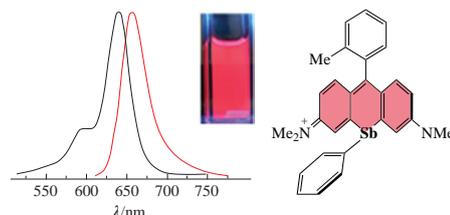ELSEVIER

Synthesis of an antimony rhodamine analog

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We describe the synthesis, structure and characterization of an antimony-rhodamine derivative with a phenyl-antimony moiety installed at the 10′ position of the central ring. This compound is a red fluorophore ($\lambda_{em} = 655$ nm) with a quantum yield of 12% in acetonitrile.

The incorporation of antimony in emissive derivatives is drawing a great deal of attention in our research because of application in anion sensing.[1–4] Examples of such compounds include organoantimony derivatives functionalized by fluorescent units such as anthrancene,[5] pyrene,[6] perylene[6] and BODIPY,[7] among others. In all cases, the antimony moiety stands at the periphery of the fluorophore. Efforts to integrate the antimony atom within the chromophore structure, as in the case of compounds **1**,[8,9] **2**,[10] and **3**[11] are much scarcer (Figure 1). These compounds are appealing because of the intimate connection that exists between the antimony atom and the π-conjugated chromophore. Absent from the literature are efforts describing the inclusion of antimony into prominent organic fluorophores such as rhodamines. This situation is somewhat surprising especially if one considers that many other main group moieties have been successfully incorporated at the rhodamine 10′-position occupied by an oxygen atom in the parent compound.[12–16] Looking at the lower part of the p-block, it is also worth noting that main group rhodamines based on tin,[17] tellurium,[18,19] and bismuth ([**4**]⁺, see Figure 1)[20] are known, making the absence of the antimony analog even more noticeable. As part of our ongoing program in the chemistry of antimony-based fluorescent materials, we now describe the synthesis, structure and properties of an antimony-rhodamine, also referred to as a stibarhodamine.

Based on literature precedents,[21] the starting dibromide **5** was lithiated in THF at –78 °C and allowed to react with PhSbCl₂ (Scheme 1). After warming up the reaction mixture and allowing it to reflux for several hours, all volatile components were removed and the residue was oxidized with *p*-chloranil in the

presence of trifluoroacetic acid (TFAH). The resulting stibarhodamine ([**6**][TFA]) was purified by chromatography and obtained in a 5% yield. The ¹H NMR spectrum of [**6**][TFA] displays the expected resonances including one at 3.37 ppm corresponding to dimethylamino group. The trifluoroacetate anion ([TFA]⁻) was exchanged with [PF₆]⁻ using a large excess of KPF₆ which was added to a methanol solution of [**6**][TFA]. Crude salt [**6**][PF₆] was isolated by evaporation of the mixture and washing with water.

Suitable single crystals of [**6**][PF₆] were obtained from the slow diffusion of diethyl ether into a dichloromethane solution of the salt.† Salt [**6**][PF₆] crystallizes in the triclinic $P\bar{1}$ space group with two cations of [**6**]⁺ and two [PF₆]⁻ anions in the asymmetric unit. The two independent molecules of [**6**]⁺ display very similar structures (Figure 2). The central ring of the rhodamine unit is
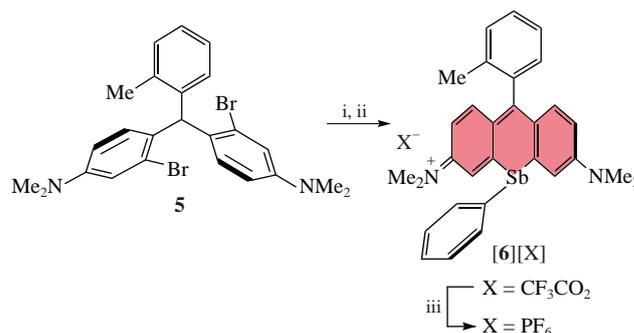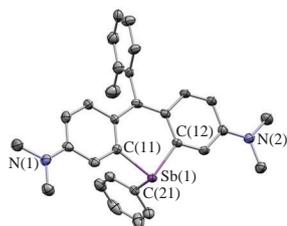

