Supporting Information

**Metal Free Efficient Dye Sensitized Solar Cells based on Thioalkylated Bithiophenyl Organic Dyes**

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Source of materials:

Titanium(IV) tetraisoproproxide (TTIP, >98%) and chenodeoxycholic acid (CDCA, ≥ 95%) were received from Sigma Aldrich. Cis-diisothiocyanato bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium (II) bis(tetrabutylammonium) (N719 dye), transparent TiO₂ paste (TL paste, Ti-nanoxide HT/SP, average diameter ~20 nm), and Surlyn® (SX1170-25, 25 μm) were acquired from Solaronix (S.A., Aubonne, Switzerland). Tert-butyl alcohol (tBA, 96%) and 4-tert-butylpyridine (tBP, 96%) were obtained from Acros. Acetonitrile (ACN, 99.99%) and dichloromethane (DCM, 99.8%) were purchased from J. T. Baker. Lithium iodide (LiI, synthetical grade), iodine (I₂, synthetical grade), and poly(ethylene glycol) (PEG, MW~20,000) were obtained from Merck. 1,2-Dimethyl-3-propylimidazolium iodide (DMPII) was brought from Tokyo Chemical Industry Co. Ltd. 3-Methoxypropionitrile (MPN, 99%) was bought from Alfa Aesar. Commercial light-scattering TiO₂ particles (ST-41) with an average particle size of 200 nm were acquired from Ishihara Sangyo, Ltd.
**Synthesis details:**

![Scheme S1. Synthetic route for the dyes studied in this work.]

**Compound 9a:**

The title compound was obtained as a light yellow solid (yield = 67%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.48 (d, $J = 6.6$ Hz, 2 H), 7.33-7.28 (m, 4 H), 7.21 (s, 1 H), 7.17-7.06 (m, 9 H), 2.89-2.81 (m, 4 H), 1.66-1.54 (m, 4 H), 1.48-1.35 (m, 4 H), 0.88 (t, $J = 7.2$ Hz, 6 H); $^{13}$C NMR (125 MHz, CDCl$_3$): 147.87, 147.35, 144.17, 134.46, 132.88, 132.76, 132.36, 131.89, 130.39, 129.39, 127.25, 126.56, 125.73, 124.70, 123.36, 112.62, 35.93, 35.91, 31.67, 31.58, 21.89, 21.85, 13.67. HRMS (m/z, FAB+) calcd for C$_{34}$H$_{34}$BrNS$_3$ 663.0757, found 663.0762.

**Compound 9b:**

The title compound was obtained as a light yellow solid (yield = 64%). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.48 (br, 2 H), 7.32-7.27 (m, 5 H), 7.16-7.04 (m, 9 H), 2.74-2.71 (br, 4 H), 1.87-1.78
(m, 1H), 1.44-1.34 (m, 1H), 0.99 (d, \( J = 6.9 \) Hz, 6 H); HRMS (m/z, FAB+) calcd for C\(_{34}\)H\(_{34}\)BrNS\(_{4}\) 663.0757, found 663.0764.

**Compound 9c:**

The title compound was obtained as a light yellow solid (yield = 65%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.48 (d, \( J = 8.7 \) Hz, 2 H), 7.30-7.25 (m, 4H), 7.21 (s, 1H), 7.13-7.06 (m, 9 H), 1.29 (d, \( J = 7.2 \) Hz, 18 H); HRMS (m/z, FAB+) calcd for C\(_{34}\)H\(_{34}\)BrNS\(_{4}\) 663.0757, found 663.0766.

**Compound 9d:**

The title compound was obtained as a light yellow solid (yield = 59 %). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta \) 7.46 (d, \( J = 6.6 \) Hz, 2 H), 7.30-7.25 (m, 4H), 7.18 (s, 1H), 7.11-7.04 (m, 9 H), 3.01-2.97 (m, 2 H), 1.94-1.81 (m, 4 H), 1.72-1.59 (m, 4 H), 1.31-1.18 (m, 12 H); \(^{13}\)C NMR (125MHz, CDCl\(_3\)): 147.82, 147.35, 143.48, 136.96, 134.41, 132.92, 130.97, 130.11, 129.37, 127.37, 127.31, 126.52, 124.66, 123.41, 123.31, 112.28, 48.66, 48.62, 33.37, 33.33, 28.29, 26.79, 26.08, 26.01, 25.69, 25.66, 17.31, 14.14, 13.62. HRMS (m/z, FAB+) calcd for C\(_{38}\)H\(_{38}\)BrNS\(_{4}\) 715.1070, found 715.1070.
**Compound 9e:**

The title compound was obtained as a light yellow solid (yield = 54 %). $^1$H NMR (300 MHz, CDCl$_3$): δ 7.38 (d, $J = 8.5$ Hz, 2 H), 7.28-7.13 (m, 14H), 7.10-6.89 (m, 9H), 6.86 (s, 1H); HRMS (m/z, FAB+) calcd for C$_{38}$H$_{26}$BrNS$_4$, 703.0131, found 703.0132.

