Electronic Supplementary Information

Boron-dibenzopyrromethene-based organic dyes for application in dye-sensitized solar cells

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1. Synthesis of intermediates

Difluoro[5-(3-hexyl-5-(5,5-dimethyl-[1,3]dioxane-2-yl)thiophen-2-yl)-1-[5-(3-hexyl-5-(5,5-dimethyl-[1,3]dioxane)thiophene-2-yl)-3-(2-methoxyphenyl)-2H-isooindole-1-yl]methylene]-3-(2-methoxyphenyl)-1H-isooindolate-N1,N2]boron (6)

To a solution of 4 (1.50 g, 2.27 mmol), 5 (2.78 g, 6.81 mmol), and K2CO3 (6.28 g, 45.4 mmol) in THF (75 mL)/H2O (10 mL) was added Pd(PPh3)4 (0.80 g, 0.69 mmol). The resulting solution was refluxed overnight under a N2 atmosphere. After evaporation of THF, the subsequent solution was extracted with CH2Cl2 (150 mL). And the organic layer was then washed with water (150 mL) and dried with Na2SO4. After the removal of solvent in vacuo, the residue was chromatographed on silica gel (Wacogel C-300) using CH2Cl2/hexane (1:1 v/v) as an eluent. In this way, 984 mg of 6 was obtained (41% yield). 1H NMR (500 MHz, CDCl3) δ (ppm) 0.79 (s, 6H), 0.83 (t, 6H, J = 6.92 Hz), 1.18–1.22 (m, 12H), 1.28 (s, 6H), 1.47–1.53 (m, 4H), 2.56 (t, 4H, J = 7.82 Hz), 3.63 (d, 4H, J = 10.95 Hz), 3.69 (s, 3H), 3.76 (d, 4H, J = 10.95 Hz), 3.76 (s, 3H), 5.59 (s, 3H), 6.95 (d, 1H, J = 8.35 Hz), 6.99 (s, 2H), 6.99–7.01 (m, 2H), 7.06 (t, 1H, J = 7.33 Hz), 7.36 (s, 1H), 7.37 (s, 1H), 7.38–7.42 (m, 2H), 7.49 (d, 2H, J = 8.35 Hz), 7.54 (d, 1H, J = 7.55 Hz), 7.66 (d, 1H, J = 7.30 Hz), 7.81 and 7.82 (s, 1H), 7.89 (d, 1H, J = 8.45 Hz), 7.90 (d, 1H, J = 8.55 Hz); FAB MS: m/z 1064 [M]+.

Difluoro[5-(3-hexyl-5-formylthiophene-2-yl)-1-[5-(3-hexyl-5-formylthiophene-2-yl)-3-(2-methoxyphenyl)-2H-isooindole-1-yl]methylene]-3-(2-methoxyphenyl)-1H-isooindolate-N1,N2]boron (7)

To a solution of 6 (980 mg, 0.920 mmol) in THF (120 mL) was added a solution of p-toluene sulfonic acid monohydrate (270 mg, 1.42 mmol) in water (20 mL). The resulting solution was stirred at 40°C overnight under dark conditions. After evaporation of THF, the subsequent solution was extracted with CH2Cl2 (100 mL). And the organic layer was then washed with water (100 mL × 2) and dried with Na2SO4. After the removal of solvent in vacuo, the residue was reprecipitated from CH2Cl2/hexane to give 7 as a deep-blue solid (723 mg, 88%). 1H NMR (500 MHz, CDCl3) δ (ppm) 0.84 (t, 6H, J = 6.92 Hz), 1.18–1.22 (m, 12H), 1.28 (s, 6H), 1.47–1.53 (m, 4H), 2.66 (t, 4H, J = 7.80 Hz), 3.72 (s, 3H), 3.80 (s, 3H), 6.99 (d, 1H, J = 8.65 Hz), 7.03 (t, 1H, J = 8.00 Hz), 7.08 (t, 1H, J = 7.15 Hz), 7.41–7.43 (m, 2H), 7.45 (s, 1H), 7.46 (s, 1H), 7.52–7.54 (m, 2H), 7.56 (d, 1H, J = 7.65 Hz), 7.63 (s, 2H), 7.69 (d, 1H, J = 7.55 Hz), 7.88 and 7.89 (s, 1H), 7.96 (d, 1H, J = 8.45 Hz), 7.97 (d, 1H, J = 8.05 Hz), 9.84 (s, 2H); FAB MS: m/z 892 [M]+; Elemental analysis: Calcd for C53H51BF2N4O6S2: C, 71.29; H, 5.76; N, 3.14, found: C, 71.39; H, 6.12; N, 2.98.
(Z)-N'-[(1-(5-Bromo-2-hydroxyphenyl)ethylidene)-2-methoxybenzohydrazide (9)

