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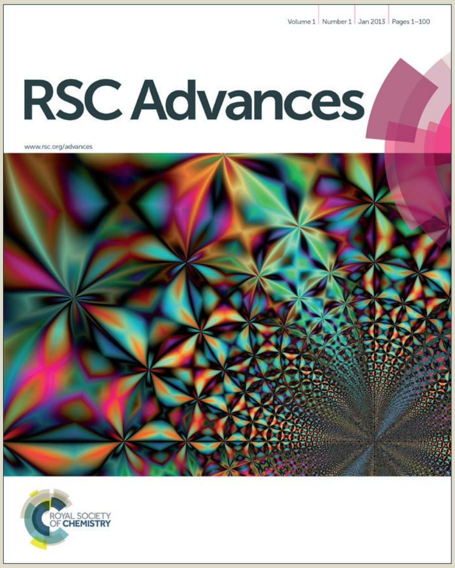

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A colorimetric and ratiometric fluorescent probe for selective detection of cyanide anions in aqueous media and living cells

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A new carbazole derivative 2-[(1E)-2-[6-(benzothiazolyl)-9-ethyl-9H-(carbazol-3-yl)]-ethenyl]-3-methyl-benzothiazolium iodide (BCB) was synthesized and its anion sensing property was studied. BCB acts as an efficient colorimetric and ratiometric fluorescent probe for detection of cyanide ions in aqueous solution even in the presence of other anions such as F^-, AcO^-, $H_2PO_4^-$, SO_4^{2-}, SO_3^{2-}, S^{2-}, SCN^-, Cl^-, Br^-, I^-, N_3^-, ClO_4^-, NO_2^-, HCO_3^- and CO_3^{2-}. The cyanide addition to the benzothiazolium group induces an obstruction in an intramolecular charge transfer (ICT) and produces a dramatic hypsochromic shift in the absorption (152 nm) and emission (165 nm) profiles of BCB. The change in color of the solution was prominent and could be easily seen by the naked eye. Probe BCB forms a 1:1 adduct with CN^- with detection limit of 0.09 μ M. The probe was successfully applied for the detection of CN^- in natural water samples as well as in live HeLa cells.

Introduction

Among anions cyanide (CN^-) is one of the most lethal poisons to living organisms. Absorption of cyanide through the lungs, gastrointestinal tract and skin, can lead to vomiting, convulsions, loss of consciousness, and ultimately death.[1,2] It is known that 0.5 − 3.5 mg per kg of body weight is fatal for humans.[3] According to the World Health Organization (WHO), the permissible level of CN^- in drinking water is 1.9μ M.[4] Nevertheless, the increased usage of cyanide in gold mining, electroplating, tanning, polymer production and metallurgy,[2] etc., along with its necessary transportation, drastically raises the potential for contamination in the environment and increases the risk of human exposure. Therefore, the detection as well as the quantitative determination of cyanide in biological and environmental samples is of considerable importance for environment protection and human health.

In recent years, a number of efforts have been made to develop colorimetric or fluorometric CN^- selective chemosensors based on versatile mechanisms, among which the reaction based probes have attracted much attention due to their unique selectivity over other anions.[5] However, majority of the reactions can only take place in an organic solvent and the water soluble CN^- sensors are still very limited in number.[6] Moreover, fluorescence based detection usually depends on the intensity change at a single wavelength, which may be influenced by variations in the sample environment. By contrast, a ratiometric method measuring the ratio of fluorescence intensities at two wavelengths provides a built-in correction for environmental effects and therefore the reliability of the measurements is substantially enhanced.[7] So far, only a limited number of ratiometric fluorescence probes for cyanide have been reported in the literature.[8] Therefore, it is of high interest to develop fluorescence chemosensors for cyanide that can show both color and fluorescence changes in an aqueous medium in a ratiometric manner.

