Formation of 8-RS-BODIPYs *via* direct Substitution of 8-MeS-BODIPY by RSH; R = Et, Pr, Bu, ^{t}Bu, *n*-$C_{12}H_{25}$, C_6H_5, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, and 2,6-$Me_2C_6H_3$

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Abstract

Reactions between 8-RS-BODIPY (R = Me, **1**) and alkyl and aryl thiols were readily accomplished in dichloromethane (DCM) to provide a synthetic pathway to a range of new 8-organothio-BODIPYs in good yield. The new alkyl 8-RS-BODIPYs, R = Et, **2**; Pr, **3**; Bu, **4**; ^{t}Bu, **5,** *n*-Dodecyl, **6**; exhibit absorption and emission properties essentially unchanged from those of **1** whereas the arylthio analogs, R = Ph, **7**; 2,6-$Me_2C_6H_3$, **8**; *p*-MeC_6H_4, **9**; *p*-$MeOC_6H_4$, **10**, exhibit no fluorescence with the exception of **7**, and then only in hexane. In common with other related 8-substituted BODIPYs the new 8-alkylthio-BODIPY dyes show decreasing fluorescence intensity as solvent polarity increases. Compounds **2**, **3**, **7**, and **8** were characterized *via* single crystal X-ray analysis; the alkyl derivatives **2** and **3** exhibited planar BODIPY cores with co-planar organothio- substituents, whereas the aryl derivatives exhibited both BODIPY core deformation and significant twisting about the S-C(8) bond removing co-planarity between the aryl group and the distorted BODIPY core. These deformations coincide with the significantly reduced emission properties.

Keywords

BODIPY; fluorescence; thiolation; structure.

Introduction

Boron dypyrromethene (BODIPY) molecules are of current interest due to such properties as strong photostability, high quantum yield emission, and high extinction coefficients.[1,2,3] These features may be tweaked by substituting the BODIPY backbone, Figure 1, at a number of positions hence resulting in a large family of materials. Because of this versatility, the molecule has been used for the quantification of transition metals in cells,[4,5,6] chemo-sensing,[7] protein tags,[8] and laser dyes purposes.[9]

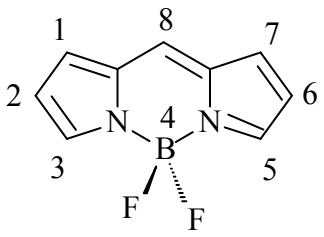
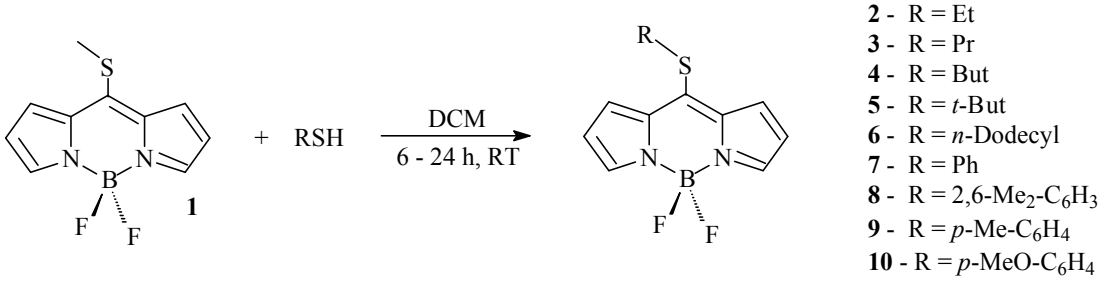


Figure 1. Boron Dipyrromethene (BODIPY)

We have recently reported that 8-methylthio-BODIPY, a molecule first described by Biellmann, *et al*.,[10] is a very potent reagent for derivatizing the BODIPY core at the 8-position. Thus, we explored the substitution of the methylthio- group by aryl- moieties,[11,12] using Liebeskind-Srogl cross-coupling reactions,[13] the substitution of the methylthio group by primary and secondary amines[14] and alcohols,[15] and more recently multi-substitution by aryl thiols in THF.[16] Herein we report the simple one-step substitution of the MeS group by a range of thiols that requires no catalyst. We also report on their structural and optical properties and draw conclusions that relate the two sets of data.