2-Acetyl-4-bromophenol 8 (4.87 g, 22.6 mmol) and 2-methoxybenzohydrazine (3.76 g, 22.6 mmol) were dissolved in dry EtOH (46 mL). The resulting mixture was stirred for 4 days at 85 °C to give 7.81 g of 9 as a light yellow solid in 95% yield. 1H NMR (500 MHz, CDCl3) δ (ppm) 2.35 (s, 3H), 4.10 (s, 3H), 6.94 (d, 1H, J = 8.75 Hz), 7.05 (d, 1H, J = 8.10 Hz), 7.17 (td, 1H, J = 7.57 and 0.95 Hz), 7.35 (dd, 1H, J = 2.43 and 8.80 Hz), 7.52–7.55 (m, 2H), 8.35 (dd, 1H, J = 1.80 and 7.85 Hz), 11.03 (s, 1H), 12.93 (s, 1H); FAB MS : m/z 363 [M]+.

1-(5-Bromo-2-(2-methoxybenzoyl)phenyl)ethanone (10)

To a solution of compound 9 (4.00 g, 11.0 mmol) in THF (200 mL) was dropwisely added Pb(OAc)4 (5.99 g, 13.5 mmol) under an icy condition and then the mixture was stirred for 6 h at room temperature to give 10 as a brown solid with quantiative yield (3.97 g). 1H NMR (500 MHz, CDCl3) δ (ppm) 2.47 (s, 3H), 3.65 (s, 3H), 6.94 (d, 1H, J = 8.40 Hz), 7.05 (td, 1H, J = 7.50 and 0.85 Hz), 7.25 (d, 1H, J = 8.30 Hz), 7.51 (ddd, 1H, J = 8.35, 7.40 and 1.80 Hz), 7.61 (dd, 1H, J = 1.90 and 8.20 Hz), 7.66 (dd, 1H, J = 1.80 and 7.70 Hz), 7.74 (d, 1H, J = 1.90); FAB MS : m/z 333 [M]+.

(Z)-6-Bromo-1-[(6-bromo-3-(2-methoxyphenyl)-2H-isindol-1-yl)methylene]-3-(2-methoxyphenyl)-1H-isindole (11)

To a solution of 10 (301 mg, 0.902 mmol) in EtOH (10 mL) and AcOH (2 mL) was added NH4OAc (459 mg, 5.96 mmol) and NH4Cl (50.5 mg, 0.945 mmol) at 65 °C. The resulting mixture was stirred overnight at 90 °C. The resulting solution was poured into water (50 mL) and then was extracted with AcOEt (160 mL). The organic layer was dried with Na2SO4. After removal of the solvent in vacuo, the residue was chromatographed on silica gel (Wacogel C-300) using CH2Cl2/hexane (1:1 v/v) as an eluent to give 149 mg of 11 as a purple solid in 54% yield. 1H NMR (500 MHz, CDCl3) δ (ppm) 3.75 (s, 6H), 7.04 (d, 2H, J = 8.20 Hz), 7.11 (td, 2H, J = 7.57 and 0.95 Hz), 7.32 (dd, 2H, J = 1.75 and 8.60 Hz), 7.40 (ddd, 2H, J = 8.25, 7.43 and 1.54 Hz), 7.49 (s, 1H), 7.69 (d, 2H, J = 8.50 Hz), 7.88 (dd, 2H, J = 1.70 and 7.70 Hz), 8.06 (d, 2H, J = 1.40 Hz); FAB MS : m/z 614 [M]+.