Keeping this in view, in the present manuscript we have designed and synthesized a new carbazole-derived (scheme 1) intramolecular charge transfer (ICT) probe for cyanide in aqueous solution. Carbazole moiety is a strong electron-donating group and thus is suitable as a donor in an intramolecular charge transfer (ICT) system. Positively-charged benzothiazolium moiety, an electron-withdrawing group, was selected as the CN^- reaction site, which may not only render the probe water-soluble but also manipulate an ICT process. We envisioned that there is a strong ICT process in BCB. Interaction of cyanide would interrupt the π -conjugation and block the ICT process to produce significant ratiometric spectroscopic responses. As expected, here we observed dramatic hypsochromic shift in absorption and in emission profiles of BCB on reaction with cyanide, which could be utilized as a selective colorimetric and ratiometric fluorescent probe for CN^- in aqueous solution.

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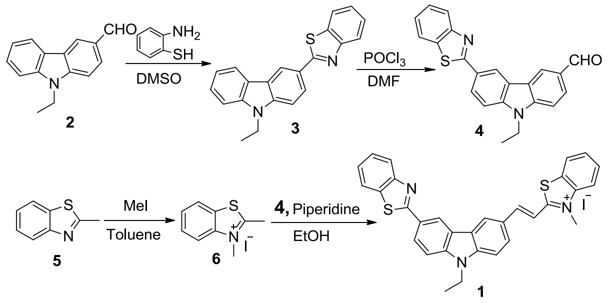

Scheme 1 Synthesis of probe BCB

Results and discussion

Chemosensing of CN^-

The anions sensing ability of BCB was investigated by UV-vis and fluorescence spectroscopy in a DMSO-H_2O (1: 9, v/v, pH 7.4) HEPES buffer solution. As shown in Fig. 1a, absorption spectrum of BCB is characterized by a higher energy band at around 320 nm due to a $\pi \rightarrow \pi^*$ transition and a lower energy band at 472 nm for the intramolecular charge transfer (ICT). On addition of increasing amounts of cyanide the absorbance at 472 nm gradually decreased, but at 320 nm it gradually increased. The absorption stabilized after the amount of added CN^- reached 2 equiv. and a significant color change from orange-red to colorless could be observed easily (Fig. 3). The observed spectral changes suggest that the π-conjugation and ICT were both inhibited by the nucleophilic addition of CN^- at the benzothiazole ring carbon adjacent to the quaternary nitrogen.[8e] The electronic delocalization was thus ruptured and the ICT band at 472 nm gradually disappeared accordingly. The presence of a clear isosbestic point at 385 nm indicated a clean conversion of the reactant to the product. The spectrophotometric titration of BCB with CN^- shows a linear dependence of the ratio of the absorbance at 472 nm and 320 nm (A_{472}/A_{320}) as a function of CN^- concentration, which enables ratiometric quantification of CN^-. Good linearity was observed in the range of 2 – 20 μM (the inset in Fig. 1a).

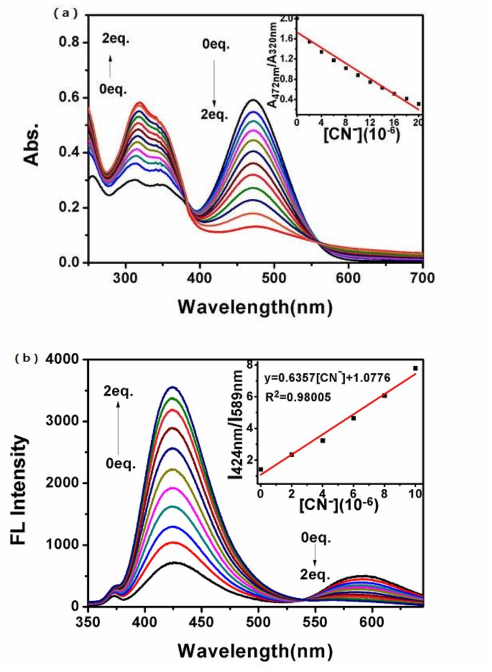

Fig.1 (a) UV-vis and (b) fluorescence spectral changes of BCB (10 μM) in the presence of various concentrations of CN^- (0–20 μM). Inset in (a): Ratiometric absorbance changes (A_{472}/A_{320}) of BCB upon gradual addition of CN^-; (b): Ratiometric calibration curve I_{424}/I_{589} as a function of CN^- ion concentration.

