 7.33 (d, $J$ = 15.6 Hz, 1 H), 7.43 (m, 3 H), 7.60 (d, $J$ = 4.0 Hz, 1 H), 7.64 (m, 2 H), 7.85 (d, $J$ = 15.6 Hz, 1 H). $^{13}$C NMR (400 MHz, CDCl$_3$) $\delta$ 120.5, 122.9, 128.5, 129.0, 131.4, 131.8, 134.5, 144.7, 147.1, 180.9. Elemental analysis calcd for C$_{13}$H$_9$BrOS (291.96): C 53.26, H 3.09, S 10.94; found: C 52.90, H 3.26, S 13.23.

Synthesis of compound 4a

Compound 4a was synthesized according the general procedure 2 and obtained as an orange solid. Yield 99 %. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 2.43 (s, 3 H), 2.84 (s, 6 H), 3.13 (dd, $J$ = 17.4, 5.1 Hz,
1 H), 3.88 (dd, J = 17.4, 11.9 Hz, 1 H), 5.55 (dd, J = 11.9, 5.1 Hz, 1 H), 6.68 (d, J = 8.9 Hz, 2 H), 7.06 (d, J = 8.9 Hz, 2 H), 7.07 (d, J = 8.8 Hz, 2 H), 7.15 (d, J = 3.9 Hz, 1 H), 7.26 (d, J = 4.0 Hz, 1 H), 7.28 (d, J = 8.8 Hz, 1 H), 7.81 (br, 2 H), 7.84 (d, J = 8.9 Hz, 2 H).

**13C NMR (400 MHz, DMSO)** δ 20.9, 43.1, 62.4, 112.6, 113.0, 113.2, 121.5, 121.6, 123.0, 126.4, 127.7, 128.1, 128.4, 126.4, 127.7, 128.1, 128.4, 128.6, 131.2, 134.0, 134.3, 137.0, 144.8, 145.3, 149.8, 151.8, 166.2. HRMS (ESI, m/z): [M + H]^+ calcd for C_{38}H_{28}N_4O_4S_3, 573.0777; found, 573.0760.

**Synthesis of compound 4b**

Compound 4b was synthesized according the general procedure 2 and obtained as a yellow solid. Yield 85 %. **1H NMR (400 MHz, acetone-d_6)** δ 0.87 (t, J = 7.0 Hz, 3 H), 1.33 (m, 4 H), 1.45 (m, 2 H), 1.73 (m, 2 H), 2.45 (s, 1 H), 3.20 (dd, J = 17.3, 5.7 Hz, 1 H), 3.96 (t, J = 6.5, 2 H), 4.00 (dd, J = 17.4, 12.1 Hz, 1 H), 5.60 (dd, J = 12.1, 5.7 Hz, 1 H), 6.92 (d, J = 8.8 Hz, 2 H), 7.08 (d, J = 3.9 Hz, 1 H), 7.14 (d, J = 8.9 Hz, 2 H), 7.17 (d, J = 3.9 Hz, 1 H), 7.26 (d, J = 8.7 Hz, 2 H), 7.28 (br, 1 H), 7.77 (br, 1 H), 7.78 (d, J = 8.3 Hz, 1 H), 7.90 (d, J = 9.0 Hz, 2 H). **13C NMR (400 MHz, (CD_3)_CO)** δ 14.3, 21.4, 23.3, 26.4, 32.3, 44.2, 64.1, 68.6, 114.1, 114.3, 115.9, 122.2, 122.8, 125.1, 128.0, 128.5, 128.7, 129.1, 131.9, 134.4, 135.5, 135.6, 138.9, 145.4, 146.9, 153.5, 159.8, 167.4. Elemental analysis calcd for C_{33}H_{32}BrN_3OS_2 (630.66): C 62.85, H 5.11, N 6.66, S 10.17; found: C 63.21, H 5.12, N 6.90, S 9.63.

