



# Effect of the change of heteroatom on phenyl capped benzazole: Photophysical and electrochemical properties from the structural viewpoint



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## ARTICLE INFO

### Keywords:

Donor-acceptor-donor  
Benzazole  
Solid-state fluorescence  
Oligomer  
Quantum yield

## ABSTRACT

Donor-acceptor-donor type phenyl capped benzazoles were synthesized and their photophysical properties were studied. By changing the heteroatom (N, O, S and Se) of central acceptor benzazole unit, the emission color was varied from blue to green. Phenyl capped benzotriazole (1) and benzoaxadiazole (2) were characterized by single crystal X-ray crystallography. The absolute solid state fluorescence quantum yields of these compounds were obtained in the range of 0.05–0.93 by a calibrated integrating sphere method. High solid state quantum yield can be attributed to the non-planarity and absence of strong intermolecular interactions in the solid state. Except phenyl capped benzotriazole (1), all compounds showed reversible reduction peak in cyclic voltammetry experiments which reflects the considerable n-type nature.

## 1. Introduction

Designing and synthesis of organic fluorophores with high quantum efficiency have attracted considerable interest because of their potential applications in optoelectronics as materials for organic light-emitting diodes (OLEDs) [1], full-color flat panel displays [2], organic light-emitting field-effect transistors (OLEFETs) [3] and solid-state laser [4]. Highly efficient white organic light-emitting diodes (WOLEDs) are good alternative for future energy-saving lighting sources. Importantly, white light can be generated from OLEDs by judiciously combining primary-color emitters (red-green-blue, R-G-B). Conjugated polymeric material such as poly(phenylenevinylene) (PPV) [5], poly(2,7-(9,9'-dialkyl) fluorenes) (PFs) [6], and poly(*p*-phenylene) (PPP) [7] are established as good materials for organic luminescent devices and has been extensively studied during the last few years. Working with small molecules has some advantages compared to their polymeric counterparts, because of their relatively simple synthesis and purification, well-defined structures, and better batch-to-batch reproducibility.

Optical and electronic properties of the conjugated molecules can be tuned by tuning highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap. One of the important strategy to tune the HOMO-LUMO gap (or band gap) of the conjugated system by structural modification and it can be achieved either by the introduction of alternate donor and acceptor units (D-A) in the conjugation [8,9], or by atomistic approach. By structural modification of

spirobifluorene, silole, indole, pyrene, and anthracene, high quantum efficiency can be achieved in different color region [10]. Proper selection of donor and acceptor in D-A conjugated system can tune the HOMO-LUMO gap relying on the moderate to excellent intramolecular charge transfer (ICT) interaction between donor and acceptor units. Altering heteroatom in either donor or acceptor unit of a D-A polymer or oligomers, is an important strategy in order to tune the HOMO-LUMO gap (or band gap) [11]. Electron-withdrawing imine group (C=N) acts as acceptor-type building blocks of the three most popular benzazoles; [2,1,3]benzothiadiazole (BDT) [12], [2,1,3]benzoselenadiazole (BDS) [11b,13], and [2,1,3]benzotriazole (BTaz) [14]. Recently oxygen analogue [2,1,3]benzoaxadiazole (BDO) has been explored as a strong electron acceptor in the conjugated systems [15].

Due to the several quenching processes in the solid state the fluorescence efficiency of organic conjugated compounds generally decreases, although many of them have very high emission intensity in the solution phase. Organic fluorophores with high quantum yield in solid state are very few especially those exhibiting strong solid state emission in the blue region because of their intrinsic characteristics such as wide energy gap and low lying HOMO energy levels. Therefore, designing conjugated molecules with pure blue emission is difficult [16]. Here we introduced donor-acceptor-donor type phenyl capped benzazoles of which 1–3 showed high quantum efficiency in both solution and solid state. Upon changing the heteroatom (N, O, S and Se) of central benzazole acceptor unit, the emission color varies from blue to green

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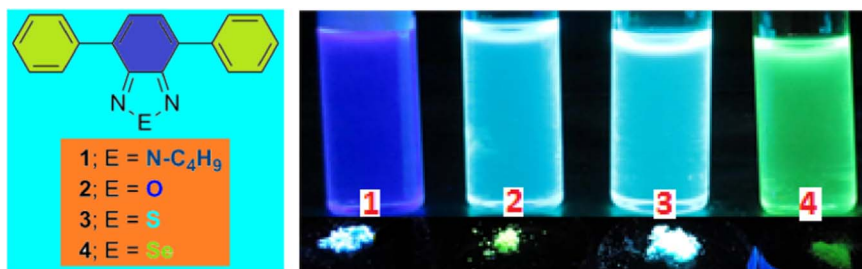


Fig. 1. Photograph of 1–4 in toluene solution and solid state under 365 nm UV-lamp.

(Fig. 1). Some of the recent papers [17] studied the effect of variation of donor group on optical and structural properties [18]. In this report we tried to address the issue by varying only one heteroatom over the acceptor moiety.

## 2. Experimental section

### 2.1. General method

All reactions were performed under nitrogen atmosphere to maintain the inert condition. Dry toluene and THF were distilled from sodium/benzophenone prior to use. Phenylboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub> and tetrabutylammonium perchlorate (TBAPC) were purchased from Aldrich and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the compounds were recorded on Jeol ECS 400 MHz spectrometer with CDCl<sub>3</sub> as the solvent, and chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to tetramethylsilane as the internal standard. Electrochemical studies were carried out with a Princeton Applied Research 263A potentiostat using platinum (Pt) disk electrode as the working electrode, a platinum wire as counter electrode and an AgCl-coated Ag wire as the reference electrode. Nonaqueous Ag/AgCl wire was prepared by dipping silver wire in a solution of FeCl<sub>3</sub> and HCl. Pt disk electrodes were polished with alumina and washed with water, and acetone and were dried with nitrogen gas before use to remove any incipient oxygen.