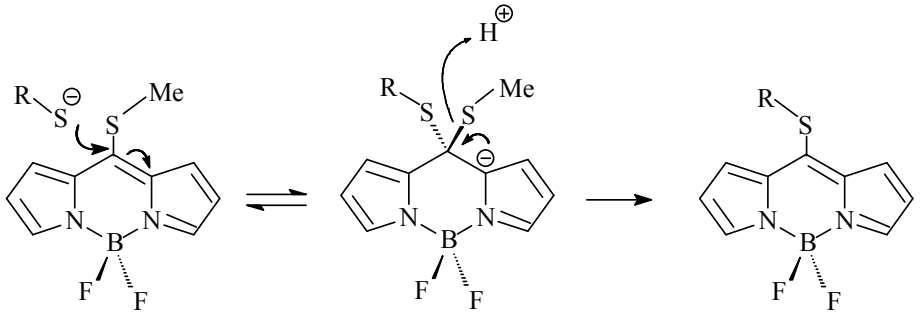
Results and Discussion

The 8-methylthio- group in **1** was substituted by a range of alkyl and aryl thiols, by simply mixing the reagents in dichloromethane (DCM) for ~ 6-24 hours, Scheme 1. The reaction does not require acidic or basic conditions, requires no catalyst or co-reagent;[17] it is therefore very simple and convenient.



Scheme 1. Reaction of 8-methylthio-BODIPY (**1**) with thiols.

Trans-thio-esterification is a well-established transformation,[18,19] and since the 8-thio-BODIPYs possesses the R-S-C(sp^2) linkage and it is attached to an electron-withdrawing moiety (the BODIPY core), electronically similar to thioesters,[20] we propose a mechanism similar to that transformation, Scheme 2. A further significant driving force for this reaction is the formation of methylthiol in the gas phase, thereby reducing the possibility of significant reformation of **1**.



Scheme 2. Proposed mechanism for the *trans*-thio-esterification of 8-MeS-BODIPY

The nucleophilicity of the sulfur is enough for the reaction to occur under the same conditions as the previously reported substitution with amines and alkoxides (the latter in the presence of a catalyst), only at slower pace.[15]

Optical spectroscopy

In general, the absorption and emission wavelengths of the new 8-RS-BODIPYs are little changed with respect to those of **1** indicating the extended alkyl chains bonded to the S atom do not modify the π-system conjugation in the BODIPY core. The absorbance spectrum shape for 8-RS-BODIPYs is, however, different compared to other BODIPYs previously reported.[1] Compounds **1-6** exhibit two absorbance peaks at ~495 nm and ~515 nm when recorded in hexane. However, the peak at ~515nm tends to decrease for all dyes as more polar solvents are utilized, as illustrated for **2** in Figure 2. Furthermore, the vibronic shoulder present in other BODIPYs seems to be absent in the compounds herein reported.

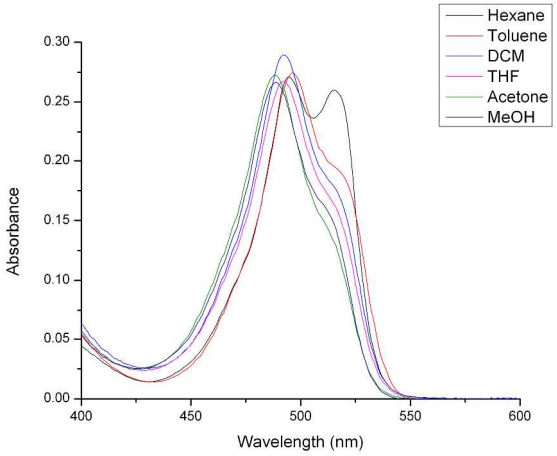


Figure 2. Absorbance of **2** as a function of solvent

The new 8-RS-BODIPYs have molar extinction coefficients ranging from 20,000 to 40,000 M^{-1} cm^{-1}, in accordance with the observations made by Biellmann.[10] As expected, based upon the

absorbance data set, the emission spectra of **2-6** are similar to **1**, again as illustrated for **2** in Figure 3. Their emission wavelength remains constant at ~530 nm and, as previously noted for the 8-amino-BODIPYs,[14] the fluorescence intensity is large in non-polar solvents such as hexane, and progressively declines as the solvent polarity increases.

