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Synthesis and electronic properties of *meso*-furyl boron dipyrromethenes

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ABSTRACT

Four *meso*-furyl boron-dipyrromethenes (BODIPYs) were synthesized and characterized. The X-ray structures solved for three *meso*-furyl BODIPYs indicated the presence of an intramolecular hydrogen bond between *meso*-furyl 'O' and 'H' of boron-dipyrromethene core resulting in decrease of dihedral angle between the *meso*-furyl group and boron-dipyrromethene core leading to better electronic interaction. However, the hydrogen bonding is absent in solution as confirmed by NMR studies in different solvents. The presence of *meso*-furyl group alters the electronic properties of BODIPY which reflected in the downfield shifts in ^{1}H NMR, bathochromic shifts in absorption and emission bands compared to the *meso*-tolyl BODIPY. The electrochemical studies indicated that the *meso*-furyl BODIPYs are easier to reduce compared to *meso*-tolyl BODIPYs. DFT studies showed that the HOMO-LUMO energy gap is decreased in *meso*-furyl BODIPYs compared to *meso*-tolyl BODIPY which is in agreement with the experimental observations.

1. Introduction

Boron-dipyrromethene fluorophores (BODIPYs) have received much interest in various research fields as labeling reagents, fluorescent switches, chemosensors, light-harvesting systems and dye sensitized solar cells owing to their advantageous photophysical properties such as photostability, high absorption coefficients and high fluorescent quantum yields [1–3]. BODIPY dyes are amenable to modifications, and the properties can be fine-tuned by introduction of suitable substituents at appropriate positions of the boron-dipyrromethene framework. Various approaches have been attempted by different research groups to create new BODIPYs with altered electronic properties that include (1) introduction of electron-donating moieties [4–12], (2) replacement of *meso* C atom by a N atom [13–16], (3) rigidification of rotatable moieties [17–20], (4) extension of the π-conjugation [21–23], and (5) the extension of the π-conjugation by the fusion of aryl moieties [24,25]. Although all the above mentioned approaches have brought substantial changes in the electronic properties of the BODIPY dyes, there are relatively few reports on BODIPY dyes containing five membered heteroaryl moieties such as thienyl, furyl, pyrrole, imidazole etc in their framework [26,6,27,28]. Umezawa et al. [29] reported recently that the furan fused BODIPY dye **I** exhibited significant red-shifts in absorption and fluorescence spectral bands with very high fluorescence yields (Chart 1). Recently, it is reported that the substituents present at the 3,5-positions would be involved in intramolecular hydrogen bonding with fluoride atoms which in turn would alter the electronic properties of boron-dipyrromethene [30]. Cohen and co-workers [30] showed that the two amide substituents at 3,5-positions in BODIPY **II** involved in intramolecular hydrogen bonding with boron-bound fluoride atoms help in rigidifying the chromophore resulting in significant alteration in electronic properties. Dehaen and co-workers [31,32] also showed the presence of intramolecular hydrogen bonding in their 3-anilino BODIPY **III** and 3,5-dianilino BODIPY **IV** compounds. These are few 3-monosubstituted or 3,5-disubstituted BODIPYs where the presence of intramolecular hydrogen-bonding alters the electronic properties of boron-dipyrromethenes. Interestingly, there is no report on BODIPY in which the *meso*-substituent is involved in intramolecular hydrogen-bonding with any atom on boron dipyrromethene core. In this paper, we report the examples of intramolecular hydrogen bonded *meso*-furyl dipyrromethenes **2**–**5** (Chart 2) in which the *meso*-furyl "O" is involved in hydrogen bonding with pyrrole "H" of boron-dipyrromethene core in solid state. While our study was in progress, Churchill and co-workers [33] reported the effect of five membered heteroaryl groups such as furyl, thienyl and selenyl at *meso*-position on structural and electronic properties of BODIPY. Interestingly, they did not discuss about the intramolecular hydrogen bonding present in **2** in solid state. Our study indicated that in *meso*-furyl BODIPYs **2**, **3** and **4**, the presence of intramolecular hydrogen bonding along with the small size of furyl group helps in reducing the dihedral angle between *meso*-furyl group and boron-dipyrromethene unlike *meso*-phenyl boron-dipyrromethene [35] in which the six membered phenyl group is relatively more out-of-plane orientation with the boron-dipyrromethene core. However, the hydrogen bonding is not present in solution for *meso*-furyl BODIPYs **2**–**5**

