



Synthesis of phenanthroimidazole-based four coordinate organoboron compounds

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ABSTRACT

The synthesis of N,C-coordinated organoboron compounds (**B1–B4**) based on phenanthroimidazole described. All the compounds were characterized by various spectroscopic techniques. Single crystal X-ray diffraction analysis of the compounds **B1** and **B3** revealed that the vicinity around the boron atom adopts tetrahedral geometry. Except compound **B4**, other organoboron compounds (**B1–B3**) does not show solvatochromism. All our newly synthesized organoboron compounds exhibited moderate to good solution state quantum yields (0.07–0.88) and moderate solid state quantum yields.

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1. Introduction

Organoboron compounds have drawn much attention with their fascinating structural and attractive photophysical properties [1]. Luminescent four coordinated boron compounds have been utilised in various optoelectronic materials owing to their better stability over tri coordinated boron compounds [2]. Among the four coordinated boron compounds, N,N coordinated boron dipyrromethene (BODIPY) are highly fluorescent in solution and studied extensively over other four coordinated boron compounds. Recently, new chelating groups such as N,O; N,C; C,C; C,O and O,O for the boron have resulted new and interesting four-coordinated boron compounds [3]. These four coordinated boron compounds have been employed as materials for sensors, organic light emitting diodes, and solar cells [4]. Recently it has been observed that some of the four coordinated N,C-chelated boron compounds have exhibited unusual photoisomerization [5].

Imidazoles are nitrogen containing heterocyclic compounds found applications in diverse fields [6]. In recent years, considerable efforts have been paid to the development of imidazole based luminescent materials due to their ease of synthesis and their

potential application in the field of organic light emitting diodes (OLEDs) [7,8]. For instance, 9,10-phenanthro based imidazoles studied as electroluminescent materials [8]. Incorporation of boron is an effective method to tune the conjugation of imidazole molecules. Taking advantage of this approach, we recently synthesized boron embedded imidazoles and studied their photophysical properties [9]. As phenanthroimidazoles possess large Stokes shifts and solid state emissive property, we extended our investigation to make phenanthroimidazole based N,C-chelated boron complexes. In this article, we report synthesis of four new phenanthroimidazole based four coordinated organoboron complexes and their photophysical properties.

2. Experimental section

All reagents were used as received from Spectrochem, Alfa-aeasar and Sigma-Aldrich unless otherwise noted. The 4-(9H-carbazol-9-yl)benzaldehyde and 4-(diphenylamino)benzaldehyde were prepared according to known literature procedures [10]. Electrophilic aromatic borylation reaction has been carried out adopting a similar procedure reported in the literature [3e]. All solvents were purchased from Spectrochem India. Dichloromethane and toluene were dried using calcium hydride and Na/benzophenone respectively. All experiments were monitored by analytical thin layer chromatography (TLC) under

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hand held UV lamp at 254 nm. All ^1H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR were recorded at room temperature on Bruker ARX 400 spectrometer. Residual protonated solvents were used as internal standards for ^1H and ^{13}C NMR. ^{11}B NMR spectra were referenced externally to $\text{BF}_3\cdot\text{Et}_2\text{O}$ in CDCl_3 ($\delta = 0$ ppm). ESI mass spectra were recorded with Bruker micro TOF-QII mass spectrometer. UV–Visible spectra were recorded on Perkin-Elmer Lambda 750 UV–Visible spectrometer. The fluorescence spectra were recorded using Edinburgh FS5 spectrofluorometer. Absolute fluorescence quantum yields in solution and solid state were measured by integrating sphere method using Edinburgh FS5 spectrofluorometer. Single crystals of compound **B1** and **B3** were grown from dichloromethane-ethanol solvent mixture. Single crystal X-ray diffraction data were collected on Bruker APEX-II CCD diffractometer at 100 K using Mo-K α radiation (0.71073 Å). The structures were solved by direct methods using shelXT program and refined with least squares minimization with shelXL [11] using Olex2. The disordered carbon atoms (for **B3**) (C44 & C45) of the alkyl chain were treated and refined with two independent positions. The H atoms were placed at calculated positions (except hydrogens attached to C44 & C45 of **B3**) were refined as riding atoms. Crystallographic data for the structure **B1** and **B3** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1851933-1851934. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

2.1. General procedure for the synthesis of compounds **L1-L4**

In a round bottom flask 9,10-phenanthrenequinone, 4-hexylaniline, arylaldehyde and ammonium acetate were taken. Acetic acid (150 mL) used as a solvent and refluxed for 24 h under nitrogen atmosphere. The reaction mixture was poured into water (200 mL) and extracted with dichloromethane (2 × 200 mL). The combined organic layers were washed with aqueous NaHCO_3 and brine solution, dried over Na_2SO_4 and concentrated using rotavapor. The crude reaction mixture was purified by 100–200 silica gel column chromatography using *n*-hexane/dichloromethane mixture as a mobile phase.