Difluoro[6-bromo-1-[(6-bromo-3-(2-methoxyphenyl)-2H-isindole-1-yl)methylene]-3-(2-methoxyphenyl)-1H-isindolate-N1,N2]boron (12)

Triethylamine (0.6 mL, 7.27 mmol) was added to a solution of 11 (1.00 g, 1.63 mmol) in dry toluene (130 mL), followed by the addition of BF3·Et2O (2 mL, 16.3 mmol) at 80 °C. The mixture was stirred for 18 h at 100°C. After cooling, the solution was poured into water (100 mL) and extracted with AcOEt (200 mL), the organic layer
was washed with water (400 mL) and dried with Na$_2$SO$_4$. After removal of the solvent \textit{in vacuo}, the residue was chromatographed on silica gel (Wacogel C-300) using CHCl$_3$/hexane (1:1 v/v) as an eluent. In this way, 960 mg of \textbf{12} was obtained in 89\% yield.\textsuperscript{1}H NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm) 3.66 (s, 3H), 3.72 (s, 3H), 7.01 (td, $J = 7.53$ and 0.68 Hz), 7.07 (td, 1H, $J = 7.48$ and 0.80 Hz), 7.17 (d, 1H, $J = 8.15$ Hz), 7.21 (d, 1H, $J = 8.20$ Hz), 7.27 (d, 2H, $J = 8.75$ Hz), 7.37–7.40 (m, 3H), 7.45 (d, 1H, $J = 7.60$ Hz), 7.50 (td, 2H, $J = 7.87$ and 1.13 Hz), 8.36–8.37 (m, 2H), 8.82 (s, 1H); FAB MS: $m/z$ 662 [M$^+$]; Elemental analysis: Calcd for C$_{31}$H$_{21}$BBr$_2$F$_2$N$_2$O$_2$ $\cdot$ H$_2$O: C, 54.74; H, 3.41; N, 4.12, found: C, 54.59; H, 3.22; N, 3.98

\textbf{Difluoro[6-(3-hexyl-5-(5,5-dimethyl-[1,3]dioxane-2-yl)thiophen-2-yl)-1-[6-(3-hexyl-5-(5,5-dimethyl-[1,3]dioxane)thiophene-2-yl)-3-(2-methoxyphenyl)-2H-isooindole-1-yl]methylene]-3-(2-methoxyphenyl)-1H-isooindolate-N$_1$N$_2$]boron (13)}

To a solution of \textbf{12} (425 mg, 0.427 mmol) and \textbf{5} (655 mg, 1.60 mmol) in THF (33 mL), 2 M K$_2$CO$_3$ aq. (6.5 mL) was added and the resulting solution was degassed by freeze-pump-thaw cycles. After adding Pd(PPh$_3$)$_4$ (0.16 g, 0.139 mmol) into the frozen flask under a N$_2$ atmosphere, the reaction mixture was stirred at 70\°C overnight, poured into water (20 mL), and then extracted with AcOEt (100 mL). The organic layer was washed with water (230 mL) and dried with Na$_2$SO$_4$. After the removal of solvent \textit{in vacuo}, the residue was chromatographed on silica gel (Wacogel C-300) using CH$_2$Cl$_2$/hexane (3:2 v/v) as an eluent. In this way, 446 mg of \textbf{13} was obtained (65\% yield).\textsuperscript{1}H NMR (500 MHz, DMSO-$d_6$) $\delta$ (ppm) 0.77 (t, 6H, $J = 6.93$ Hz), 1.19 (s, 12H), 1.20–1.25 (m, 12H), 1.57 (quint, 4H, $J = 7.31$ Hz), 2.70 (t, 4H, $J = 7.70$ Hz), 3.67 (s, 8H), 3.69 (s, 3H), 3.75 (s, 3H), 5.70 (s, 2H), 7.02 (td, 1H, $J = 7.50$ and 0.63 Hz), 7.08 (td, 1H, $J = 7.58$ and 0.73 Hz), 7.10 (s, 2H), 7.19 (d, 1H, $J = 8.35$ Hz), 7.22 (d, 1H, $J = 8.10$ Hz), 7.31 (d, 1H, $J = 8.50$ Hz), 7.31 (d, 1H, $J = 8.35$ Hz), 7.37 (d, 2H, $J = 8.45$ Hz), 7.41 (d, 1H, $J = 7.50$ Hz), 7.47 (dd, 1H, $J = 1.48$ and 8.15 Hz), 7.50 (td, 2H, $J = 7.98$ and 1.42 Hz), 8.20 (s, 2H), 8.78 (s, 1H); FAB MS: $m/z$ 1065 [M$^+$].

