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Development of non-symmetric thiophene-fused BODIPYs

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ABSTRACT

A series of non-symmetric BODIPYs containing thieno[3,2-*b*]pyrrole moiety were synthesized in 21–63% yields. The absorption and emission maxima covered from the visible green to red region (λ_{abs}=532–647 nm; λ_{em}=547–664 nm; Φ_f=0.19–0.45). X-ray analysis indicated that the S–C bond lengths were shorter than those of thienopyrrole and thienohelicene by 0.03–0.05 Å. The crystal packing pattern suggested that strong π–π interaction, intermolecular C–*H*···*F* interaction, and weak *S*···π interaction existed. The tunable emission was achieved by structure modifications. Oxidation of BODIPY (λ_{em}=547 nm) with *m*-CPBA generated thiophene-1,1-dioxide derived BODIPY (λ_{em}=528 nm). Knoevenagel-type condensation of BODIPY with *N*,*N*-dimethylaminobenzaldehyde led to BODIPY (λ_{em}=693 nm) with extended conjugation.

1. Introduction

4,4′-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (abbreviated as BODIPY) dyes are well-known and widely used fluorescent dyes with intense absorption, and high quantum yields. BODIPYs acted as good candidates for biological labeling, photonic molecular systems, laser dyes, organogelators, and light-emitting devices.[1] Very recently, furo[3,2-*b*]pyrrole derived BODIPY **1** was declared as a fluorescent dye with long absorption and high brightness, which is insensitive to solvent polarity (Fig. 1).[2] Thieno[3,2-*b*]pyrroles are useful scaffolds of biologically active compounds, photochromic compounds, and organic field effect transistors.[3] The unique electronic properties of thiophene moiety have attracted many research studies in electro-optical devices.[4] Our recent research interest lies in the novel BODIPY family of fluorescent dyes.[5] We are interested in thieno[3,2-*b*]pyrroles derived BODIPYs as bright and tunable fluorescent dyes. During the preparation of this manuscript, a thieno[3,2-*b*]pyrrole-containing symmetric BODIPY **2** carrying bromine atoms was reported by You et al. as a photodynamic therapy reagent.[6] Herein we communicate our studies on thieno[3,2-*b*]pyrrole-containing non-symmetric BODIPYs as highly fluorescent dyes.

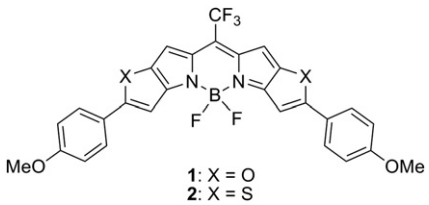
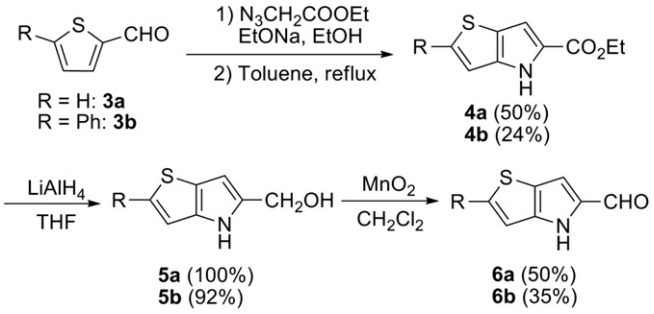


Fig. 1. Reported heterocycle fused [3,2-*b*]pyrroles derived BODIPYs.

2. Result and discussion

The precursors thieno[3,2-*b*]pyrrole-5-carbaldehyde **6a** and **6b** were synthesized in three steps from thiophene-2-carbaldehydes **3a** and **3b**, respectively, as outlined in Scheme 1. Non-symmetric



Scheme 1. Synthetic route of thieno[3,2-*b*]pyrrole-5-carbaldehyde.

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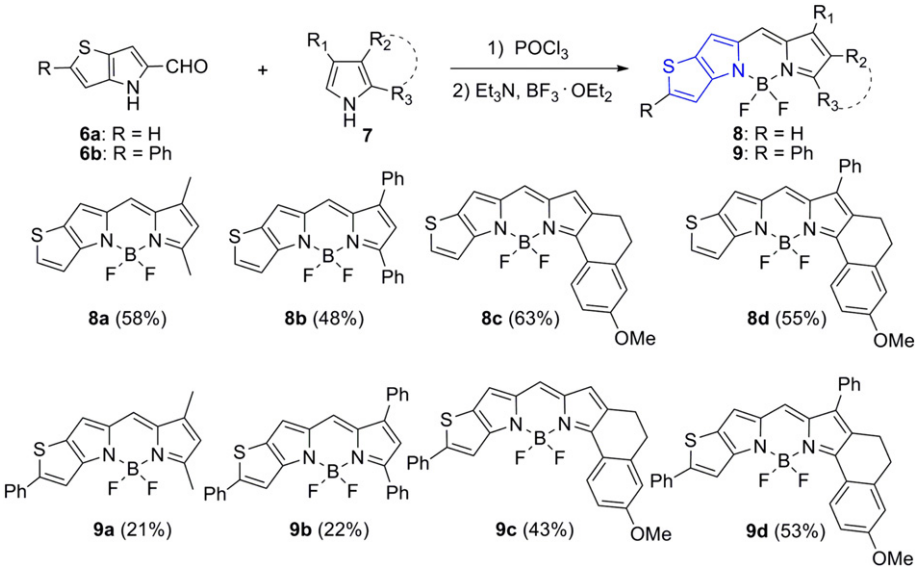
thiophene-fused BODIPYs **8a**–**9d** were obtained in 21–63% yields by the reaction of pyrrole carbaldehyde **6** with another pyrrole moiety **7**[3e,5d] (Scheme 2).[7] It was found that the yields of the dyes **8a**–**8d** from **6a** were generally higher than those of the corresponding dyes **9a**–**9d** from **6b** with a phenyl group.