**Synthesis of compound 4c**

Compound 4c was synthesized according the general procedure 2 and obtained as a yellow solid. Yield 52 %. **1H NMR (400 MHz, CDCl_3)** δ 0.88 (t, J = 7.0 Hz, 3 H), 1.37 (t, J = 7.1 Hz, 3 H), 2.46 (s, 3 H), 3.11 (dd, J = 17.3, 5.7 Hz, 1 H), 3.85 (dd, J = 16.9, 12.4 Hz, 1 H), 4.36 (q, J = 7.1, 2 H), 5.41 (dd, J = 12.3, 6.3 Hz, 1 H), 6.78 (d, J = 3.8 Hz, 1 H), 6.98 (d, J = 3.9 Hz, 1 H), 7.01 (d, J = 8.9 Hz, 2 H), 7.24 (d, J = 8.4 Hz, 1 H), 7.35 (d, J = 8.3 Hz, 2 H), 7.62 (s, 1 H), 7.85 (d, J = 8.3 Hz, 1 H), 7.86 (d, J = 8.9 Hz, 2 H), 8.03 (d, J = 8.4 Hz, 2 H). **13C NMR (400 MHz, CDCl_3)** δ 14.3, 21.4, 23.3, 26.4, 32.3, 44.2, 64.1, 68.6, 114.1, 114.3, 115.9, 122.2, 122.8, 125.1, 128.0, 128.5, 128.7, 129.1, 131.9, 134.4, 135.5, 135.6, 138.9, 145.4, 146.9, 153.5, 159.8, 167.4. Elemental analysis calcd for C_{30}H_{24}BrN_3O_2S_2 (602.56): C 59.80, H 5.11, N 6.66, S 10.64; found: C 59.51, H 5.08, N 7.29, S 10.55.

**Synthesis of compound 4d**

Compound 4d was synthesized according the general procedure 2 and obtained as a yellow solid. Yield 28 %. **1H NMR (400 MHz, CDCl_3)** δ 2.46 (s, 3 H), 3.13 (dd, J = 16.9, 6.2 Hz, 1 H), 3.84 (dd, J = 16.9, 12.3 Hz, 1 H), 5.38 (dd, J = 12.3, 6.2 Hz, 1 H), 6.78 (d, J = 3.9 Hz, 1 H), 6.98 (d, J = 3.9 Hz, 1 H), 7.05 (d, J = 8.9, 2H), 7.23 (m, 6 H), 7.62 (s, 1 H), 7.84 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 8.9 Hz, 2 H). **13C NMR (400 MHz, CDCl_3)** δ 20.9, 43.0, 62.6, 112.9, 113.4, 121.5, 121.6, 123.3, 125.6,
Elemental analysis calcd for C$_{27}$H$_{20}$BrN$_3$S$_2$ (529.03): C 61.13, H 3.80, N 7.92, S 12.09; found: C 61.53, H 4.22, N 7.73, S 11.59.

Synthesis of compound 5a

Compound 5a was synthesized according the general procedure 3 and obtained as a yellow solid. Yield 86 %.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 2.43 (s, 3 H), 2.84 (s, 6 H), 3.18 (dd, $J = 17.3, 4.9$ Hz, 1 H), 3.93 (dd, $J = 17.3, 12.0$ Hz, 1 H), 5.60 (dd, $J = 11.9, 4.9$ Hz, 1 H), 6.69 (d, $J = 8.8$ Hz, 2 H), 7.09 (d, $J = 8.5$ Hz, 2 H), 7.11 (d, $J = 8.6$ Hz, 2 H), 7.29 (d, $J = 8.4$ Hz, 1 H), 7.34 (d, $J = 3.8$ Hz, 1 H), 7.62 (d, $J = 3.9$ Hz, 1 H), 7.65 (d, $J = 3.9$ Hz, 1 H), 7.82 (d, $J = 8.4$ Hz, 2 H), 7.86 (d, $J = 8.9$ Hz, 2 H), 8.03 (d, $J = 4.0$ Hz, 1 H), 9.91 (s, 1 H).

$^{13}$C NMR (400 MHz, DMSO) δ 20.9, 43.1, 62.6, 112.6, 113.1, 121.5, 121.6, 123.2, 125.8, 126.4, 127.5, 127.7, 128.1, 128.4, 129.3, 134.0, 134.3, 135.8, 136.6, 139.2, 141.5, 144.8, 145.1, 149.8, 151.8, 166.1, 183.8. Elemental analysis calcd for C$_{34}$H$_{28}$N$_4$O$_3$S$_3$ (604.81): C 67.52, H 4.67, N 9.26, S 15.91; found: C 67.56, H 4.70, N 9.19, S 14.98.