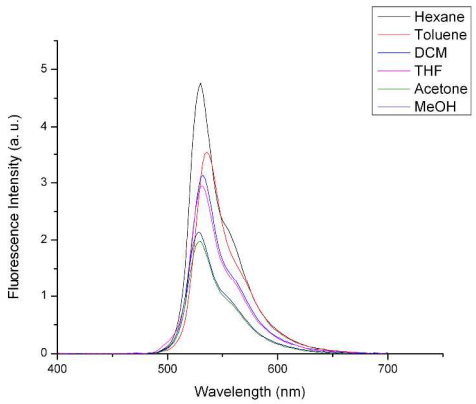


Figure 3. Emission of **2** as a function of solvent

The 8-arylthio-BODIPYs **7-10** behave differently to 8-alkylthio-BODIPYs **1-6**. Compound **7,** previously synthesized by Leen, *et al*. *via* nucleophilic substitution of 8-chloro-BODIPY in the presence of a base,[21] was reported to exhibit no emission in THF; however, we note that in the non-polar hexane it possesses a significant emission. Compounds **8-10**, with variously substituted phenylthio functionalities do not exhibit fluorescence in any organic solvent. The analogous 8-anilino-BODIPY has been reported to exhibit a similar absence of emission.[10] The absorbance and emission spectra data for **3 -10** are presented in the supplementary material, Figures S34 – S40, and listed in Table S1 along with their various quantum yields where appropriate.

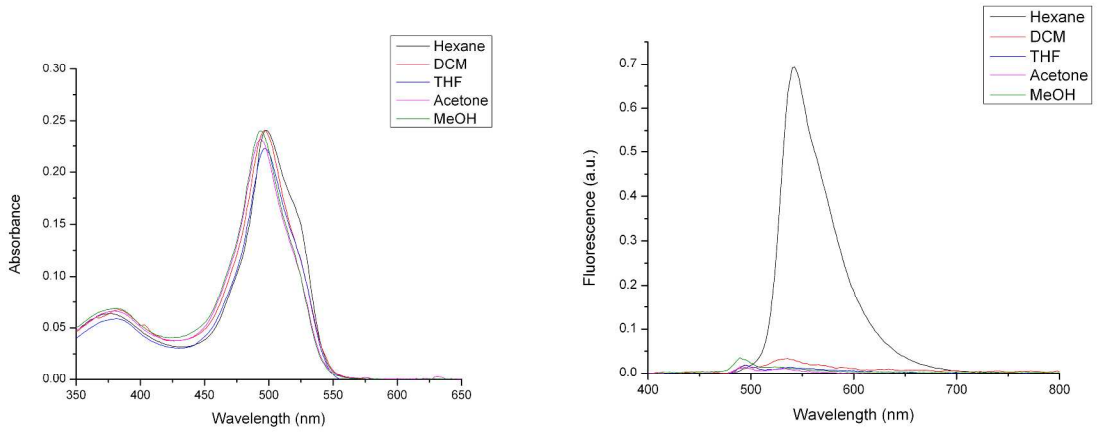


Figure 4. Absorbance (left) and Fluorescence (right) of compound **7**

NMR Studies

All the new 8-RS-BODIPY dyes exhibit sharp ^{13}C and ^{1}H NMR resonances (presented in the supplementary material, Figures S1 - S33) with no broadening due to any restricted rotation about the S-C(8) bond at 298 ^{o}K. This suggests that there is no strong multiple bonding component to the structure of these dyes, a result in direct contrast to the related 8-amino materials.[14a] In the latter case the various C and H atoms are NMR distinguishable as noted by their differentiation by color and symbol in Figure 5.

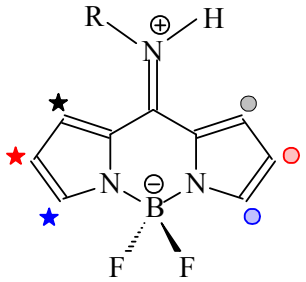


Figure 5. Resonance contribution to 8-NHR-BODIPY

The ^{19}F NMR spectra of the new materials exhibit the expected resonances located at ~-145 - 146 ppm.

Structural Analyses.

As is common in the field of BODIPY chemistry, the new 8-RS-BODIPY compounds were readily crystallized to provide crystals suitable for X-ray analysis which has proved useful for the understanding of various aspects of their emission properties. The molecular structures of **2**, **3**, and **7**,[17] and **8**, are illustrated in Figures 6 and 8, respectively. Pertinent bond lengths and various other geometrical data related to the structures are presented in Table 1, crystal and refinement data are presented in Table 2.

