ESI

A styryl-containing aza-BODIPY as near-infrared dye

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1 General

The melting points were measured using a SGW® X-4 melting point apparatus. $^1$H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. $^1$H NMR chemical shifts ($\delta$) are given in ppm downfield from Me$_4$Si, determined by chloroform ($\delta$ = 7.26 ppm). $^{13}$C NMR spectra were recorded on a Bruker AVANCE III 125 MHz spectrometer. $^{13}$C NMR chemical shifts ($\delta$) are reported in ppm with the internal CDCl$_3$ at $\delta$ 77.0 ppm as standard. ESI was measured by LCQ Deca XP.

Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone, $n$-hexane was distilled over Na, and other solvents were distilled over CaH$_2$. Merck silica gel 60 was used for the column chromatography.

Fluorescence spectra were recorded on F-4600 spectrophotometer. UV/Vis spectra were recorded on UV-2550 spectrophotometer at room temperature. The refractive index of the medium was measured by 2 W Abbe’s refractometer at 20 °C.

The fluorescence quantum yields ($\Phi_f$) of the BODIPY systems were calculated using the following relationship (equation 1):

$$\Phi_f = \frac{\Phi_refF_{sampl} A_{sampl} n_{sampl}^2}{F_{ref} A_{ref} n_{ref}^2}$$  \hspace{1cm} (1)

Here, $F$ denotes the integral of the corrected fluorescence spectrum, $A$ is the absorbance at the excitation wavelength, ref and sampl denote parameters from the reference and unknown experimental samples, respectively. The reference systems used was boronazadipyrromethene compound aza-BODIPY ($\Phi_f = 0.36$ in chloroform).$^1$

The MO calculations were performed at the DFT level, and the frontier molecular orbitals of BODIPYs 2a and 4 at the B3LYP/6-31G(d) level with Gaussian 03.$^2$
2. Synthesis

(E)-4-phenyl-2-styryl-1H-pyrrole 1a

Under N₂, LDA (1.0 mmol) in THF (3 mL) was added to (E)-4-phenylbut-3-en-2-one (146 mg, 1.0 mmol) in THF (8 mL) at −78 °C. Then, 3-phenyl-2H-azirine (175 mg, 1.5 mmol) in THF (5 mL) was added and the resulting mixture was stirred for 1 h at the same temperature. The reaction was allowed to warm up to room temperature slowly. It was quenched with water, neutralized with dilute HCl to a pH about 7. The mixture was extracted with CH₂Cl₂ (2 × 50 mL), and the organic layer was washed with brine (2 × 50 mL) and dried over anhydrous MgSO₄. After removal of the solvents by evaporation, the resulting crude mixture was separated by column chromatography (n-hexane : CH₂Cl₂ = 1 : 2) to afford 1a as green solids (110 mg, 45%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.36 (br s, 1H), 7.54 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.17-7.24 (m, 2H), 7.02-7.11 (m, 1H), 6.98 (d, J = 16.5 Hz, 1H), 6.73 (d, J = 16.5 Hz, 1H), 6.64-6.67 (m, 1H).

(E)-2-(4-methoxystyryl)-4-phenyl-1H-pyrrole 1b

(E)-4-(4-methoxyphenyl)but-3-en-2-one (176 mg, 1.0 mmol) were used as the starting material, and 1b was obtained as green solids (137 mg, 50%). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.33 (br s, 1H), 7.53 (d, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 7.07-7.08 (m, 1H), 6.88 (d, J =
7.5 Hz, 2H), 6.84 (d, J = 16.5 Hz, 1H), 6.78 (d, J = 16.5 Hz, 1H), 6.61-6.62 (m, 1H), 3.82 (s, 3H).

Styryl-containing aza-BODIPY dye 2a

Sodium nitrite (6.9 mg, 0.1 mmol) was added to a suspension of 2,4-diphenyl-1H-pyrrole (21.9 mg, 0.1 mmol) in acetic acid (1 mL) at 0 °C, and was stirred for 10 min. The color changed from colorless to brown, then green, and finally brown was observed. The second pyrrole moiety 1a (24.5 mg, 0.1 mmol) was added, followed by addition of acetic anhydride (0.4 mL). The mixture turned blue immediately. After 0.5 h stirring, the mixture was heated at 80 °C for 0.5 h. Crushed ice was added to the mixture, the resulted blue dye was filtered, washed with water. The blue dye was dissolved in CH₂Cl₂, filtered through a pad of alumina (activity III). Solvent was removed under reduced pressure, and the residue was dissolved in dry 1,2-dichloroethane. Triethylamine (0.28 mL, 2.0 mmol) was added, followed by dropwise addition of BF₃·Et₂O (0.50 mL, 4.0 mmol) with stirring at room temperature. The mixture was stirred for 0.5 h, then heated in 80 °C for 0.5 h. The reaction was quenched with crushed ice, extracted with CH₂Cl₂, and purified by chromatography on silica gel followed by recrystallization from CH₂Cl₂/n-hexane to afford 2a (15.7 mg, 30%) as coppery solids. M.p.: 91.0–91.8 °C (decomp.). ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.05-8.11 (m, 4H), 7.30 (s, 1H), 7.31-7.67 (m, 18H), 7.02 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 141.4, 135.8, 132.7, 132.0, 131.9, 130.5, 130.4, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.6, 128.5, 128.4, 128.3, 118.9, 115.5, 48.3, 47.0, 29.6, 18.8, 8.6. MS (ESI(+) ): m/z = 523.2 [M]⁺, found 522.9.
Styryl-containing aza-BODIPY dye 2b

Pyrrole 1b (27.6 mg, 0.1 mmol) were used as the starting material, and BODIPY 2b was obtained as coppery solids (18.3 mg, 34%). M.p.: 240.1–241.0 °C (decomp.). \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ (ppm) 8.09 (d, \(J = 7.0 \text{ Hz}, 4\)H), 8.09 (d, \(J = 8.5 \text{ Hz}, 2\)H), 7.63 (d, \(J = 9.0 \text{ Hz}, 2\)H), 7.39-7.57 (m, 11H), 7.30 (s, 1H), 6.99 (s, 1H), 6.94 (d, \(J = 8.5 \text{ Hz}, 2\)H), 3.87 (s, 3H). MS (ESI(+)): m/z = 553.2 [M]+, found 553.8.