**Compound 10a:** The title compound was obtained as a yellow solid (yield = 76 %). $^1$H NMR (300 MHz, CDCl$_3$): δ 9.89 (s, 1 H), 7.81-7.80 (m, 1 H), 7.72-7.70 (m, 1H), 7.49-7.43 (m, 3H), 7.34-7.30 (m, 4 H), 7.25-7.07 (m, 9 H), 2.93-2.86 (m, 4H), 1.66-1.20 (m, 8 H), 0.88 (t, $J=7.2$Hz, 6H); $^{13}$C NMR (125MHz, CDCl$_3$): 182.81, 148.30, 147.68, 146.66, 144.83, 142.35, 137.61, 135.39, 135.06, 133.43, 133.12, 130.79, 129.84, 129.77, 127.51, 126.93, 126.18, 125.10, 124.77, 123.75, 123.65, 36.78, 36.71, 32.32, 29.95, 29.76, 29.59, 29.13, 23.09, 14.52. HRMS (m/z, FAB+) calcd for C$_{39}$H$_{37}$NOS$_3$, 695.1479, found 695.1475.
Compound 10b: The title compound was obtained as a yellow solid (yield = 72 %). $^1$H NMR (500 MHz, CDCl$_3$) δ 9.90 (s, 1 H), 7.71 (d, $J = 3.8$ Hz, 1 H), 7.51-7.48 (m, 2H), 7.35-7.29 (m, 6H), 7.25-7.23 (br, 1H), 7.17-7.15 (m, 4H), 7.11-7.07 (m, 4H), 2.79 (br, 4H), 1.91-1.81 (m, 2H), 1.03 (d, $J = 6.5$ Hz, 12H); $^{13}$C NMR (125MHz, CDCl$_3$): 182.47, 147.95, 147.32, 146.28, 144.43, 141.97, 137.31, 134.99, 134.53, 133.38, 133.03, 130.25, 129.40, 129.23, 127.13, 126.56, 126.45, 125.77, 124.73, 124.43, 123.39, 123.30, 45.38, 45.30, 29.73, 28.70, 28.67, 27.87, 26.87, 22.01, 17.58, 13.65. HRMS (m/z, FAB+) calcd for C$_{39}$H$_{37}$NOS$_5$ 695.1479, found 695.1485.

Compound 10c: The title compound was obtained as a yellow solid (yield = 69 %). $^1$H NMR (300 MHz, CDCl$_3$) δ 9.87 (s, 1 H), 7.69 (d, $J = 3.3$ Hz, 1 H), 7.49 (d, $J = 7.8$ Hz, 2H), 7.36 (s, 1H), 7.30-7.24 (m, 7 H), 7.14-7.03 (m, 8 H), 1.30 (d, $J = 3.3$ Hz, 18 H); $^{13}$C NMR (125MHz, CDCl$_3$): 182.46, 147.91, 147.32, 146.45, 144.14, 141.96, 141.01, 137.27, 136.67, 133.80, 133.58, 130.35, 129.95, 129.85, 129.38, 127.19, 126.54, 124.76, 124.36, 123.39, 123.36, 48.69, 48.65, 31.21, 31.16. HRMS (m/z, FAB+) calcd for C$_{39}$H$_{37}$NOS$_5$ 695.1479, found 695.1486.
**Compound 10d:** The title compound was obtained as a yellow solid (yield = 65 %). 1H NMR (500 MHz, CDCl₃): δ 9.89 (s, 1 H), 7.71 (d, J = 3.8 Hz, 1 H), 7.52 (d, J = 8.4 Hz, 2H), 7.37 (s, 1H), 7.33-7.29 (m, 5 H), 7.26 (s, 1H), 7.16 (d, J = 7.9 Hz, 4 H), 7.13-7.07 (m, 4 H), 3.12-3.06 (m, 2H), 1.97 (br, 4H), 1.79 (br, 4H), 1.71-1.62 (m, 4H), 1.42-1.38 (m, 4H), 1.34-1.27 (m, 4H); 13C NMR (125MHz, CDCl₃): 182.46, 147.92, 147.33, 146.39, 143.87, 141.94, 137.35, 137.23, 134.52, 132.98, 131.23, 130.92, 129.41, 127.51, 127.19, 126.57, 124.72, 124.44, 123.40, 123.36, 48.83, 48.77, 33.42, 33.37, 29.74, 27.90, 26.89, 26.09, 26.02, 25.71, 17.60, 13.68. HRMS (m/z, FAB+) calcd for C₄₃H₄₁NOS₅ 747.1792, found 747.1801.

