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Asymmetrical aza-boron-dipyridomethene derivatives with large Stokes shifts: synthesis and spectroscopic properties

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ABSTRACT

The synthesis and characterization of three asymmetrical aza-boron-dipyridomethene derivatives **3–5** are reported. Single crystal X-ray structures are described and the spectroscopic properties of the dyes have been investigated in depth based on an analysis of the optical spectroscopy and the results of theoretical calculations. In contrast with what is normally observed with symmetrical aza-boron-dipyridomethene dyes, very large apparent Stokes shifts are observed for **3–5** and the emission spectra are strongly solvent dependent. DFT calculations have been carried out to explore the structure/property relationships and substituent effects.

Introduction

There is a continuing strong research focus on the synthesis of novel fluorescent chromophores, due to their wide range of possible applications, such as their use as photosensitizers in photodynamic therapy, as molecular probes, and their incorporation in various molecular materials.[1] In recent years, boron dipyrromethenes (BODIPYs), have emerged as one of the most important types of chromophore in this regard and are probably now the subject of the largest number of investigations within this field. BODIPY dyes have many favorable properties such as: (i) their chemical versatility, (ii) their strong ground-state absorption and intense fluorescent emission, (iii) their high molar extinction coefficients and fluorescence quantum yield, and (iv) their excellent photostability.[2] Recently, the effects of modifying the BODIPY core by forming boron-dipyridomethenes and aza-boron-dipyridomethenes have been investigated (Fig. 1).[3] These compounds may find applications as laser dyes, since they display moderate emission efficiency both in solution and in the solid state, and have relatively high photostabilities compared to other blue-emitting dyes.[3] However, small Stokes shift (below 10 nm) has been observed for most BODIPY dyes. The synthesis of low symmetry BODIPY analogues provides an opportunity to make the potential energy surfaces of the ground and excited states more distinct and hence to form dyes with larger apparent Stokes shifts.[4] Herein, we describe the synthesis and optical properties of a series of asymmetric boron(III) aza-dipyridomethene derivatives. DFT calculations have been carried out to explore the effect of the substituent.

Results and discussion

Synthesis

The preparation of asymmetric aza-boron-dipyridomethenes **3–5** can readily be achieved through a three-step reaction (Scheme 1). The precursor, **1**, was prepared in high yield by heating equivalent amounts of 2-aminopyridine and 2,5-dibromopyridine.[5] The difluoroboron complexes were then obtained by reacting **1** with $BF_3{\cdot}OEt_2$ under basic conditions in CH_2Cl_2 at room temperature.[6] Asymmetric aza-boron-dipyridomethenes were then synthesized from bromo-aza-boron-dipyridomethene through reactions with phenylboronic acid, phenylacetylene, and phenylethylene, respectively, by using the Suzuki–Miyaura, Hagihara–Sonogashira, and Heck cross-coupling protocols.[7] These dyes were characterized by ^1H and ^{13}C NMR spectroscopy and high-resolution MALDI MS. Molecular ion peaks were observed at 296.1168 (calcd for $[M+H]^+ = 296.1168$) for **3**, 320.1178 (calcd for $[M+H]^+ = 320.1168$) for **4**, and 322.1330 (calcd for $[M+H]^+ = 322.1325$) for **5**. The isotopic patterns were in accordance with the target structures.

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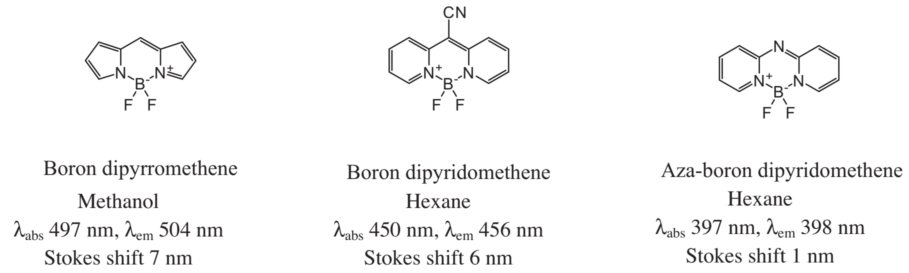
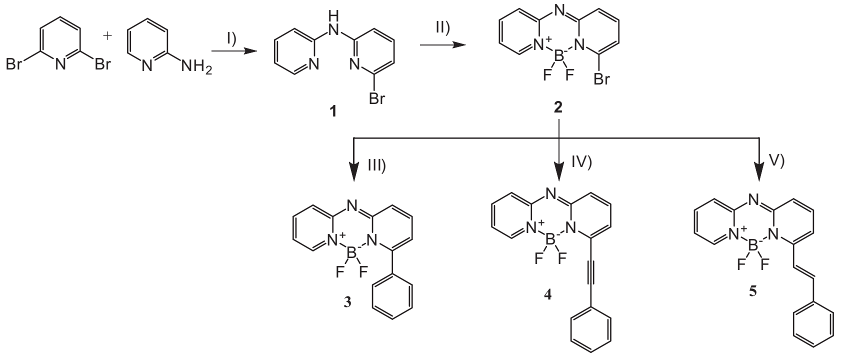


Figure 1. Stuctures and spectroscopic properties of boron dipyrromethene, boron dipyridomethene, and aza-boron dipyridomethene.



