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Nucleophilic addition of CN^- ion to —C=N bond of aza-BODIPY leading to turn-on fluorescence sensor

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ABSTRACT

We report for the first time that 1,3,5,7-tetraaryl aza-BODIPYs can be used as an exclusive chemodosimetric, colorimetric and turn-on fluorescence sensor for CN^- ion. We demonstrated that CN^- ion attacks the —C=N bond of aza-BODIPY core via nucleophilic addition reaction and the resultant compound show significant alteration in electronic properties because of disruption of conjugation as verified by spectral and electrochemical studies. Specially, the aza-BODIPY which exhibit moderate fluorescence in NIR region changes to fluorescent compound which emits strongly in the visible region and thus the 1,3,5,7-tetraaryl aza-BODIPY can be used as turn-on fluorescence sensor for CN^- ion. We also used 2-formyl-1,3,5,7-tetraaryl aza-BODIPY which has both —C=N and —CHO active sites for nucleophilic attack by CN^- ion and showed that CN^- ion prefer —C=N over —CHO as demonstrated here.

1. Introduction

Aza-BODIPYs (8-aza-boradiazaindacenes) resulted from the replacement of *meso*-carbon of BODIPY with nitrogen exhibit ~100 nm bathochromic shift in absorption band in the region of ~600–800 nm when compared to BODIPY [1–5]. Thus, aza-BODIPY exhibits all the valuable characteristic like BODIPYs such as narrow absorption and emission bands with high absorption coefficients and quantum yields, etc. but absorbs and emits in visible–NIR region which is important for their potential use in the areas of photodynamic therapy, sensors and photosynthetic model systems capable of harvesting light energy [6–10]. Interestingly, BODIPYs have been used extensively for sensing various types of cations and anions. Surprisingly, the reports on anion/cation sensing behaviour of aza-BODIPYs are very few which is due to their relatively difficult synthetic procedures and unavailability of appropriate aza-BODIPY derivatives [11–15]. However, unlike BODIPY, the aza-BODIPY has active *meso* —C=N bond which is prone for nucleophilic attack by anions and thus the aza-BODIPYs can be used as chemical reaction based sensors for anions. With this assumption in mind, we tested the anion sensing behaviour of aza-BODIPY with various anions. Our study indicated that the aza-BODIPY can be used as selective turn-on fluorescence sensor for CN^- ion. Due to the exceptional nucleophilicity of CN^- ion, the CN^- ion attacks the —C=N bond of 1,3,5,7-tetraaryl aza-BODIPY **1** and converts to new derivative **2** (Scheme 1) which resulted in clear change in colour from blue to highly fluorescent yellow with significant hypsochromic shift (~100 nm) and enhancement of fluorescence band. Thus, in this paper, we report the 1,3,5,7-tetratolyl aza-BODIPY **1** as a specific chemodosimetric turn-on fluorescence sensor for CN^- ion as verified by spectral and electrochemical techniques. Cyanide ion causes a major health rise to humans due to its high toxicity. Cyanide is a potent inhibitor for metallo-enzymes and non-metalloenzymes which leads to diseases in the vascular, cardiac, visual, endocrine, central nervous and metabolic systems [16]; hence, the development of fast turn-on fluorescence sensors are highly desirable. There are several literature reports on colorimetric probes for cyanide ion but colorimetric as well as turn-on fluorimetric probes for cyanide ion are less common [17–26]. Furthermore, there is no precedence in literature that —C=N bond of aza-BODIPY core can be used for nucleophilic addition reaction. In this paper, we demonstrate for the first time that the —C=N bond of aza-BODIPY core can be used for nucleophilic addition by cyanide ion and the resulted compound **2** exhibit altered electronic properties which can be monitored by following the changes in colour, absorption, electrochemical, fluorescence, mass and NMR properties and thus the 1,3,5,7-tetraaryl