**Compound 10e:** The title compound was obtained as a yellow solid (yield = 63 %). 1H NMR (300 MHz, CDCl₃): 9.86 (s, 1 H), 7.66 (s, 1 H), 7.40 (d, J = 7.5 Hz, 2H), 7.26-7.14 (m, 15 H), 7.13-7.05 (m, 10 H); This material was insufficiently soluble to obtain a 13C NMR spectrum. HRMS (m/z, FAB+) calcd for C₄₃H₂₉NOS₅ 735.0853, found 735.0859.
**Compound 1:** The title compound was obtained as a reddish brown solid (yield = 83 %). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.09 (s, 1H), 7.68 (d, $J$ = 4.2 Hz, 1H), 7.62-7.59 (m, 3H), 7.33 (t, $J$ = 8.1 Hz, 4H), 7.11-7.04 (m, 5H), 6.98 (d, $J$= 8.7 Hz, 2 H), 2.96 (t, $J$= 6.6Hz, 4H), 1.54-1.45 (m, 4H), 1.40-1.30 (m, 4H), 0.82 (t, $J$= 7.2Hz, 6H); This material was insufficiently soluble to obtain a $^{13}$C NMR spectrum. HRMS (m/z, FAB+) calcd for C$_{42}$H$_{38}$N$_2$O$_2$S$_5$ 762.1537, found 762.1530.

**Compound 2:** The title compound was obtained as a reddish brown solid (yield = 82 %). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.20 (s, 1H), 7.78 (d, $J$= 3 Hz, 1H), 7.64-7.55 (m, 4H), 7.36-7.31 (m, 4H), 7.12-6.97 (m, 9H), 2.87 (d, $J$= 3.9 Hz, 4H), 1.76-1.65 (m, 2H), 0.93 (t, $J$= 6.3Hz, 12H); This material was insufficiently soluble to obtain a $^{13}$C NMR spectrum. HRMS (m/z, FAB+) calcd for C$_{42}$H$_{38}$N$_2$O$_2$S$_5$ 762.1537, found 762.1530.
**Compound 3:** The title compound was obtained as a reddish brown solid (yield = 74%). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.14 (s, 1 H), 7.72 (d, $J$ = 3.9 Hz, 1 H), 7.62 (d, $J$=8.7, 2H), 7.57 (d, $J$=3.9 Hz, 1H), 7.48 (s, 1H), 7.44 (s, 1H), 7.33 (t, $J$ = 7.8 Hz, 4H), 7.11-7.04 (m, 6H), 6.98 (d, $J$= 8.7 Hz, 2 H), 1.24 (s, 18H); This material was insufficiently soluble to obtain a $^{13}$C NMR spectrum. HRMS($m/z$, FAB+) calcd for C$_{42}$H$_{38}$N$_2$O$_2$S$_5$ 762.1537, found 762.1530.

![Image of Compound 3]

**Compound 4:** The title compound was obtained as a reddish brown solid (yield = 67 %). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.14 (s, 1H), 7.74 (d, $J$ = 3 Hz, 1H), 7.64-7.53 (m, 6H), 7.34 (t, $J$ = 7.2 Hz, 3 H), 7.12-7.05 (m, 8H), 3.01-2.97 (m, 2 H), 1.94-1.81 (m, 4 H), 1.72-1.59 (m, 4 H), 1.31-1.18 (m, 12 H); This material was insufficiently soluble to obtain a $^{13}$C NMR spectrum. HRMS($m/z$, FAB+) calcd for C$_{46}$H$_{42}$N$_2$O$_2$S$_5$ 814.1850, found 814.1850.

![Image of Compound 4]

**Compound 5:** The title compound was obtained as a red solid (yield = 58 %). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.09 (br, 1H), 7.69 (br, 1H), 7.54-7.49 (br, 3H), 7.43 (br, 1H), 7.33 (br, 8 H), 7.21-7.20 (br, 6 H), 7.06-7.03 (br, 7H), 6.95-6.92 (br, 2H); This material was insufficiently soluble to obtain a $^{13}$C NMR spectrum. HRMS($m/z$, FAB+) calcd for C$_{46}$H$_{36}$N$_2$O$_2$S$_5$ 802.0911, found 802.0912.
NMR Spectra:

Figure S1. $^1$HNMR spectra of compound 9a.
Figure S2. $^1$HNMR spectra of compound 9b.

Figure S3. $^1$HNMR spectra of compound 9c.
Figure S4. $^1$HNMR spectra of compound 9d.

Figure S5. $^1$HNMR spectra of compound 9e.
Figure S6. $^1$HNMR spectra of compound 10a.

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Figure S9. $^1$HNMR spectra of compound 10d.
Figure S10. $^1$HNMR spectra of compound 10e.

Figure S11. $^1$HNMR spectra of compound 1.

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Figure S12. $^1$HNMR spectra of compound 2.

Figure S13. $^1$HNMR spectra of compound 3.
Figure S14. $^1$HNMR spectra of compound 4.

Figure S15. $^1$HNMR spectra of compound 5.