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Journal Name

ARTICLE

Benzindolium-Triarylborane Conjugates: Ratiometric Fluorescent Chemodosimeter for the Detection of Cyanide ions in Aqueous Medium

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Based on benzo[e]indolium and dimesitylborylbenzaldehyde a new ratiometric fluorescent chemodosimeter, C₄₁H₄₃BIN (**3**) has been synthesized and characterized by ¹H, ¹³C NMR spectroscopy, mass spectrometry and single crystal X-ray crystallography. Probe **3** was found to be highly selective and sensitive toward cyanide (CN⁻) ions in aqueous medium even in the presence of other competing anions like F⁻, Cl⁻, Br⁻, I⁻, H₂PO₄⁻, HCO₃⁻ and AcO⁻. The detection limit was calculated to be 7.1 X 10⁻⁹ M, which is much lower than the maximum permissible concentration in drinking water (1.9 μM) set by the World Health Organization (WHO). In addition, the response time of the probe for CN⁻ is less than 5 seconds. The mechanism is based on nucleophilic addition reaction of cyanide ions at the polarized [>C=N<]⁺ bond of the benzindolium group thereby blocking the pi-conjugation between benzindolium and triarylborane moiety. This was further confirmed by ¹H NMR titration, ESI-MS studies and DFT calculations.

Introduction

The efficient sensing of anions and cations is a subject of considerable research interest due to their essential roles in biological, aquatic, environmental and industrial processes.¹ In this respect, the synthesis of new chemosensors for the detection of anions with high selectivity and sensitivity, have attracted a great deal of attention.² Among various anions, the detection of cyanide has drawn particular attention because of its high toxicity to biological systems arising from its widespread use in industries. Cyanide ion inhibits cellular respiration in mammals by binding strongly to a3 cytochromes even at very low concentrations and can lead to death by depressing the central nervous system.³ Accordingly, the World Health Organization (WHO) has set the maximum acceptable concentration level of cyanide in drinking water as 1.9 μM.⁴ Although severe norms have been set by different regulatory bodies still accidental release of cyanide does occur into the environment, which lead to the serious contamination of the ground and/or drinking water.⁵

Initially, hydrogen-bonding⁶ and supramolecular interactions⁷ between CN⁻ and receptors were the most popular strategies for cyanide sensors which usually had low selectivity over other interfering anions. Later, several chemodosimeters for CN⁻ have been developed based on reactivity between CN⁻ and organic functional groups such as

>C=C<,⁸ >C=N-⁹ and >C=O.¹⁰ Recently, triarylboranes¹¹ (TAB) have received much attention towards anion sensing¹² due to their excellent photophysical properties¹³ and inherent Lewis acidic character.¹⁴ On the other hand, due to the emission maximum beyond 580 nm and a relatively large Stokes shift,¹⁵ indolium dyes¹⁶ have also found numerous applications in recognition,^{17,18} cell imaging,¹⁹ pH sensors²⁰ etc. Duan, Hirai and others have broadly studied the sensing of anions using a fluorescent probe based on indolium moiety where the indolium carbon acts as an active site for nucleophilic analytes such as cyanide and sulphide.^{21,16c} However, many of these chemosensors still have some drawbacks such as solubility in aqueous medium, delayed response times or poor detection limit.²² Another strategy employed is based on the concept of "single sensor with multiple binding sites", that is, analysis of analytes by single receptor using different binding sites.²³ Further, screening samples with a single sensor with multiple binding sites would lead to faster analytical processing and possible cost reductions.

In our quest towards designing new chemosensors,²⁴ we were interested to design a chemosensor using the concept of "single sensor with multiple binding sites". With this view **3** was synthesized having both triarylborane and benzindolium groups, which can act as a dual binding receptor utilizing the Lewis acidic character of boron and the polarized [>C=N<]⁺ binding sites. However, probe **3** selectively detects cyanide ions, through polarized benzindolium moiety in presence of other interfering anions (especially F⁻ and AcO⁻).