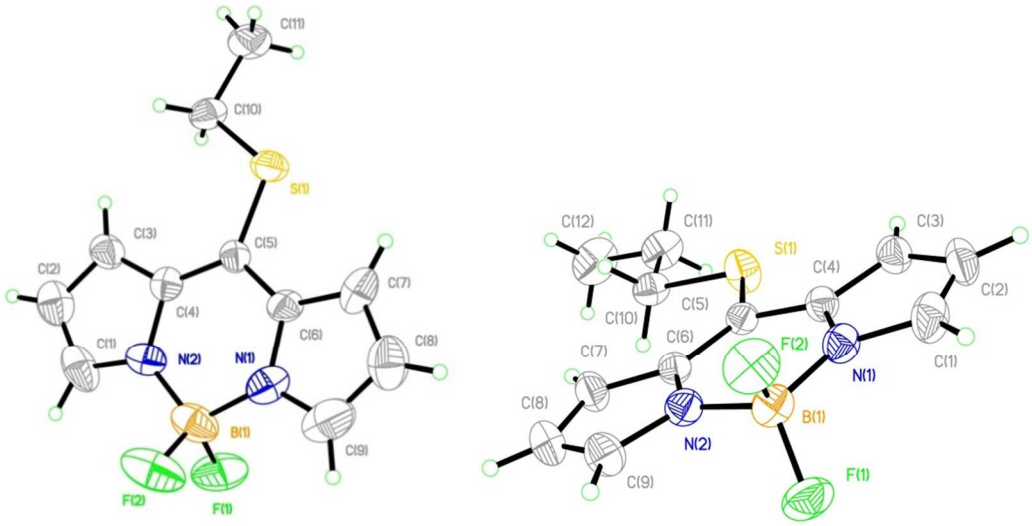


Figure 6. Molecular structure of **2** (left) and **3**

There are several general observations related to the molecular structures obtained. In the case of the 8-ethyl- and 8-propylthio-BODIPYs, Figure 6, the planarity of the BODIPY core is significantly maintained, exhibiting dihedral angles between the pyrrole rings in the range of 3-5^{o}. Also for these two compounds the thio groups are essentially coplanar with the BODIPY

core, reminiscent of the related 8-ethylamino- and 8-propylamino-BODIPY materials.[14a] This co-planarity is illustrated for **3** in Figure 7 which also illustrates a common characteristic of such molecules in terms of the crystal packing where the molecules line up in parallel columns, connected by F…H-CHS H-bonds (2.41 – 2.61 Å) with an intermolecular distance of between individual molecules of 3.44 - 3.90 Å. A detailed description of the solid state packing of these BODIPYs is beyond the scope of this article.

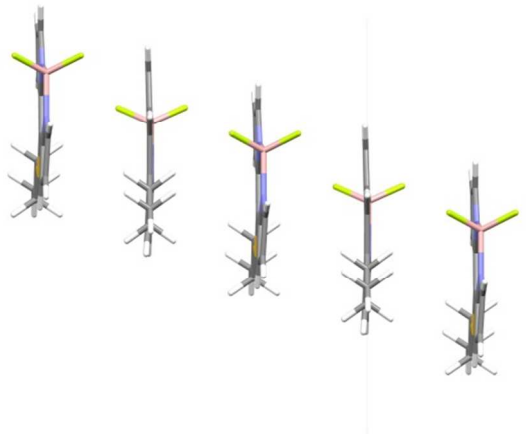


Figure 7. Coplanarity of BODIPY core and thiol substituents and solid state packing for **3**

The 8-arylthio-BODIPYs, **7** and **8**, Figure 8, differ in their generalized geometry from the alkyl analogs above. Firstly, the planarity of the BODIPY core is now moderately disturbed involving dihedral angles between the pyrrole rings of 11 and 16^{o}, respectively, as exemplified by the side on view of **7** illustrated in Figure 9.

