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Synthesis, structure, spectral, electrochemical and sensing properties of 3-amino boron-dipyrromethene and its derivatives

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ABSTRACT

We report the synthesis of 3-amino boron-dipyrromethene (3-amino BODIPY) by treating 3-bromo boron-dipyrromethene (3-bromo BODIPY) initially with sodium azide in acetonitrile followed by triphenylphosphine(PPh_3)/H_2O in tetrahydrofuran in three steps under mild reaction conditions. In this reaction, 3-azido BODIPY which formed in the first step was not isolated but the 3-iminophosphorane BODIPY which formed in the second step was isolated and characterized crystallographically. The 3-amino BODIPY was characterized by various spectroscopic and X-ray analytical techniques. To test the reactivity of amine functionality on BODIPY core, we prepared 1-(*meso*-anisyl BODIPY)-3-phenyl urea/thiourea derivatives under simple reaction conditions. Our studies indicated that 1-(*meso*-anisyl BODIPY)-3-pheny thiourea can act as specific chemodosimetric sensor for Hg^{2+} ion and 1-(*meso*-anisyl BODIPY)-3-phenyl urea as colorimetric and ratiometric sensor for F^- ion.

1. Introduction

Boron-dipyrromethenes (BODIPYs) have gained tremendous recognition as being one of the versatile fluorescent probes along with fluorescein, rhodamine and cyanine dyes in biotechnology field owing to their advantageous spectroscopic properties such as intense absorption and emission in desired regions with high absorption coefficients, fluorescence yields, singlet state life times and considerably high photostability under physiological conditions [1–3]. Besides their extensive applications in biology, these dyes are widely used as cation and anion sensors, drug delivery agents, fluorescent switches, electroluminescent films, laser dyes, light harvesters and sensitizers for solar cells [4–6]. The main reasons for the rapid growth of BODIPYs are their ease of synthesis and potential for derivatization. Several new types of BODIPY dyes have been synthesized recently by using functionalized BODIPYs since these dyes are amenable for functionalization at all positions of core [7–10]. For example, BODIPYs are subjected to halogenation at all positions and the halogenated BODIPYs have been used as building blocks to synthesize different types of new BODIPY derivatives [11–14]. Similarly, the BODIPY systems containing active methyl groups at 3,5-positions were subjected to Knoevengal reaction to synthesize π-extended conjugated BODIPY systems [15]. Ziessel et al. developed a route to introduce ethynyl functional groups in place of fluorides of BODIPY and used these dyes for the synthesis of very interesting light-harvesting systems [16–19]. Recently, BODIPYs containing one or two formyl groups have been synthesized and explored their use for the synthesis of new derivatives and their applications [20–23]. In addition to halogens and formyl groups, the most bio-compatible functional groups are amines and carboxylic acid groups on BODIPY which can be activated and linked to proteins or DNA-derivatives [24–26]. In recent literature, there are several examples in which BODIPY fluorophores were linked to proteins and bio-molecules using amine and carboxylic acid functional groups [27]. However, the functional groups in these cases were not present directly on the BODIPY core but present either on *meso*-aryl group or on long chains attached to the different positions of BODIPY core. A perusal of literature revealed that there are two reports on BODIPY having amino functional group at 3-position. Liras et al. serendipitously synthesized *meso*-free β-pyrrole substituted 3-amino BODIPY along with 3-acetamido BODIPY in one pot reaction during their attempts to synthesize 8-aza-BODIPY [28]. They carried out the reaction by treating 2,4-dimethyl-3-ethylpyrrole with aqueous sodium nitrite

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in the presence of acetic acid/acetic anhydride followed by complexation with $BF_3 \cdot OEt_2$. This reaction resulted in the formation of mixture of two compounds which were separated by column chromatography. However, this method works only for *meso*-free with pyrrole substituted 3-amino BODIPYs and may not be applicable for pyrrole unsubstituted *meso*-aryl BODIPYs. Very recently Talukdar and co-workers prepared *meso*-aryl 3-amino BODIPY by treating 3-bromo BODIPY with 15%NH_3 in CH_3CN/H_2O at room temperature [29]. Herein we report an alternate approach for the synthesis of 3-amino *meso*-anisyl BODIPY **1** (Scheme 1) under mild reaction conditions. The 3-amino BODIPY **1** was used to synthesize 1-(*meso*-anisyl BODIPY)-3-phenyl urea **3** and 1-(*meso*-anisyl BODIPY)-3-phenyl thiourea **5** (Scheme 2) [30] and demonstrated their use for cation and anion sensing applications.

2. Experimental section

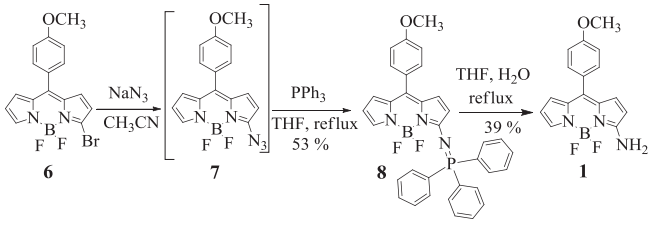
2.1. General

THF and toluene were dried over sodium benzophenone ketyl and chloroform, ethyl-acetate, methanol, acetonitrile were dried under calcium hydride. $BF_3 \cdot OEt_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) obtained from Sigma–Aldrich (USA) were used as obtained. All other chemicals used for the synthesis were reagent grade unless otherwise specified. Column chromatography was performed on silica (60–120 mesh).