\textbf{Difluoro[6-(3-hexyl-5-formylthiophene-2-yl)-1-[6-(3-hexyl-5-formylthiophene-2-yl)-3-(2-methoxyphenyl)-2H-isooindole-1-yl]methylene]-3-(2-methoxyphenyl)-1H-isooindolate-N$_1$N$_2$]boron (14)}

To a solution of \textbf{13} (445 mg, 0.426 mmol) in THF (54 mL) was added a solution of $p$-toluene sulfonic acid monohydrate (122 mg, 0.639 mmol) in water (8.5 mL) at room temperature. The resulting solution was stirred at 40\°C, and then partitioned using water (50 mL) and AcOEt (50 mL). The organic layer was washed with water (100 mL) and dried with Na$_2$SO$_4$. After the removal of solvent \textit{in vacuo}, the residue was chromatographed on silica gel (Wacogel C-300) using CH$_2$Cl$_2$/hexane (2:1 v/v) as an eluent. In this way, 283 mg of \textbf{14} was obtained
(61% yield). $^1$H NMR (500MHz, DMSO-$d_6$) $\delta$(ppm) 0.76 (t, 6H, $J = 7.00$ Hz), 1.19–1.27 (m, 12H), 1.62 (quint, 4H, $J = 7.37$ Hz), 2.78 (t, 4H, $J = 7.68$ Hz), 3.70 (s, 3H), 3.75 (s, 3H), 7.03 (t, 1H, $J = 7.78$ Hz), 7.09 (t, 1H, $J = 7.48$ Hz), 7.20 (d, 1H, $J = 8.20$ Hz), 7.23 (d, 1H, $J = 8.05$ Hz), 7.38–7.45 (m, 5H), 7.49 (d, 1H, $J = 8.25$ Hz), 7.51 (t, 2H, $J = 8.00$ Hz), 8.06 (s, 2H), 8.29 (s, 1H), 8.30 (s, 1H), 8.84 and 8.85 (s, 1H), 9.93 (s, 2H); FAB MS : m/z 892 [M$^+$].

2. Variable temperature $^1$H NMR measurements

![Diagram showing variable temperature 1H NMR measurements]
**Fig. S1** Variable temperature $^1$H NMR spectra of 1 (a), 2 (b), and 3 (c) in DMSO-$d_6$. 
3. Electrochemical properties

Fig. S2 (a) Cyclic voltammograms of 1, 2 and 3 measured in DMF/CH₂Cl₂ (1:4 v/v) containing 0.1 M TBAPF₆ at room temperature. Ferrocene (Fc) was used as an internal reference.

4. ATR-FT-IR spectra

Fig. S3 ATR-FT-IR spectra of 1 and 1-loaded TiO₂ film.
5. Characterization data of dyes

Figure S4. $^1$H NMR spectrum of dye 1 in DMSO-$d_6$ at room temperature.
Figure S5. $^{13}$C NMR spectrum of dye 1 in DMSO-$d_6$ at room temperature.
Figure S6. $^{19}$F NMR spectrum of dye 1 in CDCl$_3$-DMSO-$d_6$ (3:7 v/v) at room temperature.
Figure S7. $^1$H NMR spectrum of dye 3 in DMSO-$d_6$ at room temperature.
Figure S8. $^{13}$C NMR spectrum of dye 3 in DMSO-$d_6$ at room temperature.
Figure S9. $^{19}$F NMR spectrum of dye 3 in CDCl$_3$:DMSO-$d_6$ (3:7 v/v) at room temperature.
Figure S10. $^1$H NMR spectrum of dye 2 in DMSO-$d_6$ at room temperature.
Figure S11. $^{13}$C NMR spectrum of dye 2 in DMSO-d$_6$ at room temperature.
Figure S12. $^{19}$F NMR spectrum of dye 2 in CDCl$_3$:DMSO-$d_6$ (3:7 v/v) at room temperature.