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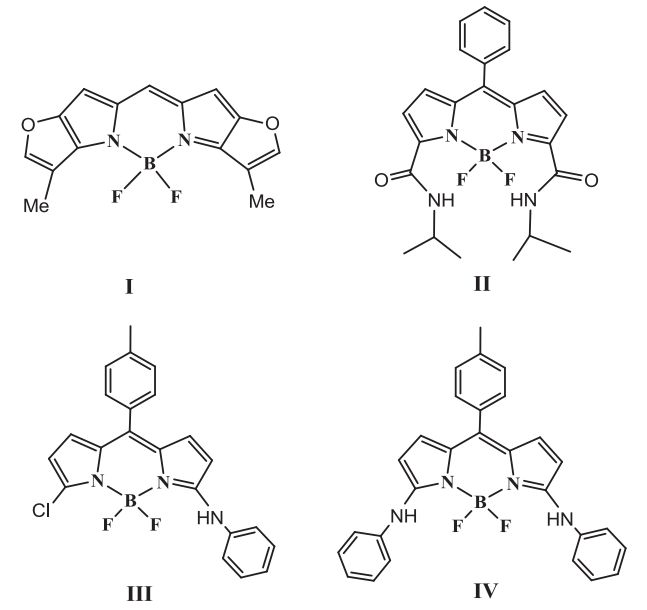

Chart 1. Molecular structures of BODIPYs **I**, **II**, **III** and **IV**.

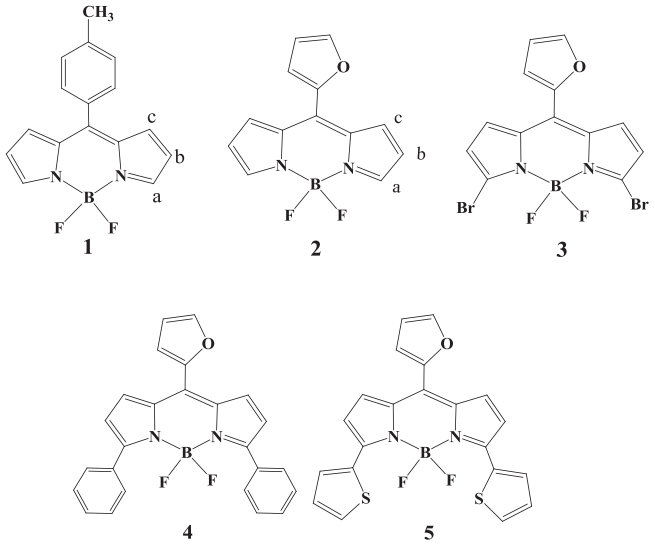

Chart 2. Molecular structures of Boron dipyrromethene dyes **1**–**5**.

unlike Cohen's BODIPY **II** in which strong intramolecular hydrogen bonding is present in solution.

2. Results and discussion

The *meso*-tolyl boron-dipyrromethene **1** was prepared by following the literature procedure [36]. The *meso*-furyl boron-dipyrromethene **2** was prepared [33] as shown in Scheme 1. The required precursor, *meso*-furyl dipyrromethane **6** was prepared in 63% yield by treating one equivalent of furan-2-aldehyde with 25 equivalents of pyrrole in the presence of catalytic amount of $BF_3{\cdot}OEt_2$ at room temperature for 15 min [37]. In the next step, the compound **6** was first oxidized with DDQ in CH_2Cl_2 at room temperature and then treated with triethylamine followed by $BF_3{\cdot}OEt_2$. After standard work-up, the crude compound was purified by silica gel column chromatography and afforded **2** as dark red fluorescent solid in 26% yield. The 3,5-dibromo boron-dipyrromethene **3** was prepared in two steps (Scheme 1) by following our earlier reported method [37]. The compounds **4** and **5** were prepared in decent yields by treating compound **3** with phenyl-2-boronic acid and thienyl-2-boronic acid, respectively in the presence of $Pd(PPh_3)_4$ in water/THF/toluene (1:1:1) at 80 °C. All reactions worked smoothly and compounds **2**–**5** are freely soluble in common organic solvents. The compounds **2**–**5** were confirmed by HR-MS mass spectral analysis and characterized by using various spectroscopic techniques. The compounds **2**, **3** and **4** were also characterized by X-ray crystallography.