similar to those found for the reported BODIPYs. The sp^3 hybridized boron center appears as slightly distorted tetrahedron geometry with the angles N1–B1–N2 of 106.8° and F1–B1–F2 of 109.0°. The side view (B) of **8a** shows a flat plane. In the crystal packing of **8a**, the neighboring BODIPY molecules are assembled by in-



Scheme 2. Synthesis of non-symmetric thiophene-fused BODIPYs **8** and **9**.

The structure of dye **8a** is confirmed by single crystal X-ray analysis (Fig. 2). The S–C distances (1.718(2) and 1.701(4) Å) in **8a** are found to be shorter than those of the thienopyrrole and thienohelicene by 0.03–0.05 Å.[8] Other bond lengths of **8a** are very

termolecular C–*H*···*F* interaction to form a one-dimensional chain along the *c* axis (top view (C), side view (D)). The average C–*H*···*F* distance (2.424 Å) is less than the sum of the van der Waals radii for hydrogen and fluorine (2.62 Å) by 0.2 Å,[9] indicating that there is

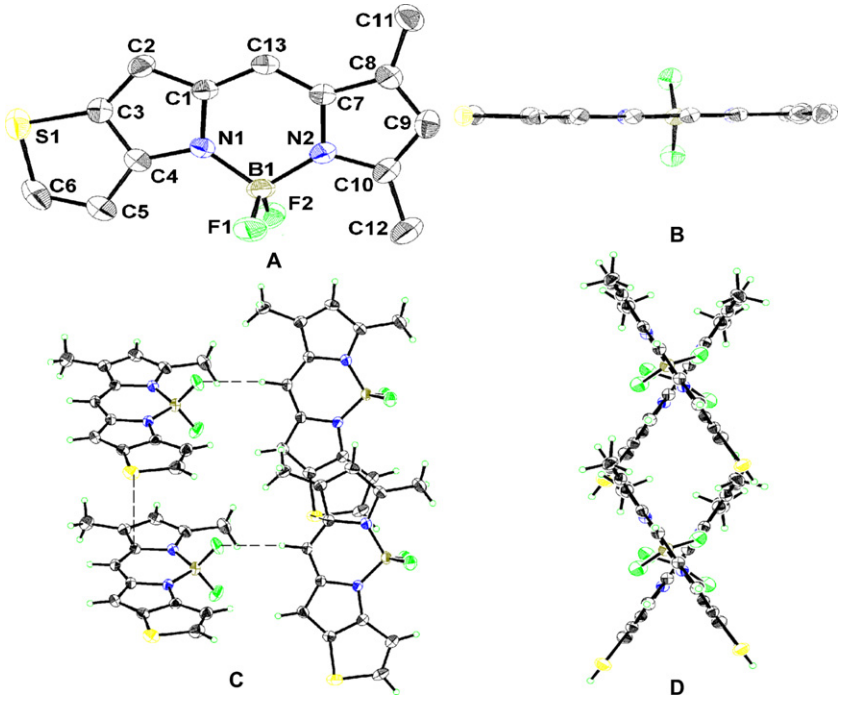


Fig. 2. Molecular structure and conformation for **8a**. Carbon, boron, nitrogen, fluorine, and sulfur atoms are depicted with thermal ellipsoids set at the 30% probability level. Top view (A). Side view (B). Selected bond lengths (Å) and angles (°) for **8a**: N1–C1, 1.375(3); N1–C4, 1.356(4); N2–C7, 1.385(3); N2–C10, 1.337(3); N1–B1, 1.520(3); N2–B1, 1.539(3); B1–F1, 1.373(3); B1–F2, 1.384(3); S1–C3, 1.718(2); S1–C6, 1.701(4); C3–C4, 1.386(3); C4–C5, 1.390(3); C5–C6, 1.347(4); N1–B1–N2, 106.80(19); F1–B1–F2, 109.0(2); C3–S1–C6, 90.41(13). A one-dimensional chain of **8a** viewed along the *c* axis. Top view (C). Side view (D). Selected bond lengths (Å) for **8a**: C–*H*···*F*, 2.424; *S*···*C*, 3.715.