In this paper we report the synthesis and anion recognition properties of a chemodosimeter consisting of benzindolium and triarylborane groups bridged through an ethylene linker.

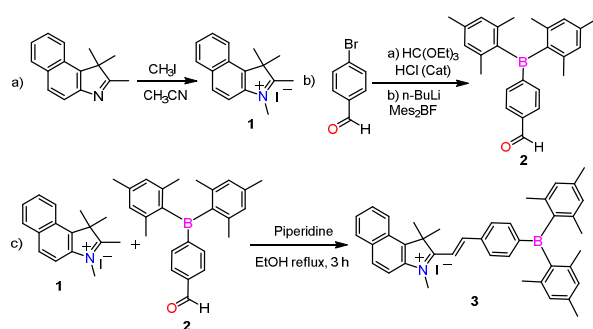
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‡ Electronic Supplementary Information (ESI) available. ¹H, ¹³C NMR, HRMS and other spectroscopic data. CCDC 1416953. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

The probe displayed exclusive visual naked-eye color change for cyanide ions in aqueous medium with a very low detection limit of 7.1 nM. The experimental results were further supported by DFT calculations.

Results and Discussions

Synthesis and characterization



Scheme 1. Synthesis of probe **3**

The synthesis of probe **3** is outlined in Scheme 1. It was readily achieved through a simple condensation of 1,2,3,3-tetramethylbenz(e)indolium (1) iodide with 4-dimesitylborylbenzaldehyde (2) in presence of one drop of piperidine in ethanol in 81 % yield. Probe **3** was characterized by ^1H , ^{13}C NMR, HRMS as well as by X-ray crystallographic analysis (ESI).

Optical properties:

The optical properties of probe **3** were studied in MeCN/water mixture (1:9, v/v) at 25 °C. The solution phase UV-Vis spectra of probe **3** shows a broad absorption band in the region 300 to 475 nm (Fig. 1). This may be attributed to π -conjugation of **3** that further leads to ICT (Intramolecular Charge Transfer) transition from triarylborane to the benzoindolium moiety through a π -conjugated spacer. Excitation at the absorption wavelength results in an emission peak at 605 nm along with a small peak at 550 nm.

Sensing Properties:

The sensing properties of probe **3** with respect to various anions (F^- , Cl^- , Br^- , I^- , CN^- , AcO^- , SCN^- , ClO_4^- , PF_6^- , NO_2^- , NO_3^- , N_3^- , HCO_3^- , CO_3^{2-} and SO_4^{2-}) were carried out in MeCN/water mixture (1:9, v/v). Fig. 1A shows absorption spectra of **3** containing various anions. The solution remains yellow upon addition of all the above anions, except for CN^- , where the solution turned almost colorless (Fig. S13, ESI). Upon gradual addition of CN^- to the solution of **3** (MeCN/water mixture, 1:9, v/v), the intensity of the absorption broad band decreases with simultaneous increase in the intensity of the bands at

