Unprecedented, One-Pot, Sequential Thiolate Substitutions of 8-methylthio-BODIPY under Mild Conditions leading to a Red Emissive BODIPY Dye 3,5,8-tris(PhS)-BODIPY.

Electronic Supplementary Information

Robinson Roacho¹, Alejandro Metta-Magaña¹, Eduardo Peña-Cabrera², Keith Pannell¹*

¹Department of Chemistry, University of Texas at El Paso. El Paso, Texas, 79968-0513, USA.
²Departamento de Química, Universidad de Guanajuato. Col. Noria Alta S/N. Guanajuato, Gto. 36050, Mexico.

Corresponding Author: Keith Pannell. kpannell@utep.edu

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**Experimental**

**Compound 2** was synthesized by reacting 1 (50 mg, 0.21 mmol purchased from Cuantico de Mexico, (Guanajuato, Mexico) with 1.5 eq. of PhSH in dry dichloromethane under nitrogen 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 a 30/70% EtOAc/Hexanes solvent system. The final product was recrystallized from a dichloromethane/hexane mixture.

**Compounds 3 and 4** were synthesized by reacting 1 (50 mg, 0.21 mmol) with 3 eq. of phenylthiol in dry tetrahydrofuran under nitrogen atmosphere. After 6 hours of stirring at room temperature silica gel thin-layer chromatography indicated that compound 3 was formed. Further stirring for 48 hours produced compound 4. The products were purified by silica gel column chromatography using 30/70% EtOAc/Hexanes. The final products were recrystallized from a dichloromethane/hexane mixture. The same results were obtained by reacting 2 with PhSH under identical conditions.

**Compound 5** was synthesized by reacting 1 (50 mg, 0.21 mmol purchased from Cuantico de Mexico, Guanajuato, Mexico) with 1.5 eq. of EtSH in tetrahydrofuran under nitrogen 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% EtOAc/Hexane solvent system. The final products were recrystallized from a dichloromethane/hexane mixture.

2: Orange crystals, yield 94%, 59.2 mg; m.pt. 134-135°C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 6.37-6.38 (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 NMR (CDCl\(_3\)) 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 (CDCl\(_3\)) -145.5 (m). Anal. Calcd. for C\(_{15}\)H\(_{11}\)BF\(_2\)N\(_2\)S: C, 60.03; H, 3.69. Found: C, 60.14; H, 3.95.

3: Red crystals, yield 59%, 51.4 mg; m.p. 163-164°C; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 5.78 (d, 1H, \(J = 4.8\) Hz), 6.34 (s, 1H), 6.92 (d, 1H, \(J = 3.42\) Hz), 7.07 (d, 1H, 4.8 Hz), 7.30-7.32 (m, 3H), 7.42-7.47 (m, 5H), 7.62-7.65 (m, 3H). \(^{13}\)C NMR (CDCl\(_3\)) 116.7 (CH), 119.7 (CH), 126.2 (CH), 128.5 (CH), 128.9 (C), 129.8 (CH), 129.9 (CH), 130.3 (CH), 130.4 (CH), 131.2 (CH), 134.3 (C), 134.4
(C), 135.3 (CH), 138.7 (C), 139.1 (CH), 139.9 (C), 152.4 (C). $^{19}$F NMR (CDCl$_3$) -147.6 (m). Anal. Calcd. for C$_{21}$H$_{15}$BF$_2$N$_2$S$_2$: C, 61.78; H, 3.70. Found: C, 61.86; H, 3.85.

4: Red crystals, yield 19%, 20.5 mg; m.pt. 92-93°C; $^1$H NMR (CDCl$_3$) $\delta$ 5.79 (d, 2H, $J$ = 4.8 Hz), 6.98 (d, 2H, $J$ = 4.14 Hz), 7.22 (d, 1H, $J$ = 7.56 Hz), 7.25-7.27 (m, 2H), 7.36-7.37 (d, 2H, $J$ = 8.22 Hz), 7.40-7.44 (m, 6H), 7.65 (d, 2H, $J$ = 8.64 Hz). $^{13}$C NMR (CDCl$_3$) $\delta$ 118.5 (CH), 127.8 (CH), 128.1 (CH), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.9 (CH), 130.0 (CH), 133.3 (C), 135.0 (CH), 135.5 (C), 138.1 (C), 157.5 (C). $^{19}$F NMR (CDCl$_3$) -147.5 (m). Anal. Calcd. for C$_{27}$H$_{19}$BF$_2$N$_2$S$_3$: C, 62.79; H, 3.71. Found: C, 61.41; H, 3.66. Note: The isolated yield of the reaction was poor due to the presence of trace compounds with similar $R_f$ values in the chromatography purification process.