a strong π–π interaction within the chain. In addition, a weak $S\cdots\pi$ interaction could also be observed among *a* and *b* axes, for example: the $S\cdots C$ distance is 3.715 Å.[8]

The absorption and emission spectra of **8a**–**9d** were outlined in Fig. 3 and Table 1 respectively. BODIPYs **8a**–**9d** absorb and emit from the visible green to red region (λ_{abs}=532–647 nm; λ_{em}=547–664 nm). In the class of **8**, **8b** possesses large Stokes shift (34 nm) and **8c** has a high quantum yield (Φ_f=0.45) compared with **2** (Φ_f=0.37) (entries 2 and 3 of Table 1).[6] For **9** carrying a phenyl substituent on thiophene, about 40 nm of bathochromic shift was noticed compared to **8**, however, with lower fluorescent quantum yield presumably due to the rotation of the phenyl group and the increased internal conversion. Notably, **9c** (λ_{em}=662 nm) and **9d** (λ_{em}=664 nm) carrying conformationally restricted pyrrole moiety have long absorption,[10] large absorption coefficients, and maintain relatively good fluorescence quantum yields.[1b,c,6]

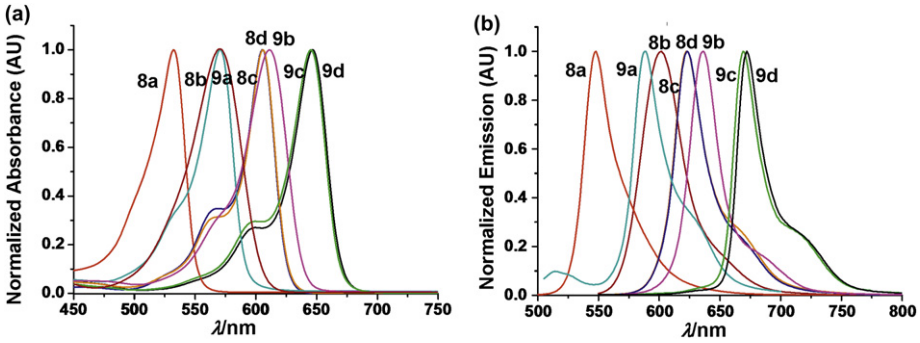


Fig. 3. (a) Normalized absorption; and (b) fluorescence spectra of **8a**–**9d** in $CHCl_3$ at 298 K.

Table 1
Spectroscopic data of **8** and **9** in $CHCl_3$ at 298 K

Entry	Dye	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (nm)	Φ_f	ε (M^{-1} cm^{-1})	Fwhm (nm)
1	**8a**	532	547	15	0.34	53,800	34
2	**8b**	570	604	34	0.41	42,100	47
3	**8c**	605	618	13	0.45	64,200	28
4	**8d**	606	618	12	0.42	82,000	27
5	**9a**	571	588	17	0.32	99,200	32
6	**9b**	611	631	20	0.38	85,300	39
7	**9c**	645	662	17	0.20	118,000	33
8	**9d**	647	664	17	0.19	143,000	32

Stokes shift: the difference in wavelength between positions of the band maxima of the emission and absorption spectra.
Fwhm: full width half maximum.

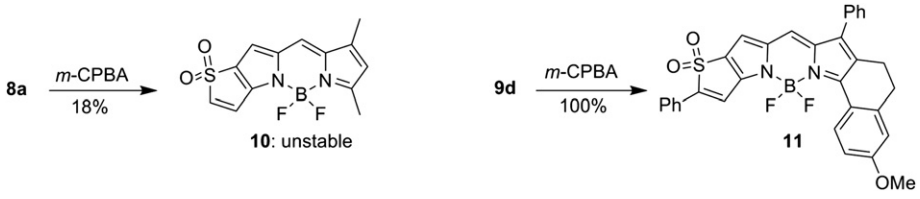
Non-symmetric thiophene-fused BODIPYs are selected to be modified, due to quantity amounts and reaction sites of non-symmetric BODIPYs.[1b,c,2,6] When **8a** and **9d** were treated with *m*-CPBA, the thiophene-1,1-dioxide derivatives (**10**: 18%; **11**: 100%) were successfully obtained (Scheme 3).[11] Unfortunately, dye **10** was unstable to air, moisture, and solvent. BODIPY **11** is more polar than the parent **9d**, and clearly differentiated from BODIPY **9d** in NMR (see: Experiment section).[11] When treated with 4,4-dimethylaminobenzaldehyde in the presence of acetic acid, piperidine, and molecular sieves in toluene, **8a** undertook a Knoevenagel-type condensation reaction and generated dye **12** in 20% yield (Scheme 4).[12]

The absorption and emission spectra of **8a**, **10**, and **12** as well as spectroscopic data of **10**–**12** are shown and collected in Fig. 4 and Table 2 respectively. As expected, oxidation of thiophene led to the hypsochromic shift of the absorption and emission (Fig. 4, and entries 1 and 2 of Table 2) because of the reduced electron donating ability. Extension of conjugation led to a dramatic bathochromic shift (146 nm), however, with decreased fluorescent quantum yield (Fig. 4, and entry 3 of Table 2).