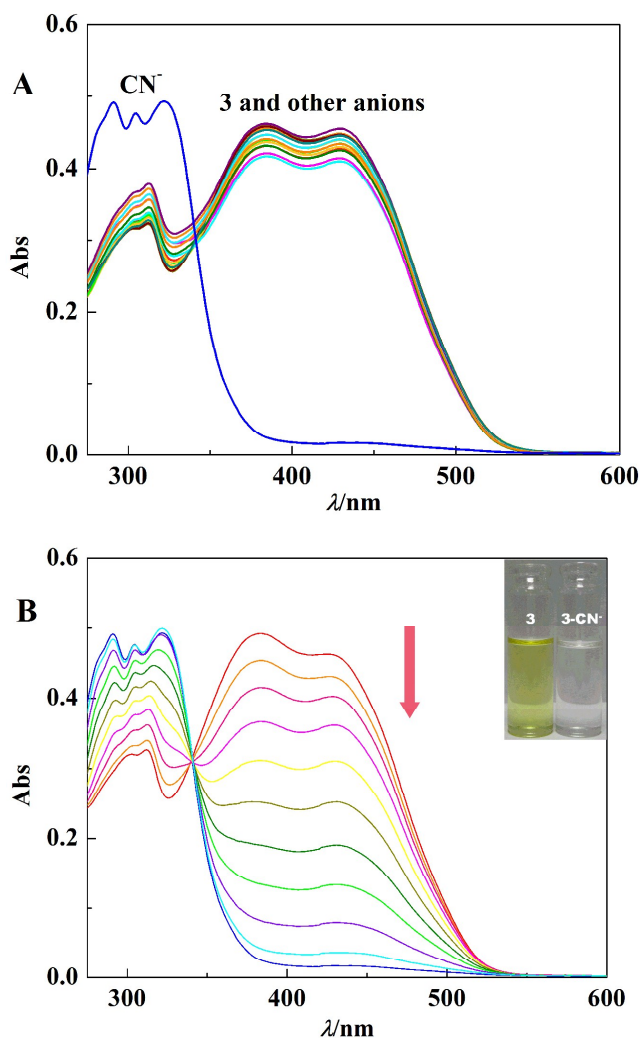


Fig. 1. (A) UV-Vis absorption spectra of probe **3** (10 μM) observed upon addition of three equivalents of various anions in $\text{CH}_3\text{CN}/\text{water}$ (1:9, v/v) at 25 °C and (B). UV-Vis absorption spectra of probe **3** (10 μM) measured upon addition of CN^- ions in MeCN/water mixture (1:9, v/v) at 25 °C.

290 and 320 nm respectively (Fig 1B). A well-defined isosbestic point at 340 nm was observed which indicates the formation of a new compound **3-CN $^-$** adduct by nucleophilic addition of CN^- to the benzoindolium moiety. These absorption changes indicate the disruption of the ICT by the nucleophilic addition of CN^- onto the $[\text{>C=N<}]^+$ moiety of **3**, inducing a break in the indolium conjugation, corresponding to a distinct color change from yellow to colorless. These results were further confirmed by NMR analyses.

In addition to serving as a colorimetric chemodosimeter, probe **3** also behaves as a fluorescent chemodosimeter for cyanide ions. The fluorescent properties of probe **3** in the presence of various anions were examined in MeCN/water

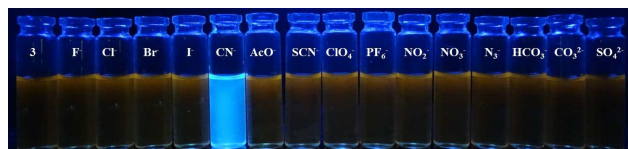


Fig. 2. Photographs of **3** in MeCN/water mixture (1:9) under UV light in the presence of different anions.

mixture (1:9, v/v) at 25 °C. Fig. 2 show the visual fluorescence colour change of **3** using UV lamp upon addition of excess amounts of various anions. On adding CN^- , a noticeable sky blue fluorescence was observed, whereas no such colour change was observed in the presence of other anions. With successive addition of CN^- , the intensity of CT emission band at 605 nm decreases while a new blue emission band at 457 nm ($\Phi = 0.32$) appears (Fig. 3A), which is characteristic of the benzoindolium emission²⁵ due to the inhibition of the charge transfer from the triarylborane moiety to the benzoindolium moiety. Job's plot²⁶ analysis of the fluorescence titrations revealed a 1: 1 binding between **3** and CN^- (Fig. S14, ESI). This was further confirmed by HRMS analysis, where the peak at m/z 609.3406 corresponds to $[\mathbf{3}\text{-CN}+\text{Na}]^+$ (m/z calcd: 609.3417) suggesting a 1:1 stoichiometry binding between **3** and CN^- . The ratio of fluorescence intensities at 457 and 605 nm (F_{457}/F_{605}) vs concentration of CN^- is shown in Fig. 3B, and the association constant for CN^- using B-H equation²⁷ (Fig. S15, ESI) was estimated to be 5.2×10^4 . The detection limit²⁸ for CN^- (Fig. S16, ESI) was measured to be 7.1 nM under the experimental conditions.