Synthesis of compound 5b

Compound 5b was synthesized according the general procedure 3 and obtained as an orange solid. This compound was used for next step without further purification.

$^1$H NMR (400 MHz, acetone-$d_6$) δ 0.88 (t, $J = 6.9$ Hz, 3 H), 1.33 (m, 4 H), 1.45 (m, 2 H), 1.74 (m, 2 H), 2.46 (s, 3 H), 3.24 (dd, $J = 17.1, 5.6$ Hz, 1 H), 3.95 (t, $J = 6.5$, 2 H), 4.04 (dd, $J = 17.1, 12.1$ Hz, 1 H), 5.62 (dd, $J = 12.0, 5.6$ Hz, 1 H), 6.91 (d, $J = 8.6$ Hz, 2 H), 7.17 (d, $J = 8.8$ Hz, 2 H), 7.27 (m, 4 H), 7.48 (d, $J = 3.8$ Hz, 1 H), 7.53 (d, $J = 4.0$ Hz, 1 H), 7.75, (s, 1 H), 7.80 (d, $J = 8.3$ Hz, 1 H), 7.93 (m, 4 H), 9.94 (s, 1 H).

$^{13}$C NMR (400 MHz, (CD$_3$)$_2$CO) δ 14.2, 21.4, 23.2, 26.3, 32.2, 44.2, 64.2, 68.4, 114.1, 115.8, 122.1, 122.7, 125.1, 125.9, 127.6, 127.8, 128.3, 129.0, 134.1, 135.3, 135.5, 137.4, 138.2, 138.9, 143.1, 145.2, 146.3, 146.5, 153.3, 160.0, 167.3, 183.5.

Synthesis of compound 5c

Compound 5c was synthesized according the general procedure 3 and obtained as an orange solid. Yield 72 %.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 1.28 (t, $J = 7.1$ Hz, 3 H), 2.43 (s, 3 H), 3.27 (dd, $J = 17.5, 5.3$ Hz, 1 H), 4.05 (dd, $J = 17.5, 12.3$ Hz, 1 H), 4.29 (q, $J = 7.1$, 2 H), 5.84 (dd, $J = 12.2, 5.3$ Hz, 1 H), 7.07 (d, $J = 8.8$ Hz, 2 H), 7.29 (d, $J = 8.4$ Hz, 1 H), 7.35 (d, $J = 3.8$ Hz, 1 H), 7.45 (d, $J = 8.3$ Hz, 2 H), 7.62 (d, $J = 4.0$ Hz, 1 H), 7.66 (d, $J = 3.9$ Hz, 1 H), 7.82 (d, $J = 8.7$ Hz, 2 H), 7.88 (d, $J = 8.9$ Hz, 2 H), 7.97 (d, $J = 8.3$ Hz, 2 H), 8.04 (d, $J = 4.0$ Hz, 1 H), 9.91 (s, 1 H).

$^{13}$C NMR (400 MHz, DMSO) δ 14.1, 20.9, 42.8, 60.6, 62.5, 113.0, 121.5, 121.6, 123.6, 125.9, 126.1, 127.5, 127.7, 128.3, 129.3, 129.7, 130.0, 134.0, 134.4, 136.1, 136.2, 139.2, 141.7, 144.7, 144.8, 145.0, 146.5, 151.8, 165.2, 166.0, 183.8. Elemental analysis calcd for C$_{35}$H$_{27}$N$_3$O$_3$S$_3$ (633.80): C 66.33, H 4.29, N 6.63, S
Synthesis of compound 5d