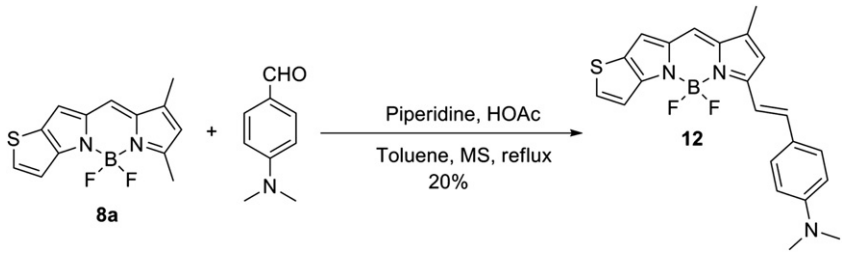
For the clear view of the effect of structure modification, pictures of the synthesized compounds in chloroform were taken under a normal condition and irradiation as well (Fig. 5). All the BODIPYs prepared exhibited relatively vivid bright fluorescence emission. The relatively distinct colors for individual dyes are differentiated by naked eye.

3. Conclusion

Utilizing the thieno[3,2-*b*]pyrrole, we successfully synthesized a series of non-symmetric thiophene-fused BODIPYs **8a**–**9d** in 21–63% yields (λ_{abs}=532–647 nm; λ_{em}=547–664 nm; Φ_f=0.19–0.45). The structure of **8a** was confirmed by X-ray analysis, and the S–C distance was shorter than that of thienopyrrole and thienohelicene by 0.03–0.05 Å. The tunable emission wavelengths were achieved by the modification of **8a**. BODIPY **8a** (λ_{em}=547 nm) reacted with *m*-CPBA to give the thiophene-1,1-dioxide derivative **10** (λ_{em}=528 nm), along with the blue shift (19 nm). BODIPY **8a** undertook a Knoevenagel-type condensation to give the NIR BODIPY **12** (λ_{em}=693 nm) and the remarkable redshift (146 nm) was achieved. Importantly, the absorption and emission maxima of such thiophene-fused BODIPYs covered the visible–near-infrared region (λ_{abs}=518–647 nm; λ_{em}=528–693 nm); in crystal packing of **8a**,



Scheme 3. Oxidation of thieno-containing BODIPY with *m*-CPBA.



Scheme 4. Synthesis of BODIPY **12** by Knoevenagel-type condensation.

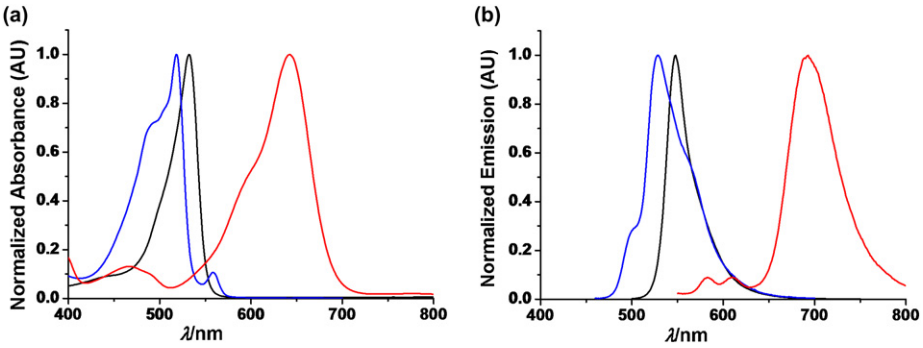


Fig. 4. The spectra of normalized absorption (a) and fluorescence (b) of **8a** (black), **10** (blue), and **12** (red) in $CHCl_3$ at 298 K.

Table 2
Spectroscopic data of **10**, **11**, and **12** in $CHCl_3$ at 298 K

Entry	Dye	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (nm)	Φ_f	ε (M^{-1} cm^{-1})	Fwhm (nm)
1	**10**	518	528	10	—[a]	—[a]	50
2	**11**	630	653	23	0.14	130,00	72
3	**12**	642	693	51	0.09	103,000	69

[a] Not measured due to the instability of **10**.