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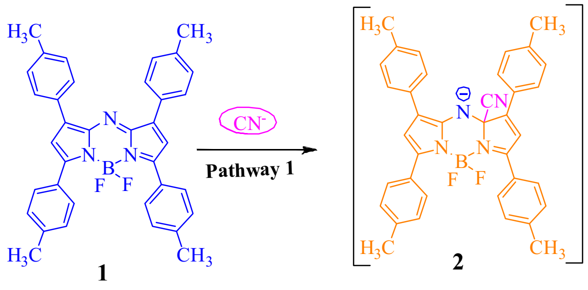

Scheme 1. Formation of compound **2** by nucleophilic addition of CN^- ion to 1,3,5,7-tetratolyl aza-BODIPY **1**.

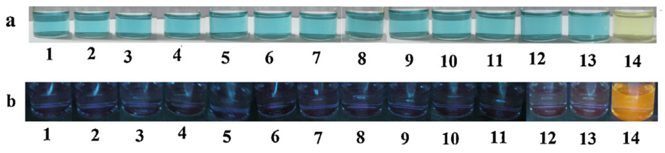

Fig. 1. Optical responses of 1,3,5,7-tetratolyl aza-BODIPY **1** (1×10^{-5} M) in the presence of 10 equiv. of different anions under (a) daylight and (b) UV lamp in CH_3CN: (1) Probe, (2) HSO_4^-, (3) ClO_4^-, (4) Br^-, (5) Cl^-, (6) I^-, (7) CO_3^{2-}, (8) NO_2^-, (9) NO_3^-, (10) N_3^-, (11) $H_2PO_4^-$, (12) AcO^-, (13) F^-, and (14) CN^-.

aza-BODIPYs can be used selectively turn-on fluorescence sensor for CN^- ion.

2. Results and discussion

To test our proposed hypothesis that —C=N bond of aza-BODIPY core is susceptible for nucleophilic attack, we added ten equivalents of different anions such as Br^-, Cl^-, I^-, ClO_4^-, HSO_4^-, NO_2^-, N_3^-, CO_3^{2-}, NO_3^-, F^-, $H_2PO_4^-$, AcO^- and CN^- to 1,3,5,7-tetratolyl aza-BODIPY **1**. Upon addition of anions to aza-BODIPY **1**, we clearly noticed change in the colour from blue to light yellow to the naked eye in the presence of CN^- ion and no visible colour change was noticed in case of other anions indicating that compound **1** can be used as specific sensor for CN^- ion (Fig. 1a). Furthermore, under UV lamp, we noted that upon addition of CN^- ion to compound **1**, the moderately fluorescent compound **1** was turned to highly yellow fluorescent compound **2** supporting that compound **1** can be used as a turn-on fluorescence sensor for CN^- ion (Fig. 1b). Thus, compound **1** can be used as specific chemodosimetric sensor for CN^- ion which we further established by absorption, fluorescence, electrochemical, mass and NMR studies.

Table 1
Photophysical and electrochemical data of aza-BODIPY compound **1**, **2** (**1** + CN^-).

Compound no.	λ [nm] (log ε)	Fluorescence λ_{exc} 420 nm, Φ_f	Redox potential (V vs SCE)
1	658 (5.00)	0.12	−0.23 V, −1.07 V
2 (**1** + CN^-)	438 (4.22)	0.21	0.35 V, −1.92 V

The absorption spectral titration of compound **1** by systematic addition of increasing amounts of TBACN in CH_3CN is shown in Fig. 2b. Upon addition of increasing amounts of CN^- ion to compound **1**, the absorption band at 658 nm gradually decreases in intensity with simultaneous appearance and increase of absorption band at 438 nm along with two clear isosbestic points at 467 and 327 nm indicating the formation of new species **2** (Fig. 2b, Table 1). However, upon addition of other anions to compound **1**, there is no significant change in absorption spectra (Fig. 2a). These observations support that the —C=N bond of aza-BODIPY **1** was converted to —C(CN)(—N⁻) to generate compound **2** by nucleophilic addition of CN^- anion (Scheme 1).