Competitive experiments:

The selectivity of **3** towards CN^- was further established by measuring the emission spectrum of $\mathbf{3}+\text{CN}^-$ in presence of other competing anions such as F^- , Cl^- , Br^- , I^- , AcO^- , SCN^- , ClO_4^- , PF_6^- , NO_2^- , NO_3^- , N_3^- , HCO_3^- , CO_3^{2-} and SO_4^{2-} (Fig. 4) in MeCN/water mixture (1:9, v/v) at 25 °C. The strong fluorescence enhancement of probe **3** (10 μM) observed in presence of CN^- remains almost unaffected even in presence of excess concentration (5 equiv.) of other anions. These investigations confirm the excellent selectivity of **3** towards cyanide anions. Moreover, the ratiometric fluorescence changes of **3** remains unchanged even in the presence of other anions.

NMR spectral studies:

In order to find the plausible mechanism of CN^- binding to probe **3**, ^1H NMR titration analysis was carried out. As expected, after addition of two equivalents of sodium cyanide in the solution of **3** a significant proton shift was observed. As depicted in Fig. 5, maximum shifts were observed for protons H_a , H_b , H_c , H_d and H_e . The resonance of H_a is shifted upfield by 1.48 ppm. Protons H_c and H_e were also shifted upfield and H_d shifted downfield. On the other hand, H_b proton splits into two peaks at 1.76 and 1.23 ppm, due to the non-equivalent nature

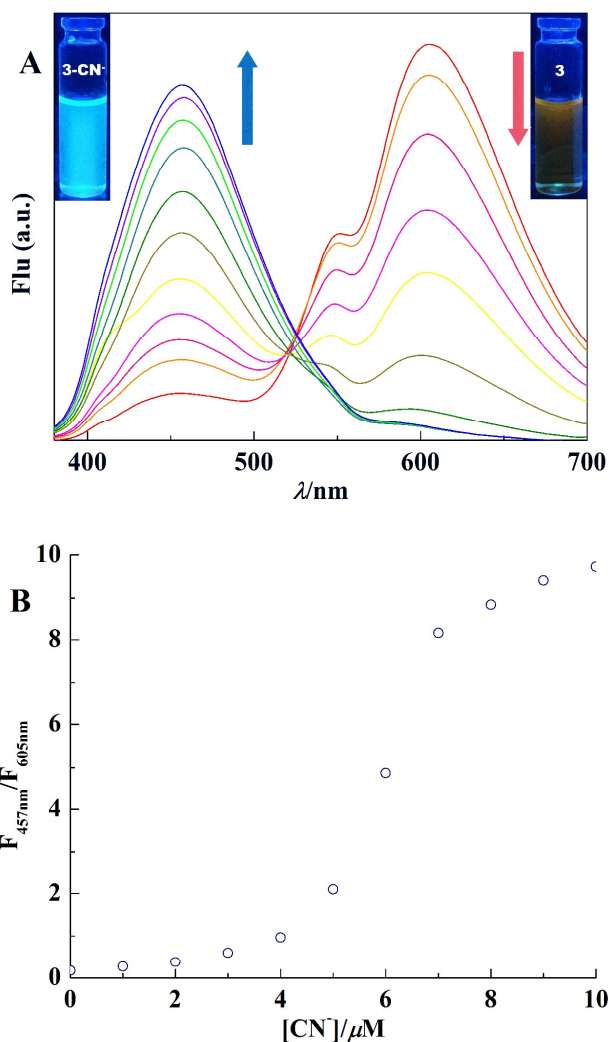


Fig. 3. (A) Fluorescence spectra of **3** (10 μM) upon addition of CN^- ions in MeCN/water mixture (1:9, v/v) at 25 °C. $\lambda_{\text{ex}} = 360$ nm, excitation and emission slit widths (5 nm/10 nm) and (B) the plot of F_{457}/F_{605} versus the concentration of CN^-