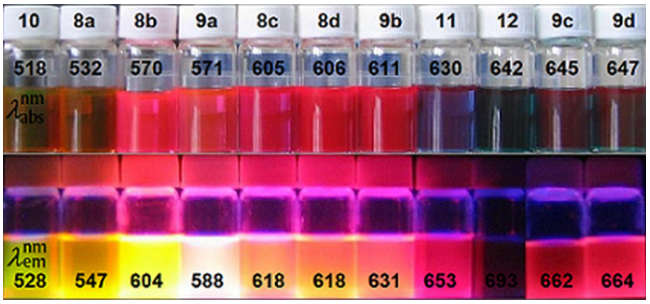


Fig. 5. Photoimages of **8a**–**9d**, **10**, **11**, and **12** under normal room illumination (upper row) and UV light (bottom row) in $CHCl_3$ at 298 K (λ_{ex}=365 nm).

a strong π–π interaction, intermolecular C–$H\cdots F$ interaction along *c* axis, and a weak $S\cdots\pi$ interaction along *a* and *b* axes exited. Such types of compounds might be used as novel organic functional materials.[13] Further modifications of these compounds and their applications in imaging and photo-electronic device studies are in progress.

4. Experiment section

4.1. General method

^{1}H NMR spectra were recorded on a VARIAN Mercury 400 MHz spectrometer. ^{1}H NMR chemical shifts (δ) are given in parts per million downfield from Me_4Si, determined by residual chloroform (δ=7.26 ppm). ^{13}C NMR spectra were recorded on a VARIAN Mercury 100 MHz spectrometer in $CDCl_3$, all signals are reported in parts per million with the internal chloroform signal at δ 77.0 ppm as standard. Mass spectrometric measurements were performed by the mass spectrometry service of the ETHZ on a Bruker Reflex MALDI as matrix (20 kV). All reactions were carried out under N_2. Tetrahydrofuran (THF) was freshly distilled from sodium. Other solvents were distilled over CaH_2. Merck silica gel 60 was used for the column chromatography.

Fluorescence spectra were recorded on FluoroSENS spectrophotometer and are reported. UV/vis spectra were recorded on Perkin–Elmer Lambda 35 UV/Vis spectrophotometer at room temperature. The fluorescence quantum yields (Φ_f) of the BODIPY systems were calculated using the following relationship:

$$\Phi_f = \Phi_{ref} F_{sampl} A_{ref} n^2_{sampl} / F_{ref} A_{sampl} n^2_{ref}$$

Here, *F* denotes the integral of the corrected fluorescence spectrum, *A* is the absorbance at the excitation wavelength, and *n* is the refractive index of the medium, ref and sampl denote parameters from the reference and unknown experimental samples, respectively. The reference systems used were Rhodamine 6G as standard [Φ_f=0.95, λ_{ex}=530 nm, in ethanol][14] for **8a**, **8b**, and **9a**, and Nile blue as standard [Φ_f=0.27, λ_{ex}=625 nm, 0.5% (v/v) 0.1 M HCl in ethanol][15] for the other compounds.

4.2. X-ray crystal structure determinations of compound 8a

A single crystal of compound **8a** was obtained by accurately controlling the sublimation temperature. The X-ray crystal structure analyses were made on a Bruker SMART CCD diffractor, using graphite-monochromated MoKα radiation (λ) 0.7107 Å. The data were collected at 298 K and the structures were refined by full-matrix least-squares on F^2. The computations were performed

with SHELEX-97 program.[16] CCDC 847774 (compound **8a**) contains the supplementary crystallographic data.

*4.2.1. Crystallographic data for **8a**.* $C_{13}H_{11}BF_2N_2S$, M=276.11, monoclinic, a=7.1072(1), b=12.2978(2), c=14.0570(1) Å, α=90°, β=92.399(2)°, γ=90°, V=1227.55(3) Å^3, T=298(2) K, space group $P2_1/c$, Z=4, data/restraints/parameters=2169/0/175, R_1=0.0431 ($I>2\sigma(I)$), wR_2 (all data)=0.1396, GOF=0.927.

4.3. Synthesis

*4.3.1. Ethyl thieno[3,2-b]pyrrole-5-carboxylate (**4a**).*[17] A solution of sodium ethoxide (8.17 g, 120 mmol, 20 wt % in ethanol) was added dropwise into a mixture of **3a** (2.8 mL, 30 mmol) and ethyl azidoacetate (15.4 g, 120 mmol) in anhydrous ethanol (50 mL) at −10 °C and stirred for 4 h at room temperature. Excess amount of saturated aqueous NH_4Cl solution was added. The mixture was extracted with ethyl acetate (2×80 mL), the organic layer was washed with brine (2×60 mL), and dried over anhydrous Na_2SO_4. After removing the solvents by evaporation, the resulting residue was dissolved in toluene (30 mL) and heated to reflux for 1 h. After cooling, the solvent was evaporated. The residue was separated by column chromatography (*n*-hexane/CH_2Cl_2=2:1) to afford **4a** as white solid (2.93 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (br s, 1H), 7.32 (d, J=5.2 Hz, 1H), 7.14 (d, J=0.8 Hz, 1H), 6.96 (dd, J=5.2, J=0.8 Hz, 1H), 4.38 (q, J=7.6 Hz, 2H), 1.39 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 141.3, 129.4, 127.1, 124.8, 111.1, 107.5, 60.7, 14.5.