5: Orange crystals, yield 82%, 43.3 mg (0.17 mmol); m.p. 92-93°C; $^1$H NMR (CDCl$_3$) $\delta$ 1.40–1.42 (t, 3H, $J$ = 7.74 Hz), 3.34-3.38 (q, 2H, $J$ = 7.56 Hz), 6.51 (d, 2H, $J$ = 4.14 Hz), 7.41 (d, 2H, $J$ = 4.14 Hz), 7.79 (s, 2H). $^{13}$C NMR (CDCl$_3$) $\delta$ 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 (CDCl$_3$) -145.8 (m). Anal. Calcd. for C$_{11}$H$_{11}$BF$_2$N$_2$S: C, 52.41; H, 4.40. Found: C, 52.74; H, 4.25.

The new compounds were characterized by NMR spectroscopy using a Bruker 600 MHz NMR; UV-vis spectroscopy recorded in a Cary 50 spectrometer; fluorescence spectroscopy recorded on an Olis DM 45 fluorometer. Rhodamine B ($\Phi$ = 0.70 in ethanol) and cresyl violet perchlorate ($\Phi$ = 0.54 in ethanol) were used as standards for the calculation of the quantum yields.

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Table 1. Summary of the optical properties of BODIPYs 2-4.

Figure 1. Absorbance (left) and emission spectra of 2.
Figure 2. 3,8-bis(phenylthio)BODIPY 3; $^1\text{H}$ NMR
Figure 3. 3,8-bis(phenylthio)BODIPY 3; $^1$H NMR expanded
Figure 4. 3,8-bis(phenylthio)BODIPY 3; $^{19}$F NMR
Figure 5. 3,8-bis(phenylthio)BODIPY 3; $^\text{13}$C NMR
Figure 6. 3,8-bis(phenylthio)BODIPY 4; $^1$H NMR
Figure 7. 3,5,8-tris(phenylthio)BODIPY 4; $^1$H NMR expanded.
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**Figure 10.** 8-ethylthio-BODIPY 5, $^1$H NMR
Figure 11. 8-ethylthio-BODIPY 5, $^1$H NMR zoom
Figure 12. 8-ethylthio-BODIPY 5, $^{19}$F NMR
Figure 13. 8-ethylthio-BODIPY 5, $^{13}\text{C}$ NMR
Crystal Packing aspects of 2, 3 and 4

In the case of the monothio BODIPY 2, in the crystal structure can be observed the formation of ribbons or chains by the HB between the F atoms and two hydrogens in the aromatic ring (F1···H13 [2.635 Å] and F2···H11 [2.395 Å], Figure9). These chains are then interlinked by more HB through the F atoms (F1···H12 [2.514 Å] and F2···H1 [2.440 Å]) generating a 2-D structure (Figure9).

On the other hand, the presence of the second phenyl ring on the bis-adduct3 blocks the interactions with the hydrogen on the bodipy core generating a chain motif along axis b through F2···H11 [2.605 Å] and F2···H20 [2.558 Å], Figure10a. Another structural change in the crystal is the formation of dimers (Figure10b), not observed in the mono-adduct, with a distance of 3.493 Å between the mean planes of each bodipy with a close interaction of the F and S atoms of 3.054 Å, probably the driving force, because that distance is shorter than the Van der Waal’s distance by 0.216 Å. This F···S interactions interlock chain motifs generating a 2-D structure.
In the case of the tris adduct, 4, the formation of dimers is also observed (Figure 11), the distance between them (mean planes) is 3.531 Å, as expected a little longer than the bis adduct due to the increased molecular volume. Due to the same reason the F⋯S interactions are slightly longer (3.158 Å), but still below the sum of VdW radii by 0.112 Å. But in this molecule, the F⋯S interaction is not necessary as in the bis-adduct to expand the order of the architecture to 2-D, but they are collaborating with the F⋯H network, F1⋯H25 [2.551 Å], F2⋯H26 [2.464 Å], Figures 12 and 13.

Figure 16. Dimer for 4

Figure 17. Partial HB network generated from a central molecule of 4
Figure 18. HB network molecules of 4 in different color to increase clarity