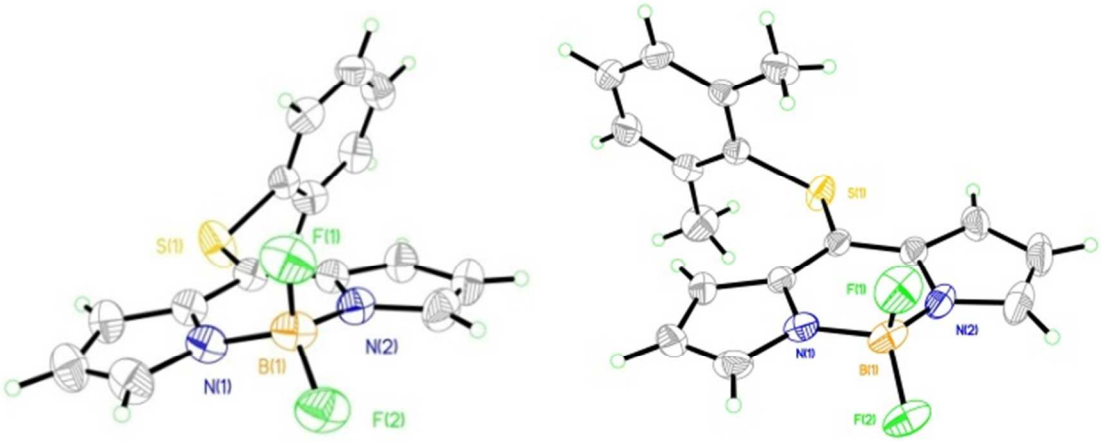


Figure 8. Molecular structure of **7** (left) and **8**

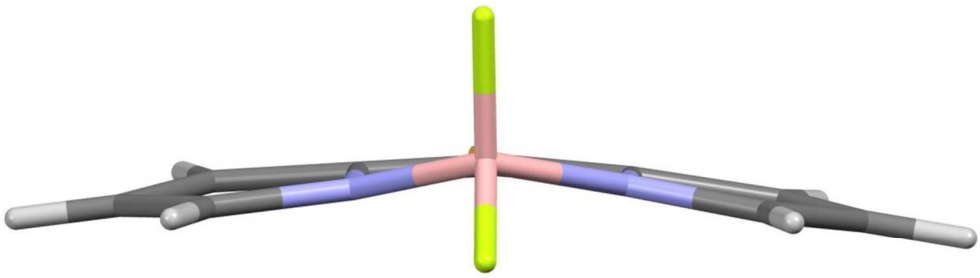


Figure 9. Side view of BODIPY **7** (phenyl group removed for clarity)

Secondly, there is a very significant non-co-planarity of the thio group with respect to the cores. Dihedral angles between the BODIPY core and the C(8)-S-C plane of 22.6^{o} and 31.2^{o} are observed for **7** and **8**, respectively, indicating a bending away from the BODIPY plane to remove

the steric interactions of the adjacent H atom. Additionally the aryl ring twists about the S-C(aryl) bond to further reduce the steric congestion by 57.7^{o} (**7**) and 66.1^{o} (**8**). As expected the increased steric bulk of the 2,5-dimethyl unit in **8** is reflected in the larger deviations in both cases. However, apart from these small angular variation the two structures, **7** and **8**, are essentially equivalent as can be noted in Figure 10 where the two structures are overlaid.

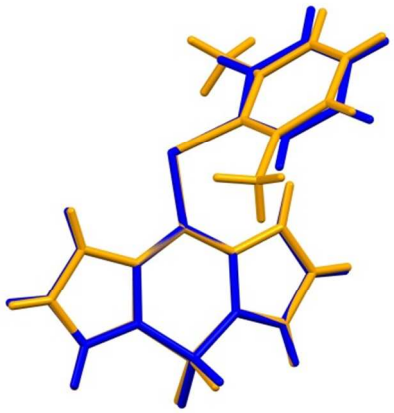


Figure 10. Overlaid structures of **7** and **8**

The various S-C bond lengths are interesting and fall within the range of 1.701(12) – 1.819(11) Å, Table 1. The degree to which any delocalization of the S lone pairs into the BODIPY π-system can, in principle, be assessed by the S-C(8) bond lengths in a manner similar to the same analysis of the N-C(8) bond lengths in the related 8-amino-BODIPY system.[14a] The average of the S-C(8) bond lengths associated with the new materials is 1.732 Å, which compares to the average S-aliphatic C bond length of 1.785 Å, a significant bond length decrease which indeed suggests such π delocalization. However, it is well to recognize that in general element bonds to carbon, E-C(sp^2) atoms exhibit small but significant shortening compared to a corresponding E-C(sp^3) bond due to the increasing contribution of the s orbital.

Conclusion

The facile substitution of 8-methylthio-BODIPY by a range of thiols has been demonstrated for the first time. When DCM is utilized as solvent, the substitution only occurs at the *meso*-(8)-position, while, as we previously noted, THF promotes a further substitution in the 3- and 5- positions.[16] Emission spectroscopy revealed that the fluorescence intensity for **1**-**6** decreases as solvent polarity increases, an effect we had previously described in 8-amino-BODIPYs, due to efficient solvation of the polar species facilitating to non-radiative relaxation. However, the wavelength remains unchanged despite bulkier alkyl groups. 8-phenylthio-BODIPY exhibits fluorescence in the most non-polar solvent (hexane); however, the other 8-arylthio-BODIPYs, **8**-**10**, do not exhibit fluorescence emission in any solvent, a result similar to the related 8-anilino-BODIPY.