#### 2.1.1. Synthesis of compound 5

A 250 mL two necked round bottomed flask fitted with a reflux condenser was charged with 20 mL of aqueous HBr (48%) and N-butylated benzotriazole (4.8 g, 22 mmol). The reaction mixture was stirred and refluxed at 100 °C for 1 h. Next bromine (7.8 g, 48 mmol) was added and the mixture was stirred at 135 °C for 4 h. After cooling to rt an aqueous solution of NaHCO<sub>3</sub> was added and the mixture was extracted with DCM. The organic layer was collected and dried under vacuum to get the crude product. The crude product was purified by flash column chromatography with hexane as the solvent. The pure product 5 was obtained as a yellow oil (yield 70%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 0.95 (t, *J* = 15.3 Hz, 3H), 1.38–1.44 (m, 2H), 2.10–2.14 (m, 2H), 4.78 (t, *J* = 14.2 Hz, 2H), 7.43 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 13.6, 19.9, 32.3, 57.3, 110.1, 129.6, 143.8; HRMS (ESI) *m/z* Calcd for C<sub>10</sub>H<sub>11</sub>N<sub>3</sub>Br<sub>2</sub> [M<sup>+</sup>] 330.9320, found 330.9312.

#### 2.1.2. General synthetic procedure for Suzuki coupling

In a 50 mL 3-necked round bottom flask 2,7-dibromobenzazole (1 mmol), potassium carbonate (420 mg) and 2-phenylboronic acid (2.5 mmol) were mixed in water (5 mL) and THF (10 mL). The reaction mixture was purged with nitrogen for 20 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (50 mg) was added to the reaction mixture. The reaction mixture was stirred for overnight at 80 °C. Solvent was removed at reduced pressure and crude product was directly loaded on column chromatography (60–120 mesh) for purification.

**2.1.2.1. Compound 1.** Colorless solid, m.p.: 90 °C; Yield: 85%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 0.99 (t, *J* = 14.5 Hz, 3H), 1.42–1.46 (m,

2H), 2.14–2.17 (m, 2H), 4.80 (t, *J* = 14.5 Hz, 2H), 7.40–7.44 (m, 2H), 7.53 (t, *J* = 16 Hz, 4H), 7.64 (s, 2H), 8.06 (d, *J* = 8.4 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 13.7, 20.0, 32.4, 56.7, 124.7, 128.1, 128.7, 128.8, 130.4, 137.6, 143.6; HRMS (ESI) *m/z* Calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub> [M<sup>+</sup>] 327.1735, found 327.1750.

**2.1.2.2. Compound 2.** Yellow colored solid, m.p.: 170 °C; Yield: 65%; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 7.48–7.49 (m, 2H), 7.55 (t, *J* = 14.5 Hz, 4H), 7.69 (s, 2H), 8.06 (d, *J* = 7.6 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 128.5, 128.8, 129.0, 129.1, 129.3, 135.4, 149.4; HRMS (ESI) *m/z* Calcd for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O [M<sup>+</sup>] 272.0950, found 272.0940.

### 2.2. Crystal structure solution and refinement

Crystal data of 1 was collected at rt on a Bruker APEX-II CCD device with graphite monochromated Mo K $\alpha$  radiation (0.71073 Å). Data processing program (SAINT) was used to process the intensity data. Absorption correction was applied using SADABS [19]. Crystal structure was determined with SHELXS-97 and the data was refined using SHELXL-97 [20]. The crystal data of 2 was recorded on a SuperNova, Dual, Mo at zero, Eos device using Mo K $\alpha$  radiation (0.71073 Å). Atomic coordinates, isotropic and anisotropic displacement parameters of all non hydrogen atoms of the compound was refined using Olex2 [21]. Crystal structure of 2 was determined using ShelXT and for refinement ShelXL [22] was used. Figures of 1 and 2 were produced by the means of X-seed version 2.0.

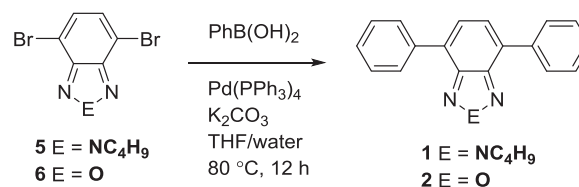
## 3. Results and discussion

### 3.1. Synthesis

To study the effect of heteroatom (N, O, S and Se) on the photo-physical and structural properties of phenyl capped benzazoles, a series of compounds, 1–4 were synthesized. Compound 1 and 2 were synthesized from compounds 5 and 6, respectively by Pd(0) catalyzed Suzuki coupling with phenylboronic acid in THF/water in high yields (Scheme 1) [14,23]. 2,7-Dibromobenzoxadiazole [15c], compound 3 [24] and 4 [17b] were synthesized by the reported procedure.

### 3.2. Optical properties

The absorption spectra of compounds 1–4 were recorded in benzene solutions (Fig. 2a). The absorption spectra of 3 and 4 showed two absorption bands; higher energy bands at 318 and 343 nm for  $\pi \rightarrow \pi^*$



Scheme 1. Synthesis of phenyl capped benzotriazole 1 and benzoxadiazole 2.

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