*4.3.2. Ethyl 2-phenyl-4H-thieno[3,2-b]pyrrole-5-carboxylate (**4b**).* Compound **3b** (78.3 mg, 0.4 mmol) was used as the starting material, and **4b** was obtained as yellow solid (23.8 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (br s, 1H), 7.62 (d, J=7.2 Hz, 2H), 7.39 (t, J=7.2 Hz, 2H), 7.30 (t, J=7.2 Hz, 1H), 7.18 (d, J=0.8 Hz, 1H), 7.13 (d, J=0.8 Hz, 1H), 4.38 (q, J=7.6 Hz, 2H), 1.40 (t, J=7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 148.1, 141.6, 135.1, 128.9, 128.0, 126.6, 125.8, 124.2, 107.8, 107.0, 60.7, 14.5; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{15}H_{13}NO_2S$: 271.0667; found: 271.0656.

*4.3.3. (4H-Thieno[3,2-b]pyrrol-5-yl)methanol (**5a**).* To a stirred solution of **4a** (78.1 mg, 0.4 mmol) in anhydrous THF (10 mL) was added $LiAlH_4$ (30.4 mg, 0.8 mmol) slowly at 0 °C. The mixture was stirred at room temperature for 3 h and then cooled to 0 °C. The mixture was diluted with Et_2O (5 mL), quenched with 15% aqueous sodium hydroxide (0.03 mL). The organic layer was washed with brine (2×10 mL), and dried over anhydrous Na_2SO_4. After removing the solvents by evaporation, the resulting residue **5a** was obtained as a gray solid (61.3 mg, 100%), which was used for next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (br s, 1H), 7.07 (d, J=5.2 Hz, 1H), 6.88 (d, J=5.2 Hz, 1H), 6.43 (s, 1H), 4.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 136.3, 123.7, 111.1, 100.1, 58.7, 29.6; HRMS-MALDI (m/z): $[M+H]^+$ calcd for C_7H_7NOS: 154.0327; found: 154.0320.

*4.3.4. (2-Phenyl-4H-thieno[3,2-b]pyrrol-5-yl)methanol (**5b**).* Compound **4b** (25.8 mg, 0.095 mmol) was used as the starting material, and **5b** was obtained as a gray solid (20.1 mg, 92%), which was used for next step without further purification.

*4.3.5. Thieno[3,2-b]pyrrole-5-carbaldehyde (**6a**).* To a stirred solution of **5a** (61.3 mg, 0.4 mmol) in CH_2Cl_2 (10 mL) was added manganese dioxide (600 mg, 4 mmol). The reaction mixture was stirred overnight, diluted with CH_2Cl_2 (10 mL), and filtered over Celite. The filtrate was concentrated, and purified by chromatography column (CH_2Cl_2/*n*-hexane=1:1) to afford **6a** as white solid (30.2 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.0 (br s, 1H), 9.61 (s, 1H), 7.46 (d, J=4.2 Hz, 1H), 7.17 (s, 1H), 7.01 (d, J=4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 144.3, 137.0, 132.8, 125.5, 113.7, 111.4.

*4.3.6. 2-Phenyl thieno[3,2-b]pyrrole-5-carbaldehyde (**6b**).* Compound **5b** (20.1 mg, 0.088 mmol) was used as the starting material, and **6b** was obtained as a yellow solid (7.0 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 9.41 (br s, 1H), 7.64 (d, J=7.2 Hz, 2H), 7.41 (t, J=7.2 Hz, 2H), 7.36 (t, J=7.2 Hz, 2H), 7.22 (s, 1H), 7.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.4, 151.4, 144.1, 136.5, 134.6, 129.1, 128.5, 126.0, 125.8, 113.5, 106.9.

*4.3.7. BODIPY (**8a**).* Under N_2, to a stirred solution of **6a** (66.5 mg, 0.44 mmol) and 2,4-dimethylpyrrole (45.0 μL, 0.44 mmol) in CH_2Cl_2 (5 mL) was added $POCl_3$ (40.0 μL, 0.44 mmol) at 0 °C. When TLC analysis showed the reaction was over, Et_3N (0.61 mL, 4.4 mmol) was added at 0 °C and stirred for 10 min. $BF_3{\cdot}OEt_2$ (0.56 mL, 4.4 mmol) was added to the mixture. The reaction mixture was stirred for 12 h at room temperature, quenched with saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, and purified by chromatography column (CH_2Cl_2/*n*-hexane=1:1) to afford BODIPY **8a** as coppery solid (69.9 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J=5.2 Hz, 1H), 7.20 (s, 1H), 7.14 (d, J=5.2 Hz, 1H), 6.97 (s, 1H), 6.18 (s, 1H), 2.62 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 155.7, 145.4, 137.7, 136.9, 124.6, 121.7, 116.7, 113.4, 46.8, 15.3, 11.4, 8.6; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{13}H_{11}BF_2N_2S$: 276.0710; found: 276.0709.