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Experimental

The thiol reagents were purchased from Sigma-Aldrich and used as received and solvents were dried prior to use by standard methods. In general NMR measurements were performed with a JEOL 600 MHz spectrometer, with the exception of samples **6**, **9** and **10** when a BRUKER 500 MHz spectrometer was used; UV-Vis data were obtained with CARY 50 UV-Vis spectrometer; fluorescence spectra were obtained on a OLIS DM45 fluorescence spectrometer using Fluorescein as standard in a 0.1 N NaOH solution for the determination of the quantum yields. The crystal structures were determined using a Bruker APEX CCD diffractometer with mono-chromatized MoK_α radiation ($\lambda = 0.71073$ Å). Elemental analyses were performed by

Galbraith Laboratories and HRMS were obtained using a JJEOL JMS-T100LC AccuToF Mass Spectrometer.

Compounds **2**, **3**, **4**, **5**, **7**, and **8** were synthesized by reacting **1** (50 mg, 0.21 mmol purchased from Cuantico de Mexico, Guanajuato, Mexico) with 1.5 eq. of the corresponding thiol in DCM under a nitrogen or argon atmosphere. After 6 hours of stirring at room temperature silica gel thin-layer chromatography indicated that the reaction was finished. The product was purified by silica gel column chromatography using 30/70% mixture of EtOAc/hexanes. The final products were recrystallized from a DCM/hexane mixture.

Compounds **6**, **9** and **10** were synthesized by reacting **1** (40 mg, 0.17 mmol) with 1.5 eq. of the corresponding thiol in DCM under nitrogen atmosphere. After 24 hours of stirring at room temperature silica gel thin-layer chromatography indicated that the reaction no longer proceeds and the reaction was stopped. The product was purified by silica gel column chromatography using 3/97 % solvent mixture of EtOAc/Hexanes. The final products were recrystallized from a DCM/petroleum ether.

The various yields, physical, spectral, and analytical data for the new compounds are reported below; NMR data reported as δ ppm values, recorded in $CDCl_3$.

2: Orange crystals, yield 82%, 43.3 mg; m.pt. 92-93^{o}C; ^{1}H NMR, 1.41 (t, 3H, J = 7.74 Hz), 3.36 (q, 2H, J = 7.56), 6.51 (d, 2H, J = 4.14 Hz), 7.41 (d, 2H, J = 4.14 Hz), 7.79 (s, 2H). ^{13}C{^{1}H} NMR, 14.9 (CH_3), 32.5 (CH_2), 118.0 (CH), 128.5 (CH), 135.1 (C), 142.2 (CH), 151.4 (C). ^{19}F NMR -145.8 (m). Anal. Calcd. for $C_{11}H_{11}BF_2N_2S$: C, 52.41; H, 4.40. Found: C, 52.74; H, 4.25.

A, 493

3: Orange crystals, yield 86%, 48.0 mg; m.pt. 95-96 ^{o}C; ^{1}H NMR, 1.05-1.07 (t, 3H, J = 7.56 Hz), 1.77 (sextet, 3H, J = 7.56 Hz), 3.31 (t, 2H, J = 7.56 Hz), 6.51 (d, 2H, J = 4.14 Hz), 7.42 (d, 2H, J = 4.14 Hz), 7.79 (s, 2H); ^{13}C{^{1}H} NMR, 13.3 (CH_3), 23.4 (CH_2), 40.3 (CH_2), 118.0 (CH), 128.5 (CH), 135.5, 142.2 (CH), 152.0 (C); ^{19}F NMR, -145.8 (m). Anal. Calcd. for $C_{12}H_{13}BF_2N$, C, 54.16; H, 4.92. Found: C, 54.04; H, 5.16.

4: Orange crystals, yield 89%, 52.3 mg; m.pt. 98-99 ^{o}C; ^{1}H NMR, 0.93 (t, 3H, J = 7.50 Hz), 1.49 (sextet, 2H, J = 7.56 Hz), 1.72 (quintet, 2H, J = 6.84), 3.33 (t, 2H, J = 7.50 Hz). 6.51 (s, 2H), 7.41 (s, 2H), 7.79 (s, 2H); ^{13}C{^{1}H} NMR, 13.6 (CH_3), 21.8 (CH_2), 31.8 (CH_2), 38.1 (CH_2), 117.9 (CH), 128.4 (CH), 135.0 (C), 142.0 (CH), 152.1 (C). ^{19}F NMR, -145.8 (m). Anal. Calcd. for $C_{13}H_{15}BF_2N_2S$: C,55.74; H, 5.40. Found: C, 55.36; H, 5.32.