2.1.1. Synthesis of compound **L1**

The quantities involved are as follows: 9,10-Phenanthrenequinone (3.00 g, 14.41 mmol), 4-hexylaniline (3.61 mL, 18.73 mmol), benzaldehyde (1.53 g, 14.41 mmol), and ammonium acetate (5.55 g, 72.05 mmol). Yield: 4.72 g, (72%). Mp: 125 °C. ^1H NMR (400 MHz, CDCl_3): δ 9.04 (d, $J = 7.8$ Hz, 1H), 8.78 (dd, $J = 8, 8.3$ Hz, 2H), 7.84 (t, $J = 7.3$ Hz, 1H), 7.71 (t, $J = 6.8$ Hz, 3H), 7.56–7.53 (m, 1H), 7.42–7.31 (m, 9H), 2.83 (t, $J = 7.4$ Hz, 2H), 1.83–1.76 (m, 2H), 1.46 (brs, 6H), 1.05 (t, $J = 8$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 150.9, 144.7, 137.3, 136.1, 130.6, 130.0, 129.4, 129.2, 128.7, 128.7, 128.2, 128.2, 128.1, 127.3, 127.2, 126.2, 125.5, 124.8, 124.0, 123.1, 123.1, 122.8, 120.8, 35.6, 31.7, 31.0, 28.7, 22.6, 14.1 ppm. HR-MS (ESI). Calcd. for $\text{C}_{33}\text{H}_{31}\text{N}_2$ ($[\text{M} + \text{H}]^+$): 455.2482, found: 455.2498.

2.1.2. Synthesis of compound **L2**

The quantities involved are as follows: 9,10-Phenanthrenequinone (3.00 g, 14.41 mmol), 4-hexylaniline (3.61 mL, 18.73 mmol), 1-naphthaldehyde (2.25 g, 14.41 mmol), and ammonium acetate (5.55 g, 72.05 mmol). Yield: 3.70 g, (51%). Mp: 174 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.91 (d, $J = 8.0$ Hz, 1H), 8.82 (d, $J = 8.0$ Hz, 1H), 8.76 (d, $J = 8.0$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 2H), 7.75 (t, $J = 7.1$ Hz, 1H), 7.68 (t, $J = 8$ Hz, 1H), 7.57–7.53 (m, 1H), 7.51–7.44 (m, 3H), 7.36 (t, $J = 8$ Hz, 1H), 7.31–7.23

(m, 4H), 7.14 (d, $J = 8.1$ Hz, 2H), 2.61 (t, $J = 8.0$ Hz, 2H), 1.63–1.56 (m, 2H), 1.31–1.24 (m, 6H), 0.89 (t, $J = 6.8$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 150.5, 144.2, 137.2, 135.4, 133.5, 133.2, 129.6, 129.5, 129.5, 129.3, 128.4, 128.2, 128.1, 127.6, 127.4, 127.3, 126.8, 126.3, 126.1, 125.6, 125.0, 124.5, 124.1, 123.2, 123.1, 122.9, 121.1, 35.5, 31.6, 30.8, 28.6, 22.6, 14.2 ppm. HR-MS (ESI): Calcd. for $\text{C}_{37}\text{H}_{33}\text{N}_2$ ($[\text{M} + \text{H}]^+$): 505.2638, found: 505.2667.