Compound 5d was synthesized according the general procedure 3 and obtained as an orange solid. This compound was used for next step without further purification. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 2.43 (s, 3 H), 3.24 (dd, $J = 17.4$, 5.1 Hz, 1 H), 4.01 (dd, $J = 17.4$, 12.1 Hz, 1 H), 5.74 (dd, $J = 12.1$, 5.1 Hz, 1 H), 7.09 (d, $J = 8.9$ Hz, 2 H), 7.27 (m, 4 H), 7.35 (d, $J = 3.9$ Hz, 1 H), 7.38 (m, 2 H), 7.61 (d, $J = 3.9$ Hz, 1 H), 7.65, (d, $J = 3.9$ Hz, 1 H), 7.81 (m, 2H), 7.87 (d, $J = 9.0$ Hz, 2 H), 8.03 (d, $J = 4.0$, 1 H), 9.91 (s, 1 H). $^{13}$C NMR (400 MHz, DMSO) δ 20.9, 43.1, 62.8, 113.0, 121.5, 121.6, 123.4, 125.6, 125.9, 127.5, 127.7, 128.2, 129.1, 129.5, 134.0, 136.0, 136.3, 139.1, 141.3, 141.6, 144.8, 144.9, 145.0, 151.8, 166.1, 183.8.

Synthesis of compound 6a

Compound 6a was synthesized according the general procedure 4 and obtained as a dark red solid. Yield 79 %. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 2.43 (s, 3 H), 2.85 (s, 6 H), 3.19 (dd, $J = 17.3$, 5.0 Hz, 1 H), 3.94 (dd, $J = 17.3$, 12.0 Hz, 1 H), 5.61 (dd, $J = 12.0$, 5.0 Hz, 1 H), 6.69 (d, $J = 8.9$ Hz, 2 H), 7.11 (dd, $J = 9.0$ Hz, 4 H), 7.29 (d, $J = 8.3$ Hz, 1 H), 7.35 (d, $J = 3.8$ Hz, 1 H), 7.61 (d, $J = 3.9$ Hz, 1 H), 7.68 (d, $J = 4.0$ Hz, 1 H), 7.82 (m, 2 H), 7.86 (d, $J = 9.0$ Hz, 2 H), 7.98 (d, $J = 4.1$ Hz, 1 H), 8.48 (s, 1 H). $^{13}$C NMR (400 MHz, DMSO) δ 20.9, 43.1, 62.6, 112.7, 113.2, 121.5, 121.6, 123.2, 126.4, 127.4, 127.7, 128.1, 128.4, 129.4, 131.0, 134.3, 135.7, 136.7, 144.8, 145.0, 149.8, 151.8, 163.3, 166.1. HRMS (ESI, m/z): [M – H]⁻ calcd for C$_{37}$H$_{29}$N$_5$O$_2$S$_3$, 670.1411; found, 670.1405.

Synthesis of compound 6b

Compound 6b was synthesized according the general procedure 4 and obtained as a dark red solid. Yield 91 %. $^1$H NMR (400 MHz, acetone-$d_6$) δ 0.84 (t, $J = 6.7$ Hz, 3 H), 1.27 (m, 4 H), 1.36 (m, 2 H), 1.66 (m, 2 H), 2.43 (s, 3 H), 3.20 (dd, $J = 17.4$, 4.7 Hz, 1 H), 3.90 (t, $J = 6.5$, 2 H), 3.96 (m, 1 H), 5.67 (dd, $J = 11.3$, 3.8 Hz, 1 H), 6.90 (d, $J = 8.5$ Hz, 2 H), 7.10 (d, $J = 8.6$ Hz, 2 H), 7.19 (d, $J = 8.5$ Hz, 2 H), 7.29 (d, $J = 8.3$ Hz, 1 H), 7.35 (br, 1 H), 7.61 (d, $J = 3.7$ Hz, 1 H), 7.69 (d, $J = 4.0$ Hz, 1 H), 7.82 (m, 2 H), 8.00 (d, $J = 4.1$ Hz, 1 H), 8.51 (s, 1 H). $^{13}$C NMR (400 MHz, (CD$_3$)$_2$CO) δ 14.2, 21.4, 23.2, 26.3, 32.2, 44.2, 64.2, 68.4, 114.1, 115.8, 122.7, 125.1, 125.9, 127.6, 127.8, 128.3, 129.0, 129.2, 134.1, 135.3, 135.5, 137.4, 138.2, 143.1, 145.2, 146.3, 146.5, 153.3, 159.7, 167.3, 183.5. HRMS (ESI, m/z): [M – H]⁻ calcd for C$_{41}$H$_{38}$N$_5$O$_3$S$_3$, 727.1877; found, 727.1869.