5: Red powder, yield 74%, 43.5 mg; m.pt. 96-97 ^{o}C; ^{1}H NMR, 1.39 (s, 9H), 6.51 (d, 2H, J = 4.08 Hz), 7.48 (d, 2H, J = 4.08 Hz), 7.87 (s, 2H). ^{13}C{^{1}H} NMR, 32.10 (CH_3), 51.3 (C), 118.5 (CH), 132.9 (CH), 140.8 (CH), 140.8 (C), 142.7 (C), 145.8 (CH). ^{19}F NMR, -145.5 (m). HRMS [M + H]: Calcd. for $C_{13}H_{15}BF_2N_2S$: 281.1095, Found. 281.1103.

6: Orange powder, yield 30%, 20 mg; m.pt. 58-59 °C; ^{1}H NMR, 7.80 (s, 2H), 7.42 (d, J = 4.1, 2H), 6.52 (d, J = 3.3 Hz, 2H), 3.33 (t, J = 7.4 Hz, 2H), 1.81 - 1.68 (m, 2H), 1.51 - 1.40 (m, 2H), 1.36 - 1.18 (m, 2H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR, 14.1 (CH_2), 28.6 (CH_2), 29.0 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_3), 29.8 (CH_2), 38.4 (CH_2), 117.8 (CH), 117.9 (CH), 128.3 (CH), 135.1 (C), 141.9 (CH), 152.2 (C). Anal. Calcd. for $C_{21}H_{31}BF_2N_2S$: C, 64.28; H, 7.96. Found: C, 64.18; H, 7.82.

7: Orange crystals, yield 94%, 59.2 mg; m.pt. 134-135 ^{o}C; ^{1}H NMR, 6.37 (d, 2H, J = 5.28 Hz), 6.95 (d, 2H, J = 4.08 Hz), 7.40-7.45 (m, 3H), 7.60 (d, 2H, J = 7.56 Hz), 7.75 (s, 2H). ^{13}C{^{1}H}

NMR, 118.0 (CH), 126.8 (CH), 130.0 (CH), 130.3 (CH), 131.9 (C), 133.1 (CH), 134.2 (C), 142.1 (CH), 150.0 (C). ^{19}F NMR, -145.5 (m). Anal. Calcd. for $C_{15}H_{11}BF_2N_2S$: C, 60.03; H, 3.69. Found: C, 60.14; H, 3.95.

8: Red crystals, yield 85%, 58.5 mg; m.pt. 151-152 ^{o}C; ^{1}H NMR, 2.84 (s, 6H), 6.34 (m, 2H), 2.74 (s, 1H), 7.24 (m, 2H), 7.36 (t, 1H, J = 7.56 Hz), 7.71 (s, 1H). ^{13}C{^{1}H} NMR, 21.7 (CH_3), 117.5 (CH), 126.0 (CH), 128.2 (C), 129.5 (CH), 131.4 (CH), 132.5 (C), 140.5 (CH), 143.3(CH), 153.7 (C). ^{19}F NMR, -145.8 (m). HRMS [M + H]: Calcd. for $C_{13}H_{15}BF_2N_2S$: 329.1095, Found. 329.1083.

9: Orange crystals; yield 66%, 35 mg; m.pt. 143-144 °C; ^{1}H NMR, 7.75 (s, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 4.1 Hz, 2H), 6.38 (d, J = 3.6 Hz, 2H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR, 21.4 (CH_3), 117.7 (CH), 127.7 (C), 128.1 (CH), 131.1 (CH), 133.4 (CH), 133.8 (C), 140.8 (C), 141.6 (CH), 151.8 (C). Anal. Calcd. for $C_{16}H_{13}BF_2N_2S$: C, 61.17; H, 4.17. Found: C, 61.29; H, 4.25.

10: Red crystals; yield 45%, 27 mg; m.pt. 171-173 °C; ^{1}H NMR: δ 7.73 (s, 2H), 7.56 (d, J = 8.8, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 4.1 Hz, 2H), 6.38 (d, J = 3.1 Hz, 2H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR, 55.5 (CH_3), 116.0 (CH), 117.6 (CH), 120.7 (C), 127.7 (CH), 133.3 (C), 135.7 (CH), 141.1 (CH), 153.2 (C), 161.7 (C). Anal. Calcd. for $C_{16}H_{13}BF_2N_2OS$: C, 58.21; H, 3.97. Found: C, 58.33; H, 4.10.