of the methyl groups after addition of CN^- . In ^{11}B NMR spectra of the receptor and cyanide adduct remain unchanged whereas ^{13}C NMR spectra of $\mathbf{3}\text{-CN}^-$ adduct shows a new peak for cyanide at 114.33 and the peak at 182.05 (benzoindolium sp^2 C) shifts to 82.72 (becomes sp^3 C). This confirms the formation of the cyanide adduct as well as its binding to the benzoindolium carbon rather than boron.

DFT Calculations:

To understand the mechanism of interaction between **3** and CN^- , density functional theory calculations DFT were performed with B3LYP functional using 6-31g(d) basis set in a Gaussian 09 program package. The optimized geometries of **3** and $\mathbf{3}\text{-CN}$ in gas phase are shown in Fig. S18. The optimized

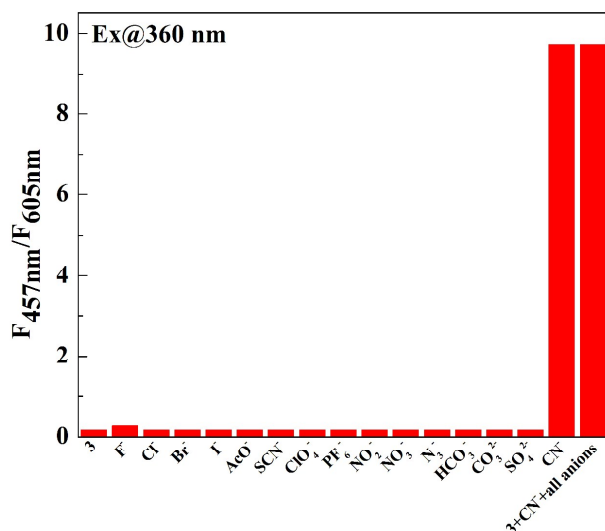


Fig. 4: The fluorescence ratio intensity of **3** at 457 nm and 605 nm in presence of various analytes (5 equiv) in MeCN/water (1:9, v/v) at 25 °C.

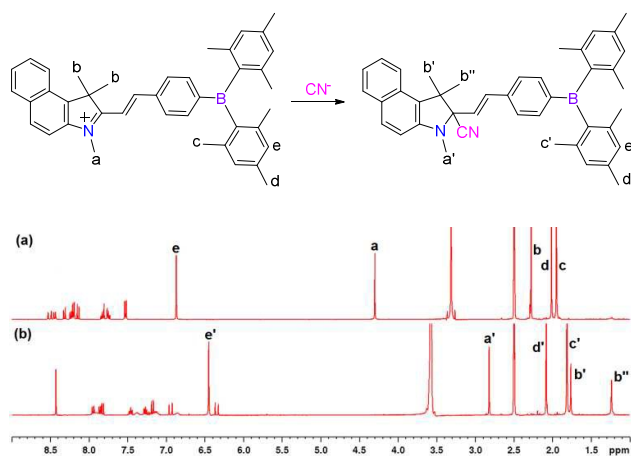


Fig. 5. Plausible binding mechanism of CN^- (top). ^1H NMR spectra (400 MHz, d_6 -DMSO- D_2O) of probe **3** measured (a) without CN^- and (b) with CN^- (2 equiv.) (bottom).

geometry of probe **3** is in good agreement with X-ray structure (Fig. S17, ESI). The phenyl groups of triarylborane unit were slightly tilted from the benzoindolium plane. The ground state optimized geometry of **3** undergoes drastic twisting upon interaction with CN^- . Thus, the π -conjugation between the benzoindolium and triarylborane was completely disturbed that resulted in a considerable blue shift in the UV-Vis spectrum with a decrease of ICT transition. Further, the HOMO-LUMO gap (Fig. 6 and Table S2) was found to be higher than the free probe **3**.