Synthesis of compound 6c

Compound 6c was synthesized according the general procedure 4 and obtained as a dark red solid. Yield 75 %. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 1.28 (t, $J = 7.1$ Hz, 3 H), 2.43 (s, 3 H), 3.27 (dd, $J = 15.18$; found: C 66.00, H 4.30, N 6.75, S 14.77.

1. H NMR (400 MHz, DMSO-$d_6$) δ 2.43 (s, 3 H), 3.24 (dd, $J = 17.4$, 5.1 Hz, 1 H), 4.01 (dd, $J = 17.4$, 12.1 Hz, 1 H), 5.74 (dd, $J = 12.1$, 5.1 Hz, 1 H), 7.09 (d, $J = 8.9$ Hz, 2 H), 7.27 (m, 4 H), 7.35 (d, $J = 3.9$ Hz, 1 H), 7.38 (m, 2 H), 7.61 (d, $J = 3.9$ Hz, 1 H), 7.65, (d, $J = 3.9$ Hz, 1 H), 7.81 (m, 2H), 7.87 (d, $J = 9.0$ Hz, 2 H), 8.03 (d, $J = 4.0$, 1 H), 9.91 (s, 1 H). $^{13}$C NMR (400 MHz, DMSO) δ 20.9, 43.1, 62.8, 113.0, 121.5, 121.6, 123.4, 125.6, 125.9, 127.5, 127.7, 128.2, 129.1, 129.5, 134.0, 136.0, 136.3, 139.1, 141.3, 141.6, 144.8, 144.9, 145.0, 151.8, 166.1, 183.8.
17.5, 5.3 Hz, 1 H), 4.04 (dd, J = 17.4, 12.3 Hz, 1 H), 4.29 (q, J = 7.1, 2 H), 5.84 (dd, J = 12.2, 5.4 Hz, 1 H), 7.08 (d, J = 8.9 Hz, 2 H), 7.29 (d, J = 8.4 Hz, 1 H), 7.36 (d, J = 3.8 Hz, 1 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.62 (d, J = 3.9 Hz, 1 H), 7.69 (d, J = 4.0 Hz, 1 H), 7.82 (m, 2 H), 7.87 (d, J = 9.0 Hz, 2 H), 7.97 (d, J = 8.5 Hz, 2 H), 8.00 (d, J = 4.3 Hz, 1 H), 8.49 (s, 1 H). ¹³C NMR (400 MHz, DMSO) δ 14.1, 20.9, 60.6, 62.6, 113.1, 116.6, 121.5, 121.6, 123.6, 125.7, 126.2, 127.4, 127.7, 128.3, 129.3, 129.8, 130.0, 134.0, 134.4, 134.6, 136.0, 136.2, 144.8, 146.5, 151.8, 163.4, 165.2, 166.0. HRMS (ESI, m/z): [M – H]⁻ calcd for C₃₈H₂₈N₄O₄S₃, 699.1200; found, 669.1199.

Synthesis of compound 6d

Compound 6d was synthesized according the general procedure 4 and obtained as a dark red solid. Yield 69 %. ¹H NMR (400 MHz, DMSO-d₆) δ 2.43 (s, 3 H), 3.24 (dd, J = 17.4, 5.2 Hz, 1 H), 4.00 (dd, J = 17.4, 12.1 Hz, 1 H), 5.74 (dd, J = 12.1, 5.1 Hz, 1 H), 7.10 (d, J = 8.9 Hz, 2 H), 7.28 (m, 4 H), 7.35 (m, 3 H), 7.61 (d, J = 3.9 Hz, 1 H), 7.69, (d, J = 4.0 Hz, 1 H), 7.81 (m, 2H), 7.87 (d, J = 9.0 Hz, 2 H), 8.00 (d, J = 4.4, 1 H), 8.51 (s, 1 H). ¹³C NMR (400 MHz, DMSO) δ 20.9, 43.0, 113.0, 113.0, 121.5, 121.6, 125.6, 127.7, 128.2, 129.1, 129.6, 134.0, 134.3, 141.3, 145.0, 151.8, 166.1. Elemental analysis calcd for C₃₅H₂₄N₄O₂S₃ (628.11): C 66.85, H 3.85, N 8.91; found: C 66.97, H 4.16, N 8.60.
Figure S1. $^{1}H$ NMR spectra of $3a$.