The compounds **2**–**5** were characterized in detail by 1D, 2D, ^{19}F and ^{11}B NMR and the selected NMR data for compounds **2**–**5** along with compound **1** are presented in Table 1. The comparison of ^1H NMR spectra of compounds **1** and **2** in selected region is shown in Fig. 1a and ^1H–^1H COSY NMR spectrum recorded for compound **2** is shown in Fig. 1b. The extensive NMR studies including ^1H, ^{13}C, ^{19}F and ^{11}B NMR for all compounds along with ^1H–^1H COSY, HSQC and HMBC NMR for compounds **2** and **4** helped in identifying the protons such as β-pyrrole protons represented as H_a, H_b and H_c and *meso*-furyl protons represented as H_d, H_e and H_f (Supporting information). The introduction of five membered furyl group at *meso*-position in place of six membered aryl group alter the electronic properties of boron-dipyrromethene core which clearly reflected in the downfield shift of certain protons [33]. In ^1H NMR spectrum of **2**, the three pyrrole protons H_a, H_b and H_c were observed as set of three signals at 7.89, 6.58 and 7.47 ppm, respectively and the three furyl protons H_d, H_e and H_f were also observed as set of three signals at 7.83, 6.71 and 7.20 ppm, respectively. A close inspection of Fig. 1a and data in Table 1 indicates that the pyrrole protons H_a and H_b experienced slight shifts in **2** compared to **1**. However, the H_c proton of compound **2** experienced ca. ~0.5 ppm downfield shift relative to compound **1**. Similarly, the corresponding carbons of H_a, H_b and H_c in compound **2** also exhibited downfield shifts compared to **1** and maximum downfield shift was noted for carbon which possess H_c proton as judged by ^{13}C NMR, HSQC and HMBC analysis. (Supporting information) Similar observations were made recently by Churchill and co-workers [33]. These results indicated that the π-delocalization is increased in **2** compared to **1** resulting in downfield shifts of pyrrole protons. This is because the *meso*-furyl group is smaller in compound **2** hence more in plane (as confirmed by X-ray crystallography) with the BODIPY core resulting in the extension of π-electron delocalization of BODIPY core into the *meso*-furyl group. On the other hand, the larger *meso*-tolyl group in compound **1** is more out-of-plane with the BODIPY core thus preventing the extension of *p*-delocalization into *meso*-tolyl group. The significant shift of H_c proton in **2** is because of its proximity to the furan "O" atom which provides more electron rich environment to H_c proton compared to H_a and H_b protons [33]. This is also clearly evident in 3,5-disubstituted *meso*-furyl boron-dipyrromethenes **3**–**5** which showed significant shifts for H_c proton compared to H_a and H_b protons (Table 1). However, the ^{19}F and ^{11}B NMR showed slight downfield shifts for compound **2** compared to compound **1** unlike Cohen's compound **II** which showed 16 ppm downfield shift in ^{19}F NMR due to the presence of strong intramolecular hydrogen bonding between fluoride and amide group present at the 3,5-position of BODIPY. However, the ^1H NMR spectra of compound **2** recorded in different solvents such as deuterated acetone, methanol and acetonitrile indicated that there is no intramolecular hydrogen bonding between *meso*-furyl "O" and the pyrrole H_c (H3 and H7) proton of boron dipyrrin unit in solution (Supporting information). The ^{19}F and ^{11}B NMR of compounds **3**, **4** and **5** showed significant downfield shifts compared to **2** which is due to presence of substituents at 3,5-positions such as bromo, phenyl and thienyl groups, respectively.