2.1.3. Synthesis of compound **L3**

The quantities involved are as follows: 9,10-Phenanthrenequinone (3.00 g, 14.41 mmol), 4-hexylaniline (3.61 mL, 18.73 mmol), 4-(9H-carbazol-9-yl) benzaldehyde (3.90 g, 14.41 mmol), and ammonium acetate (5.55 g, 72.05 mmol). Yield: 5.53 g, (62%). Mp: 211 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.96 (bs, 1H), 8.80 (d, $J = 8.0$ Hz, 1H), 8.73 (d, $J = 8.0$ Hz, 1H), 8.14 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 8.0$ Hz, 2H), 7.78 (t, $J = 8.0$ Hz, 1H), 7.69 (t, $J = 7.3$ Hz, 1H), 7.57–7.46 (m, 7H), 7.43–7.39 (m, 3H), 7.32–7.24 (m, 5H), 2.83 (t, $J = 8.0$ Hz, 2H), 1.80–1.73 (m, 2H), 1.42–1.31 (m, 6H), 0.88 (t, $J = 8.0$ Hz, 3H) ppm. ^{13}C NMR (176 MHz, CDCl_3): δ 150.1, 145.3, 140.6, 138.2, 137.6, 136.2, 130.8, 130.4, 129.7, 129.5, 128.9, 128.5, 128.4, 127.5, 127.4, 126.6, 126.4, 126.1, 125.8, 125.1, 124.2, 123.7, 123.3, 122.8, 121.1, 120.5, 120.3, 109.9, 35.8, 31.7, 31.3, 28.8, 22.7, 14.2 ppm. HR-MS (ESI): Calcd. for $\text{C}_{45}\text{H}_{38}\text{N}_3$ ($[\text{M} + \text{H}]^+$): 620.3060, found: 620.3062.

2.1.4. Synthesis of compound **L4**

The quantities involved are as follows: 9,10-Phenanthrenequinone (3.00 g, 14.41 mmol), 4-hexylaniline (3.61 mL, 18.73 mmol), 4-(diphenylamino) benzaldehyde (3.93 g, 14.41 mmol), and ammonium acetate (5.55 g, 72.05 mmol). Yield: 4.75 g, (53%). Mp: 213 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.92 (bs, 1H), 8.76 (d, $J = 8.0$ Hz, 1H), 8.70 (d, $J = 8.0$ Hz, 1H), 7.74 (t, $J = 8.0$ Hz, 1H), 7.65 (t, $J = 8.0$ Hz, 1H), 7.52–7.39 (m, 7H), 7.28–7.23 (m, 6H), 7.17 (d, $J = 8.0$ Hz, 1H), 7.10–7.03 (m, 5H), 6.94 (d, $J = 8.8$ Hz, 2H), 2.80 (t, $J = 7.6$ Hz, 2H), 1.76–1.70 (m, 2H), 1.38–1.32 (m, 6H), 0.90 (t, $J = 7.0$ Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 150.9, 148.4, 147.4, 144.9, 137.3, 136.5, 130.2, 130.1, 129.4, 129.2, 128.9, 128.3, 128.2, 127.3, 126.3, 125.5, 125.1, 124.7, 124.1, 123.5, 123.3, 123.2, 122.9, 122.1, 120.9, 35.8, 31.8, 31.2, 28.8, 22.7, 14.2 ppm. HR-MS (ESI): Calcd. for $\text{C}_{45}\text{H}_{40}\text{N}_3$ ($[\text{M} + \text{H}]^+$): 622.3217, found: 622.3209.

3. General procedure for the synthesis of compounds **B1-B4**

Oven dried two neck round bottom flask was charged with compound (**L1-L4**) and dichloromethane (80 mL) under argon atmosphere. To this solution diisopropylethylamine ($^i\text{Pr}_2\text{NEt}$) was added at 0 °C and stirred. After 10 min, BBr_3 (1.0 M in dichloromethane) was added slowly at the same temperature and allowed to warm to room temperature. After being stirred at room temperature for 24 h, saturated K_2CO_3 aqueous solution was added to the reaction mixture and extracted with CH_2Cl_2 (2 × 150 mL). The combined organic layers were washed with water, dried over MgSO_4 and concentrated using rotary evaporator to afford the crude dibromo boron compound. Without further purification (it should be noted that trace amount of $\text{RB}(\text{OH})_2$ species might have formed during workup), the dried crude product along with toluene (80 mL) was taken in a round bottom flask in an argon atmosphere. To this stirred solution, AlMe_3 (2.0 M in toluene) was added at room temperature. After being stirred for half an hour, the reaction was quenched by adding water (20 mL) and extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were washed with water, and brine. The organic layer was dried over Na_2SO_4 and concentrated using rotavap. The crude product was purified by silica gel column chromatography using *n*-hexane/dichloromethane mixture as a mobile phase.

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