*4.3.8. BODIPY (**8b**).* Compound **6a** (66.5 mg, 0.44 mmol) and 2,4-diphenylpyrrole (96.5 mg, 0.44 mmol) were used as the starting materials, and BODIPY **8b** was obtained as gold metallic color solid (82.9 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J=8.0 Hz, 2H), 7.60 (d, J=5.2 Hz, 1H), 7.60–7.45 (m, 8H), 7.42 (s, 1H), 7.15 (d, J=5.2 Hz, 1H), 7.07 (s, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 132.9, 131.9, 130.3, 129.5, 129.1, 128.9, 128.3, 119.7, 118.7, 113.6, 31.9, 29.6, 22.6, 14.1; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{23}H_{15}BF_2N_2S$: 400.1053; found: 400.1043.

*4.3.9. BODIPY (**8c**).* Compound **6a** (33.3 mg, 0.22 mmol) and 4,5-dihydro-7-methoxylbenzo[*g*]indole (43.8 mg, 0.22 mmol) were used as the starting materials, and BODIPY **8c** was obtained as blue metallic color solid (52.1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J=8.8 Hz, 1H), 7.50 (d, J=5.2 Hz, 1H), 7.20 (d, J=5.2 Hz, 1H), 7.10 (s, 1H), 7.00 (dd, J=8.8, 2.8 Hz, 1H), 6.94 (s, 1H), 6.87 (s, 1H), 6.83 (d, J=2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$), δ 162.2, 157.3, 144.4, 139.3, 136.0, 131.7, 127.4, 124.7, 120.1, 115.3, 114.5, 113.6, 112.9, 55.4, 31.9, 30.5, 29.7, 29.4, 22.7, 22.4, 14.1; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{20}H_{15}BF_2N_2OS$: 380.0962; found: 380.0961.

*4.3.10. BODIPY (**8d**).* Compound **6a** (33.3 mg, 0.22 mmol) and 4,5-dihydro-7-methoxy-3-phenylbenzo[*g*]indole (60.6 mg, 0.22 mmol) were used as the starting materials, and BODIPY **8d** was obtained as green metallic color solid (54.3 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J=8.8 Hz, 1H), 7.53 (t, J=6.8 Hz, 2H), 7.50 (d, J=5.2 Hz, 1H), 7.49 (t, J=6.8 Hz, 1H), 7.40 (d, J=6.8 Hz, 2H), 7.22 (d, J=5.2 Hz, 1H), 7.12 (s, 1H), 7.02 (dd, J=8.8, 2.8 Hz, 1H), 6.91 (s, 1H), 6.84 (d, J=2.8 Hz, 1H), 3.90 (s, 3H), 2.92 (t, J=6.4 Hz, 2H), 2.78 (t, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 156.4, 155.0, 144.4, 141.5, 138.7, 136.0, 132.0, 129.7, 128.8, 128.6, 124.6, 120.2, 115.3, 114.4, 113.6, 112.9, 55.4, 31.9, 30.6, 29.7, 22.7, 21.1, 14.1; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{26}H_{19}BF_2N_2OS$: 456.1276; found: 456.1274.

*4.3.11. BODIPY (**9a**).* Compound **6b** (50.0 mg, 0.22 mmol) and 2,4-dimethylpyrrole (22.7 μL, 0.22 mmol) were used as the starting materials, and BODIPY **9a** was obtained as green metallic color solid

(16.3 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J=7.2 Hz, 2H), 7.43 (s, 1H), 7.41 (t, J=7.2 Hz, 2H), 7.35 (t, J=7.2 Hz, 1H), 7.16 (s, 1H), 6.96 (s, 1H), 6.17 (s, 1H), 2.63 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 156.6, 155.8, 144.5, 134.5, 129.1, 126.2, 123.4, 121.3, 116.8, 109.1, 31.9, 29.7, 22.7, 15.2, 14.1, 11.5; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{19}H_{15}BF_2N_2S$: 352.1013; found: 352.1012.

*4.3.12. BODIPY (**9b**).* Compound **6b** (50.0 mg, 0.22 mmol) and 2,4-diphenylpyrrole (48.2 mg, 0.22 mmol) were used as the starting materials, and BODIPY **9b** was obtained as green metallic color solid (22.9 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J=8.0 Hz, 2H), 7.68 (d, J=8.0 Hz, 2H), 7.57–7.42 (m, 11H), 7.45 (s, 1H), 7.37 (s, 1H), 7.04 (s, 1H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 146.5, 139.7, 136.3, 134.2, 133.2, 132.2, 130.1, 129.7, 129.5, 129.1, 129.0, 128.4, 127.4, 126.3, 119.3, 118.7, 109.2, 31.9, 29.7, 29.4, 22.7, 14.1; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{29}H_{19}BF_2N_2S$: 476.1328; found: 476.1325.