Scheme 1. Synthetic procedures and structures of aza-boron-dipyridomethene derivatives **3**–**5**. (I) $(CH_3)_3COK$, benzene, N_2, reflux; (II) $BF_3{\cdot}Et_2O$, NEt_3/toluene, N_2, reflux; (III) $C_6H_5B(OH)_2$, $(PPh_3)_4Pd(0)$, Na_2CO_3, THF, N_2, reflux; (IV) $C_6H_5C{\equiv}CH$, $PdCl_2(PPh_3)_2$, CuI, PPh_3, NEt_3/toluene, N_2, reflux; (V) $C_6H_5CH{=}CH_2$, Pd $(OAc)_2$, NEt_3/DMF, N_2, reflux.

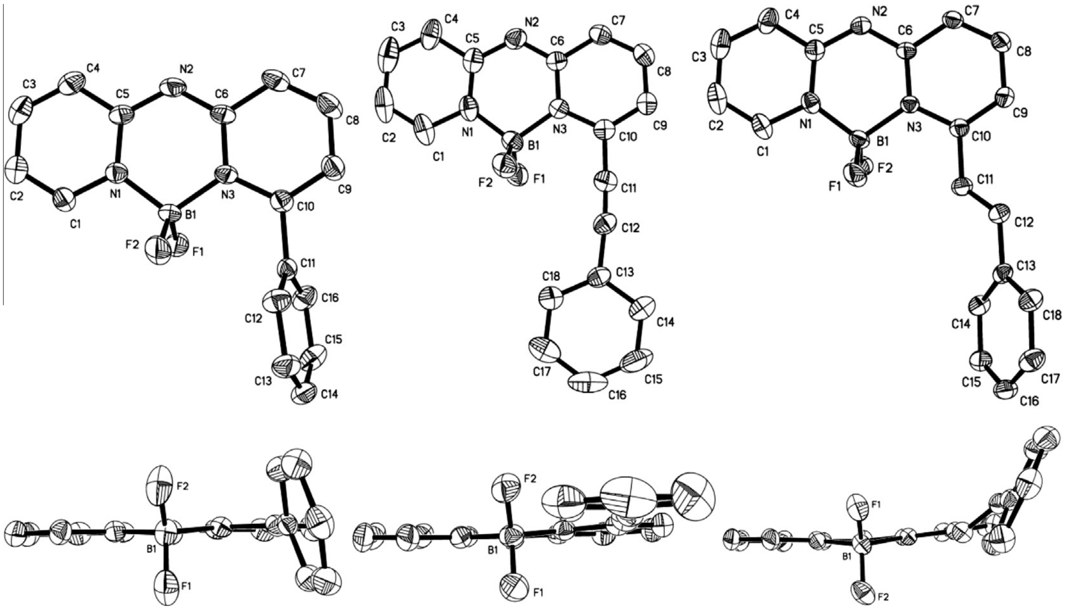


Figure 2. Front (Left) and side (Right) ORTEP views of the molecular structure of **3**–**5** with the thermal ellipsoids set at 30% probability. Selected bond lengths [Å], for **3**: B–N1 1.55(10), B–N3 1.56(11), B–F1 1.38(11), B–F2 1.37(10), C10–C11 1.52(9); for **4**: B1–N1 1.542(4), B1–N3 1.557(3), B–F1 1.382(3), B–F2 1.379(3), C11–C12 1.163(3); for **5**: B1–N1 1.547(2), B1–N3 1.561(2), B–F1 1.377(19), B–F2 1.385(2), C11–C12 1.323(2).

X-ray crystal structures

Suitable single crystals of **3**–**5** were obtained for X-ray structure analysis by slow diffusion of hexane into solutions of **3**–**5** in dichloromethane. In each structure, the boron atom is coordinated by two nitrogen atoms and two fluorine atoms in a tetrahedral geometry. The aza-boron-dipyridomethene structures are highly planar with average root-mean-square (rms) deviations of 0.168 Å for **3**, 0.0485 Å for **4**, and 0.0809 Å for **5**. The planar structure is similar to that observed previously for BODIPY dyes.[8] The dihedral angles between the indacene plane and the phenyl rings are 76.7° for **3**, 1.2° for **4**, and 62.4° for **5** (Fig. 2). The planarity of the π-system plays a key role in shaping the spectroscopic properties of aza-boron-dipyridomethenes.[9] The molecules exhibit partially overlapping head-to-head or head-to-tail π–π stacking interactions (Fig. 3).