Scheme 1 *Reagents and conditions*: i, BuⁿLi (2 equiv.), THF, –78 °C, then PhSbCl₂, reflux; ii, *p*-chloranil, CH₂Cl₂, 0 °C, 1 h, then column chromatography, Al₂O₃, 0.1% CF₃CO₂H in MeOH/CH₂Cl₂ 95:5 (v/v); iii, KPF₆, MeOH, 25 °C, 2 h.
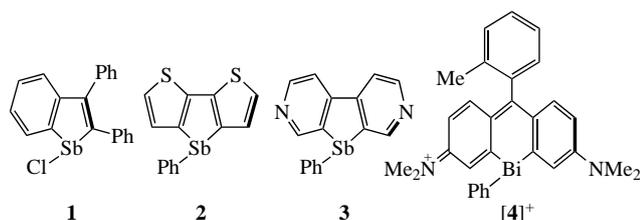
Figure 1 Examples of derivatives **1**–**3** featuring an antimony atom incorporated in a π-conjugated chromophore, and the known cationic bismuth rhodamine analog [**4**]⁺.
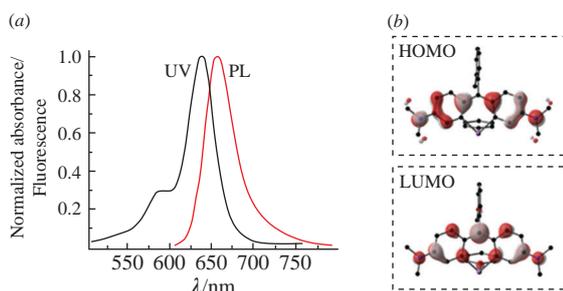
Figure 2 Crystal structure of one of the two independent molecules of [**6**]⁺ in the crystals structure of [**6**][PF₆]. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) for the molecule shown (those for the second independent molecule are provided in brackets): Sb(1)–C(11) 2.130(6) [2.131(5)], Sb(1)–C(12) 2.144(6) [2.133(6)], Sb(1)–C(21) 2.155(6) [2.167(6)], C(11)–Sb(1)–C(12) 92.2(2) [92.0(2)], C(11)–Sb(1)–C(21) 95.9(2) [94.8(2)], C(12)–Sb(1)–C(21) 91.9(2) [93.1(2)].

very slightly puckered with the antimony atom siting 0.24 or 0.25 Å above the plane defined by the five carbon atoms of the central six-member ring. With all C–Sb–C angles approaching the value of 90°, the antimony-bound phenyl group is arranged in a perpendicular fashion with respect to the planar stibarhodamine chromophore. Such an orientation is reminiscent of that observed in the case of compounds **2**,[10] and **3**.[11] The two *N*,*N*-dimethylamino groups adopt a trigonal planar geometry about nitrogen, indicating the expected conjugation of the nitrogen lone pair with the rest of the chromophore (see Figure 1).

The UV-VIS absorption spectrum of [**6**]⁺ displays a maximum absorbance at ~640 nm ($\varepsilon = 1.07 \times 10^5$ dm³ mol⁻¹ cm⁻¹) with a second, less intense, band at ~595 nm ($\varepsilon = 2.8 \times 10^4$ dm³ mol⁻¹ cm⁻¹) [Figure 3(*a*)]. The fluorescence spectrum (excitation wavelength: 595 nm) shows an emission maximum at ~655 nm. These photophysical characteristics are reminiscent of those observed for related main group containing rhodamines such as the bismuth analog [**4**]⁺ (see Figure 1) which is also red light excitable with an absorption maximum at 635 nm and an emission maximum at 658 nm when measured in buffered water at pH 7.4.[20] Given the possibility of heavy atom effect in this structure, we were eager to measure the fluorescence quantum yield of [**6**]⁺. Measurements carried out using cresyl violet as a reference afforded a value of 12%. This quantum yield is significantly higher than that of [**4**]⁺ (3.9%) indicating that heavy atom effects play a less detrimental role in the case of [**6**]⁺.[20] These effects cannot be entirely ruled out since the quantum yield of [**6**]⁺ is lower than those measured for the silicon

analogs.[15] Finally, the analogy between [**6**]⁺ and its bismuth analog [**4**]⁺ is also evident from an inspection of the frontier orbitals [Figure 3(*b*)] which were derived from DFT calculations carried out with the M062X functional and mixed basis set [Sb, cc-pVTZ-PP/ECP28; C/O/H, 6-31g; Cl, 6-311g(d)]. Indeed, both the HOMO and LUMO of [**6**]⁺ are almost analogous in shape and atomic parentage to those of [**4**]⁺.

In summary, we have successfully synthesized and characterized the first antimony rhodamine analog. Our future efforts in the chemistry of this derivative will explore the oxidation of the antimony center and the use of the resulting derivatives for anion sensing.

Online Supplementary Materials
Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.021.

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Figure 3 (*a*) UV-VIS absorption and fluorescence spectrum of [**6**]⁺ in acetonitrile. (*b*) HOMO and LUMO of cation [**6**]⁺.

The X-ray diffraction analysis was carried out on a Bruker APEX II CCD diffractometer (MoKα radiation, $\lambda = 0.71073$ Å, graphite monochromator). Semi-empirical absorption correction was performed using the TWINABS program.[22] The structure was solved by direct methods (SHELXT)[23] and refined by least-squares procedures on F^2 using SHELXL.[24] OLEX2[25] was used to prepare material for publication.

CCDC 2103824 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.