Supplementary Data. ^{1}H and ^{13}C spectra of compounds **2-10**; ^{19}F NMR spectra of compounds **2-5, 7-8**; Absorbance and emission data for **2-10**. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 959245 (**2**), 959249 (**3**), 9559249 **(7**) and

959248 (**8**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.UK).

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Table 1. Selected geometrical parameters

	2[a]	**3**	**7**	**8**
r(C_B-S)	1.701(12) 1.730(13)	1.724(4)	1.7350(19)	1.7472(16)
r(S-C_R)	1.785(11) 1.819(11)	1.800(4)	1.766(2)	1.7771(16)
∠(C_B-S-C_R)	110.5(6) 111.8(6)	111.0(2)	106.67(9)	107.43(7)
r(B-F_1)	1.407(17) 1.377(16)	1.379(6)	1.383(2)	1.387(2)
r(B-F_2)	1.397(16) 1.397(15)	1.385(5)	1.381(2)	1.377(2)
Φ_{py}	5.5 3.0	4.2	16.0	11.4
$\Phi_{Bdpy\text{-}SR}$	3.6 0.5	1.3	22.6	31.2

a Two symmetry independent molecules are found in the crystal lattice.

Table 2. Selected crystal data

R=	Et (**2**)	Pr (**3**)	Ph (**7**)	Mes (**8**)
CCDC #	959245	959247	959249	959248
Empirical formula	$C_{11}H_{11}BF_2N_2S$	$C_{12}H_{13}BF_2N_2S$	$C_{15}H_{11}BF_2N_2S$	$C_{17}H_{15}BF_2N_2S$
Formula Wt.	252.09	266.11	300.13	328.18
Crystal system	orthorhombic	orthorhombic	triclinic	triclinic
Space group	$Pca2_1$	$Pna2_1$	P -1	P -1
Z	8	4	2	2
a (Å)	7.7827(18)	7.8029(4)	9.019(5)	8.0536(6)
b (Å)	18.960(4)	20.2322(11)	9.387(5)	8.1501(6)
c (Å)	15.678(4)	7.9100(5)	9.840(5)	12.6192(9)
α (°)	90	90	103.834(10)	87.2310(10)
β (°)	90	90	111.510(11)	73.1110(10)
γ (°)	90	90	104.812(11)	77.7050(10)
Volume ($Å^3$)	2313.4(9)	1248.75(12)	696.1(7)	774.31(10)
Collection Ranges	$-10 \le h \ge 10$; $-25 \le k \ge 25$; $-19 \le l \ge 20$	$-10 \le h \ge 10$; $-17 \le k \ge 27$; $-10 \le l \ge 10$	$-12 \le h \ge 12$; $-12 \le k \ge 12$; $-13 \le l \ge 13$	$-9 \le h \ge 9$; $-9 \le k \ge 9$; $-10 \le l \ge 14$
Temp. (K)	296(2)	296(2)	296(2)	296(2)
Density g/cm^3	1.448	1.415	1.432	1.408
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Absorp. coeff (μ) (mm^{-1})	0.262	0.265	0.247	0.229
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan

F(000)	1040	552	308	340
Θ range - data collection	1.074-28.333	2.013-29.462	2.395-29.028	1.687-24.996

Table 2. Selected crystal data continued

R=	Et (**2**)	Pr (**3**)	Ph (**7**)	Mes (**8**)
Reflections collected	32959	10263	11581	6903
Independent reflections	5544	3387	3595	2703
R(int)	0.2032	0.0357	0.0241	0.0116
Data/restraints/parameters	5544/1/309	3387/1/165	3595/0/190	2703/66/268
Max shift/error	0.000	0.000	0.000	0.000
Goodness of fit on F^2	0.911	0.753	1.0024	0.642
R1 [I>2sigma(I)]	0.0651	0.0400	0.0462	0.0352
R1 (All data)	0.2326	0.0770	0.0747	0.0385
Absolute structure parameter	0.08(9)	0.09(4)	N/A	N/A
Extinction coefficient	N/A	N/A	N/A	N/A
Largest diff peak and hole (e A^{-3})	0.167, -0.232	0.153, -0.181	0.345, -0.419	0.347, -0.386

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