Styryl-containing aza-BODIPY dye 3a

Sodium nitrite (6.9 mg, 0.1 mmol) was added to a suspension of 7-methoxy-3-phenyl-4,5-dihydro-1H-benzo[g]indole\(^4\) (27.5 mg, 0.1 mmol) in acetic acid (1 mL) at 0 °C, and was stirred for 10 min. The color changed from colorless to brown, then green, and finally brown was observed. The second pyrrole moiety 1a (24.5 mg, 0.1 mmol) was added, followed by addition of acetic anhydride (0.4 mL). The mixture turned blue immediately. After 0.5 h stirring, the mixture was heated at 80 °C for 0.5 h. Crushed ice was added to the mixture, the resulted blue dye was filtered, washed with water. The blue dye was dissolved in CH\(_2\)Cl\(_2\), filtered through a pad of alumina (activity III). Solvent was removed under reduced pressure, and the residue was dissolved in dry 1,2-dichloroethane. Triethylamine (0.28 mL, 2.0 mmol) was added, followed by dropwise addition of BF\(_3\)·Et\(_2\)O (0.50 mL, 4.0 mmol) with stirring at room
temperature. The mixture was stirred for 0.5 h, then heated in 80 °C oil bath for 0.5 h. The reaction was quenched with crushed ice, extracted with CH$_2$Cl$_2$, and purified by chromatography on silica gel followed by recrystallization from CH$_2$Cl$_2$/n-hexane to afford 3a (22.0 mg, 38%) as coppery solids. M.p.: 290.2–290.9 °C (decomp.). ¹H NMR (500 MHz, CDCl$_3$): δ (ppm) 8.80 (d, J = 9.0 Hz, 1H), 8.08 (d, J = 7.5 Hz, 2H), 7.66-7.74 (m, 5H), 7.35-7.49 (m, 10H), 7.22 (s, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.87 (s, 1H), 3.93 (s, 3H), 2.97 (s, 4H). ¹³C NMR (125 MHz, CDCl$_3$): δ (ppm) 162.7, 151.3, 147.2, 144.9, 144.4, 140.2, 138.2, 137.5, 136.4, 132.7, 131.9, 130.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 127.7, 120.0, 119.2, 114.6, 113.2, 55.5, 30.5, 21.7. MS (ESI(+)): m/z = 579.2 [M]$^+$, found 579.0. HRMS-MALDI (m/z): [M+H]$^+$ calcd for C$_{37}$H$_{29}$BF$_2$N$_3$O: 580.2372; found 580.2366.

**Styryl-containing aza-BODIPY dye 3b**

Pyrrole 1b (27.6 mg, 0.1 mmol) were used as the starting material, and BODIPY 3b was obtained as coppery solids (24.9 mg, 41 %). M.p.: 253.0–253.7 °C (decomp.). ¹H NMR (500 MHz, CDCl$_3$): δ (ppm) 8.77 (d, J = 9.0 Hz, 1H), 8.08 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 8.5 Hz, 2H), 7.51-7.58 (m, 2H), 7.49 (t, J = 7.5 Hz, 2H), 7.34-7.45 (m, 4H), 7.21 (s, 1H), 7.05 (dd, J = 9.0, 2.5 Hz, 1H), 6.95 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 2.5 Hz, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 2.95 (s, 4H). ¹³C NMR (125 MHz, CDCl$_3$): δ (ppm) 162.3, 161.0, 153.3, 152.5, 146.7, 144.7, 144.4, 138.0, 137.6, 132.6, 132.1, 131.4, 130.4, 129.6, 129.3, 128.7, 128.6, 128.4, 128.2, 128.0, 120.3, 117.1, 114.4, 113.5, 113.1, 55.5, 55.4, 30.5, 21.7. MS (ESI(+)): m/z = 609.2 [M]$^+$, found 609.4. HRMS-MALDI (m/z): [M+H]$^+$ calcd for C$_{38}$H$_{31}$BF$_2$N$_3$O$_2$: 610.2478; found 610.2457.
$^1$H NMR (500 MHz, CDCl$_3$) of dye 1a
$^1$H NMR (500 MHz, CDCl$_3$) of dye 1b
$^1$H NMR (500 MHz, CDCl$_3$) of dye 2a
$^{13}$C NMR (125 MHz, CDCl$_3$) of dye 2a
$^1$H NMR (500 MHz, CDCl$_3$) of dye 2b
$^1$H NMR (500 MHz, CDCl$_3$) of dye 3a
$^{13}$C NMR (125 MHz, CDCl$_3$) of dye 3a
$^1$H NMR (500 MHz, CDCl$_3$) of dye 3b
$^13$C NMR (125 MHz, CDCl$_3$) of dye 3b
4. MS (ESI) of 2a

Relative Abundance
MS (ESI) of 2b
5. HRMS

HRMS of 3a
6. References