Detailed information about the hypsochromic shift in the absorption spectrum upon nucleophilic CN^- addition to **3** can

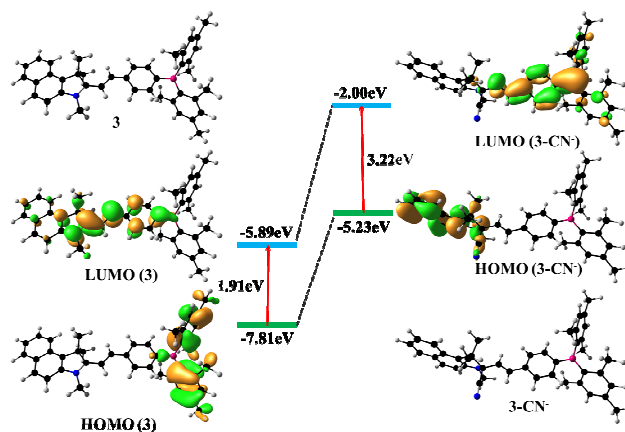


Fig. 6. Frontier molecular orbitals (iso value 0.04) of **3** and **3-CN⁻** as obtained from DFT calculations.

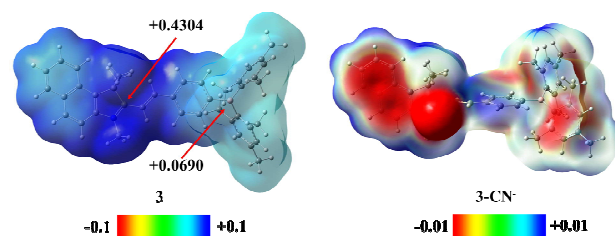


Fig. 7. ESP surfaces of **3** and **3-CN⁻** (isovalue = 0.0004).

be accomplished from time-dependent DFT (TDDFT) calculations as well. The results of transitions of **3** and **3-CN⁻** are summarized in Table S3. The calculated wavelengths in the absorption spectra of **3** and **3-CN⁻** were 423 nm and 309 nm respectively with oscillator strengths of 1.311 and 0.135. In both the cases, the predicted absorption spectra were found to be in good agreement with experimentally observed ones (Fig. S20 and S21, ESI). The $S_0 \rightarrow S_1$ transition in **3** involves mainly HOMO \rightarrow LUMO (> 88 %) with very large oscillator strength. The HOMO is concentrated on the mesityl group with a small contribution from B=C bond, while the LUMO is dominated by π orbital of the C=C bond with significant contributions from the π^* orbitals of the indolium ring and the π^* orbital of boron atom. It is reverse in the case of **3-CN⁻**, where the HOMO is mainly concentrated on the benzoindolium group and LUMO is concentrated on the triarylborane group. This confirms that the transition occurs from benzoindolium to triarylborane moiety. Electrostatic potential surfaces of molecules **3** and **3-CN⁻** and Mulliken atomic charges of indolium carbon and boron of molecule **3** are shown in Fig. 7. Indolium carbon with the Mulliken charge of +0.4304 has more positive potential than that of boron atom (Mulliken charge = +0.0690). Optimized structure of cyanide adducts at different binding sites and energy comparison of the optimized structures of **3-CN⁻** and **3-B-CN⁻** are shown in Fig. S19, ESI. The cyanide adduct of compound **3**

is stabilized by 20.2 kcal mol⁻¹ when cyanide attacks the indolium carbon atom. These results suggest that cyanide anions prefer indolium carbon atom rather than the boron atom.

Conclusions

In summary, we have developed a new chemodosimeter for highly sensitive and selective sensing of cyanide ions. The effective sensing of probe **3** to CN⁻ comes from nucleophilic addition of CN⁻ to [$>C=N<]^+$ group. The newly designed probe offers several advantages such as easily synthesizable, ability to detect CN⁻ in aqueous medium, visual colour change by naked eyes and very low detection limit (~7.1 nM).