Figure S2. $^{13}C$ NMR spectra of $3a$. 
Figure S3. $^1$H NMR spectra of 3b.

Figure S4. $^{13}$C NMR spectra of 3b.
Figure S5. $^1$H NMR spectra of 3c.

Figure S6. $^{13}$C NMR spectra of 3c.
Figure S7. $^1$H NMR spectra of 3d.

Figure S8. $^{13}$C NMR spectra of 3d.
Figure S9 $^1$H NMR spectra of 4a.

Figure S10 $^{13}$C NMR spectra of 4a.
Figure S11. H\textsuperscript{1} NMR spectra of 4b.

Figure S12. C\textsuperscript{13} NMR spectra of 4b.
Figure S13. $^1\text{H}$ NMR spectra of 4c.

Figure S14. $^{13}\text{C}$ NMR spectra of 4c.
Figure S15. H¹ NMR spectra of 4d.

Figure S16. C¹³ NMR spectra of 4d.
Figure S17. H\textsuperscript{1} NMR spectra of 5a.

Figure S18. C\textsuperscript{13} NMR spectra of 5a.
Figure S19. $^1$H NMR spectra of 5b.

Figure S20. $^{13}$C NMR spectra of 5b.
Figure S21. $^1$H NMR spectra of $5c$.

Figure S22. $^{13}$C NMR spectra of $5c$. 
Figure S23. $^1$H NMR spectra of 5d.

Figure S24. $^{13}$C NMR spectra of 5d.
Figure S25. $^1$H NMR spectra of 6a.

Figure S26. $^{13}$C NMR spectra of 6a.
Figure S27. $^1$H NMR spectra of 6b.

Figure S28. $^{13}$C NMR spectra of 6b.
Figure S29. $\text{H}^1$ NMR spectra of 6c.

Figure S30. $\text{C}^{13}$ NMR spectra of 6c.
Figure S31. H\textsuperscript{1} NMR spectra of 6d.

Figure S32. C\textsuperscript{13} NMR spectra of 6d.
Figure S33. Absorption spectra of 6a–6d adsorbed on TiO$_2$.

Table S1. Photovoltaic parameters of all obtained data measured under AM 1.5G (100 mW/cm$^2$).

<table>
<thead>
<tr>
<th>Dye</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>10.4 ± 0.1</td>
<td>656 ± 3</td>
<td>0.74 ± 0.00</td>
<td>5.1 ± 0.1</td>
</tr>
<tr>
<td>6b</td>
<td>9.53 ± 0.11</td>
<td>641 ± 0</td>
<td>0.74 ± 0.00</td>
<td>4.5 ± 0.0</td>
</tr>
<tr>
<td>6c</td>
<td>8.80 ± 0.07</td>
<td>624 ± 2</td>
<td>0.73 ± 0.01</td>
<td>4.0 ± 0.0</td>
</tr>
<tr>
<td>6d</td>
<td>9.04 ± 0.06</td>
<td>620 ± 1</td>
<td>0.73 ± 0.00</td>
<td>4.1 ± 0.0</td>
</tr>
</tbody>
</table>

The tendency between dye structure and solar cell performance was reproducible.

Table S2. Photovoltaic parameters of DSSCs with a double-layer TiO$_2$ film employing 6a–d measured under AM 1.5G (100 mW/cm$^2$).

<table>
<thead>
<tr>
<th>Dye</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6a</td>
<td>12.3</td>
<td>636</td>
<td>0.73</td>
<td>5.7</td>
</tr>
<tr>
<td>6b</td>
<td>11.4</td>
<td>622</td>
<td>0.73</td>
<td>5.1</td>
</tr>
<tr>
<td>6c</td>
<td>10.5</td>
<td>608</td>
<td>0.73</td>
<td>4.6</td>
</tr>
<tr>
<td>6d</td>
<td>10.0</td>
<td>579</td>
<td>0.70</td>
<td>4.1</td>
</tr>
</tbody>
</table>