*4.3.13. BODIPY (**9c**).* Compound **6b** (55.0 mg, 0.22 mmol) and 4,5-dihydro-7-methoxylbenzo[*g*]indole (43.8 mg, 0.22 mmol) were used as the starting materials, and BODIPY **9c** was obtained as green metallic color solid (43.6 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J=8.8 Hz, 1H), 7.71 (d, J=7.2 Hz, 2H), 7.51 (s, 1H), 7.41 (t, J=7.2 Hz, 2H), 7.34 (t, J=7.2 Hz, 1H), 7.06 (s, 1H), 7.00 (dd, J=8.8, 2.8 Hz, 1H), 6.91 (s, 1H), 6.84 (s, 1H), 6.83(d, J=2.8 Hz, 1H), 3.89 (s, 3H), 2.93 (t, J=6.4 Hz, 2H), 2.77 (t, J=6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.1, 156.3, 156.1, 155.0, 144.2, 139.1, 138.4, 134.7, 134.4, 131.4, 131.3, 129.0, 126.9, 126.1, 123.6, 120.4, 115.5, 114.4, 112.9, 109.3, 55.4, 30.6, 29.7, 22.4; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{26}H_{19}BF_2N_2OS$: 456.1276; found: 456.1274.

*4.3.14. BODIPY (**9d**).* Compound **6b** (55.0 mg, 0.22 mmol) and 4,5-dihydro-7-methoxy-3-phenylbenzo[*g*]indole (60.6 mg, 0.22 mmol) were used as the starting materials, and BODIPY **9d** was obtained as green metallic color solid (62.4 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J=8.8 Hz, 1H), 7.72 (d, J=7.6 Hz, 2H), 7.53 (t, J=7.6 Hz, 3H), 7.47 (t, J=7.6 Hz, 1H), 7.42 (s, 1H), 7.41 (t, J=7.6 Hz, 3H), 7.35 (t, J=7.6 Hz, 1H), 7.08 (s, 1H), 7.03 (dd, J=8.8, 2.8 Hz, 1H), 6.89 (s, 1H), 6.85 (d, J=2.8 Hz, 1H), 3.91 (s, 3H), 2.93 (t, J=6.8 Hz, 2H), 2.78 (t, J=6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 155.8, 154.9, 144.2, 141.0, 138.6, 134.7, 132.2, 131.5, 129.7, 129.0, 128.8, 128.5, 126.1, 123.4, 120.4, 115.5, 114.3, 112.8, 109.3, 55.4, 31.9, 30.6, 29.7, 29.4, 22.7, 21.1, 14.1; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{32}H_{23}BF_2N_2OS$: 532.1590; found: 532.1587.

*4.3.15. BODIPY (**10**).* To a stirred solution of **8a** (20.7 mg, 0.075 mmol) in CH_2Cl_2 (5 mL) was added *m*-CPBA (92.4 mg, 0.375 mmol) and stirred for 4 h. The reaction mixture was evaporated and purified by TLC (*n*-hexane/CH_2Cl_2=1:1) to give **10** as yellow solid (4.1 mg, 18%); HRMS-MALDI (m/z): $[M+H]^+$ calcd for $C_{13}H_{12}BF_2N_2O_2S$: 309.0677; found: 309.0675.

*4.3.16. BODIPY (**11**).* Compound **9d** (21.3 mg, 0.04 mmol) was used as the starting material, and **11** was obtained as dark green solid (22.6 mg, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J=8.8 Hz, 1H), 7.72 (d, J=7.6 Hz, 2H), 7.56–7.39 (m, 9H), 7.04 (s, 2H), 6.87 (s, 2H), 3.93 (s, 3H), 2.93 (t, J=7.6 Hz, 2H), 2.78 (t, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 151.2, 145.6, 131.1, 130.5, 129.6, 129.2, 129.1, 127.9, 126.7, 123.0, 119.4, 115.9, 114.6, 113.4, 55.6, 37.1, 31.9, 30.4, 30.0, 29.7, 29.6, 29.4, 27.1, 22.7, 21.1, 19.7, 14.1; HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{32}H_{23}BF_2N_2O_3S$: 564.1500; found: 564.1496.

*4.3.17. BODIPY (**12**).* 4-Dimethylaminobenzaldehyde (59.7 mg, 0.4 mmol), **8a** (27.6 mg, 0.1 mmol), AcOH (0.15 mL), and piperidine (0.15 mL) were stirred for 24 h at 95 °C in dry toluene (3 mL) in the presence of a small amount of activated 4 Å molecular sieves. The mixture was cooled to room temperature, quenched with water, extracted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, evaporated, and purified by TLC (*n*-hexane/CH_2Cl_2=1:1) to afford **12** as dark green solid (8.0 mg, 20%); HRMS-MALDI (m/z): $[M]^+$ calcd for $C_{22}H_{20}BF_2N_3S$: 407.1435; found: 407.1434.

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Supplementary data

^{1}H and ^{13}C NMR spectra, and a CIF file giving crystallographic data for **8a**. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.09.011. These data include MOL files and InChiKeys of the most important compounds described in this article.

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