We also studied CN^- ion sensing behaviour of compound **1** by fluorescence studies since the compound **1** which is moderately fluorescent changes to brightly fluorescent in the presence of CN^- ion. The compound **1** showed one weak fluorescent band at 691 nm with a quantum yield of 0.12. Upon addition of increasing amounts of CN^- ion to compound **1** results in gradual decrease in the intensity of the fluorescence band at 691 nm and appearance and increase in the intensity of a new fluorescence band at 602 nm with a quantum yield of 0.21 (Table 1) due to formation of compound **2** with an isoemissive point at 678 nm (Fig. 3b). The significant hypsochromic shifts in absorption and fluorescence bands due to formation of compound **2** was attributed to arrested conjugation in compound **2**. Similar observations were made in case of OH^- ion also which could be ascribed to the nucleophilic attack of OH^- ion to 1,3,5,7-tetratolyl aza-BODIPY **1.** Since nucleophilicity of OH^- ion is relatively less compared to CN^- ion, we require ~40 equiv. of OH^- ion (required more equiv. of OH^- ion compared to CN^- ion) to saturate the 1,3,5,7-tetratolyl aza-BODIPY **1** in CH_3CN solution.

We have performed time-dependent fluorescence study on aza-BODIPY **1** in presence of 10 equiv. CN^- ion. Our study showed that the aza-BODIPY **1** is very reactive towards CN^- ion and required ~6 min for the completion of reaction (Fig. S3, SI). Furthermore, to investigate reversibility of probe, we have performed protonation study (absorption and fluorescence studies) of species **2** (1×10^{-5} M) in presence of 10 equiv. of TFA solution in CH_3CN,

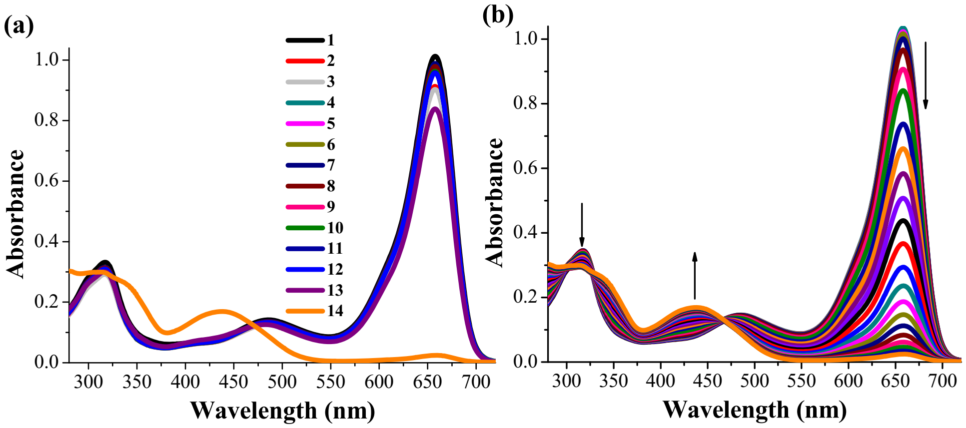

Fig. 2. (a) Absorption titration spectra of 1,3,5,7-tetratolyl aza-BODIPY **1** (1×10^{-5} M) in presence of various anions (1) Probe, (2) HSO_4^-, (3) ClO_4^-, (4) Br^-, (5) Cl^-, (6) I^-, (7) CO_3^{2-}, (8) NO_2^-, (9) NO_3^-, (10) N_3^-, (11) $H_2PO_4^-$, (12) AcO^-, (13) F^-, and (14) CN^- (10 equiv.) in CH_3CN solution. (b) Absorption titration spectra of 1,3,5,7-tetratolyl aza-BODIPY **1** (1×10^{-5} M) upon addition of different amounts of CN^- (TBACN) ion (0–10 equiv.) in CH_3CN solution.