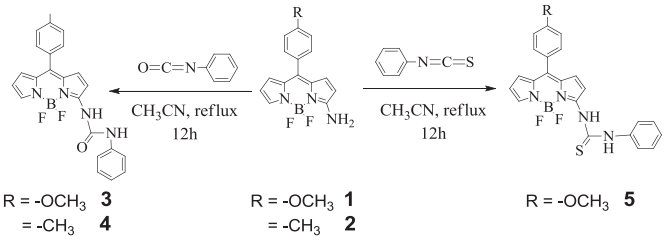
2.2. Instrumentation

All the NMR spectra were recorded in $CDCl_3$ on Bruker 400 MHz instrument using tetramethylsilane ($Si(CH_3)_4$) as internal standard. Absorption and steady state fluorescence spectra were obtained with Perkin–Elmer Lambda-35 and PC1 photon counting spectrofluorometer manufactured by ISS, USA instruments, respectively. The fluorimeter is corrected for the wavelength dependence of the monochromator and the sensitivity of the detector throughout the experiment. Square Wave Voltammetric (SWV) studies were carried out with BAS electrochemical system utilizing the three electrode configuration consisting of a Glassy carbon (working electrode), platinum wire (auxillary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The HR mass spectra were recorded with a Q-Tof micro mass spectrometer. The quantum yields were calculated using Rhodamine 6G as reference ($\Phi = 0.88$ in ethanol, $\lambda_{exc} = 488$ nm) [6]. All Φ are corrected for changes in refractive index. The association constant of the anion complex formed in solution has been estimated by using the standard Benesi–Hildebrand equation, viz.,

$$\frac{1}{I - I_0} = \frac{1}{I_1 - I_0} + \frac{1}{(I_1 - I_0)K_a[A^-]}$$



Scheme 1. Synthesis of 3-amino BODIPY **1**.



Scheme 2. Synthesis of BODIPYs **3**, **4** and **5**.

where I_0 is the intensity of the compounds **3** and **5** before addition of anion, where I is the intensity in the presence of A^-, I_1 is intensity upon saturation with A^-, and K_a is the association constant of the complex formed. The solutions of Bu_4N salts and metal perchlorates were prepared (1×10^{-2} M) in CH_3CN. The solution containing compounds **3** and **5** was placed in quartz cell (1 cm width), and Bu_4NF and $Hg(ClO_4)_2$ solutions were added in an incremental fashion. Their corresponding UV–Vis and fluorescence spectra were recorded at 298 K. In ^1H NMR titration, the spectra were measured on 400 MHz NMR spectrometer. A solution of **3** and **5** in DMSO-d_6 was prepared (5×10^{-3} M), and a 0.4 mL portion of this solution was transferred to a 5-mm NMR tube. A small aliquots of Bu_4NF and $Hg(ClO_4)_2$ in DMSO-d_6 were added in an incremental fashion, and their corresponding spectra were recorded.

2.3. X-ray crystallography

X-ray intensity data measurements of BODIPYs **1**, **4** and **8** were carried out on a SMART APEX II CCD diffractometer with graphite-monochromatized ($MoK_\alpha = 0.71073$ Å) radiation at 297 (2) K. Data were collected with ω scan width of 0.5° at different settings of Φ and 2θ with a frame time of 10 s keeping the sample-to-detector distance fixed at 50 mm. The X-ray data collection was monitored by APEX2 program [31]. The data was corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs. SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2 [32]. All the H-atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. The asymmetric unit contained two molecules of acetonitrile along with one molecule of BODIPY **2**, thus the host to guest ratio is 1:2.

2.4. General method for the synthesis of 4,4-difluoro-4-bora-3a,4a-diaza-3-amino-8-(4-methoxyphenyl)-s-indacene (*1*–*2*)

Samples of 3-bromo BODIPY **6** (0.13 mmol) and sodium azide (0.13 mmol) were dissolved in acetonitrile (10 mL) and reaction mixture was stirred at room temperature for 4 h. Progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure and mixture was washed with CH_2Cl_2 and water to obtain 3-azido BODIPY which without purification proceeded for 3-Amino BODIPY reaction. The crude mixture of 3-azido BODIPY was reacted with triphenylphosphine (0.26 mmol) in THF solvent we got corresponding phosphine intermediate of BODIPY compound **8**, which intern hydrolysis to give corresponding 3-Amino BODIPY **1**. The crude product was subjected to silica gel column chromatography using petether/ethylacetate (75:25) to afford pure compound **1** as stable brown solid in 46% yield.

2.4.1. BODIPY *8*

Yield 54%. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 3.83 (s, 3H; $-OCH_3$), 5.16–5.18 (d, ^3J (H, H) = 4.8 Hz, 1H; py), 6.29–6.30 (m, 1H;