Experimental

General procedures and instrumentation. Unless otherwise mentioned, all reagents were obtained from commercial suppliers and were used without further purification. 1,2,3,3-tetramethylbenz[e]indolium iodide, **1** and 4-dimesitylborylbenzaldehyde, **2** were synthesized following literature procedure methods.^{21a,12b} The ¹H, ¹³C and ¹¹B NMR spectra were recorded on 400 or 500 MHz FT NMR spectrometers, using TMS as an internal reference. HRMS (ESI) spectra were carried out using Qtof Micro YA263 HRMS instrument. Absorption spectra were recorded on an Evolution 300 (Thermo Scientific) or Jasco V-650 UV-Vis spectrophotometers at 298 K. Fluorescence spectra were taken with Jasco FP-6300 spectrofluorimeter. Quinine sulfate was used as standards for the determination of fluorescence quantum yields.

Synthesis of **3**.

1,2,3,3-tetramethylbenz[e]indolium iodide (351 mg, 1 mmol) and 4-dimesitylborylbenzaldehyde (354 mg, 1 mmol) were dissolved in ethanol (20 ml). To this was added 2 drops of piperidine and the resulting solution was refluxed for 3 h. The reaction mixture was cooled to room temperature and after chromatographic workup compound **3** was obtained as an orange solid.

3: Eluent (DCM/MeOH, 98:2), orange solid, yield 560 mg (81%). ¹H NMR [400 MHz, CDCl₃, SiMe₄, *J* (Hz), δ (ppm)]: 8.28 (1H, d, *J* = 16.4), 8.18 (1H, d, *J* = 8.4), 8.13 (1H, d, *J* = 8.9), 8.07 (1H, d, *J* = 8.0), 8.04 (2H, d, *J* = 8.1), 7.87 (1H, d, *J* = 16.4), 7.80 (1H, d, *J* = 8.9), 7.68-7.78 (2H, m), 7.66 (2H, d, *J* = 8.1), 6.83 (4H, s), 4.62 (3H, s), 2.32 (6H, s), 2.11 (6H, s), 2.00 (12H, s). ¹³C NMR [100 MHz, CDCl₃, SiMe₄, δ (ppm)]: 183.2, 152.7, 140.8, 139.3, 136.5, 134.0, 131.9, 130.0, 128.6, 128.4, 127.7, 122.7, 113.6, 112.4, 54.5, 37.9, 26.4, 23.4, 21.2. HRMS (ESI): calcd for (M⁺) 560.3489, measd 560.3502

Titration studies:

Stock solution of **3** was prepared (1x 10⁻⁴ mol L⁻¹) in CH₃CN/H₂O (1:9, v/v) then diluted to 10 μ M. Anions (as their Na or K salts) in double distilled water were added to the diluted probe solution and used for the selectivity and titration experiment. For titration experiments quartz cuvette (1 cm x 1 cm) was used and the solutions were added using a micropipette. In fluorescence studies excitation and emission slit width were 5 nm and 10 nm respectively. Spectral data were recorded after 5 minutes of the addition of CN⁻ ions to ensure completion of the reaction.

Computational details:

All calculations (DFT and TD-DFT) were carried out with the program package Gaussian 09 Revision C.01²⁹. The ground-state geometries were optimized without symmetry constraints using the B3LYP functional³⁰ in combination with the 6-31G(d) basis set.³¹ The optimized geometries were confirmed to be local minima by performing vibrational frequency calculations and obtaining only positive (real) frequencies. TD-DFT calculations done, using the Coulomb-attenuated functional CAMB3LYP³² in combination with the 6-31G(d) basis set.

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SYNOPSIS TOC

Benzindolium-Triarylborane Conjugates: Ratiometric Fluorescent Chemodosimeter for the Detection of Cyanide ions in Aqueous Medium

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A new ratiometric fluorescent chemodosimeter has been synthesized and characterized that exhibits high selectivity and sensitivity toward CN^- ion in aqueous medium.