The excitation of the probe BCB at 330 nm produced a dual emission with peaks at 424 nm and 589 nm (Fig. 1b). The band at 589 nm is attributed to the ICT emission band, while the band at 424 nm can be ascribed to the benzothiazolyl carbazole moiety. The successive addition of CN^- into a solution of BCB caused a gradual quenching in fluorescence at 589 nm and a prominent enhancement at 424 nm. It led to a bright blue emission which is clearly visible by the naked eye under the irradiation of a hand held UV-lamp at 365 nm. A clear isoemissive point at 538 nm also indicated the formation of the BCB – CN adduct. Thus, probe BCB can offer fluorescent detection of cyanide at two different emission channels. There is a ca. 26.4-fold variation in the fluorescence ratio (I_{424}/I_{589}) from 1.42 in the absence of CN^- to 37.5 in the presence of 2 equiv. of CN^-. A good linear relationship between the intensity ratio (I_{424}/I_{589}) and the concentration of CN^- could be obtained in the range of 1.0×10^{-6} – 10×10^{-6} M (R^2 = 0.98005). This ratiometric fluorescence change could be potentially useful for quantitative determination of CN^-. The detection limit of BCB toward CN^- was obtained as 0.09 μM,

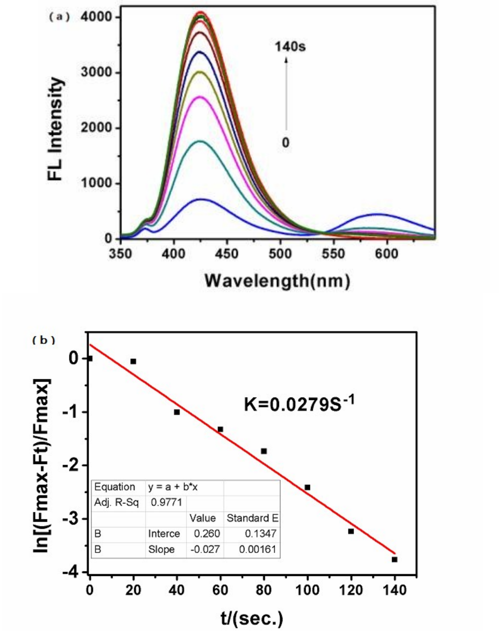

Fig.2 (a) Time-dependent changes in the fluorescence spectra of BCB (1.0×10^{-5} mol L^{-1}) treated with KCN (2.0×10^{-5} mol L^{-1}) in DMSO: H_2O (1:9, v/v, HEPES buffer, pH 7.4). and (b) Pseudo-first-order kinetic plot of the reaction of BCB (1.0×10^{-5} mol L^{-1}) with CN^- (2.0×10^{-5} mol L^{-1})

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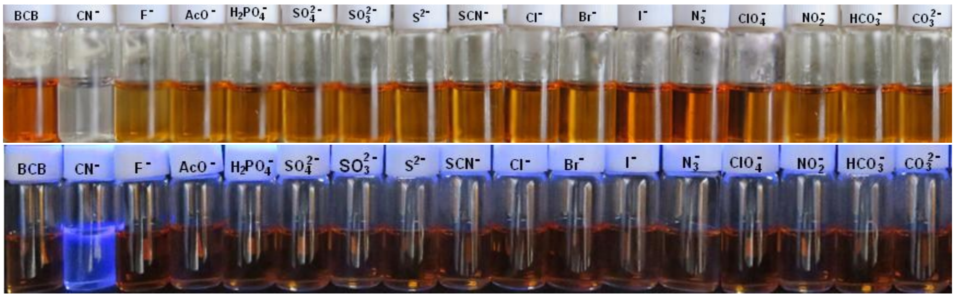


Fig.3 Chromogenic response of BCB added with 10 equiv. of different anions under daylight (above) and the corresponding fluorogenic response (below) under UV light. All the images were obtained after 1.5 min upon the addition of anions.

which is much lower than the WHO cyanide standard in drink water (1.9 μM), indicating that BCB is a promising fluorescence ratiometric sensor for the detection of low levels of cyanide ions in samples.

The benzothiazolyl carbazole moiety was itself fluorescent and when it was coupled with the methyl salt of 2-methylenebenzothiazole in BCB, fluorescence was greatly reduced due to extensive π-conjugation and the ICT mechanism. The nucleophilic addition of CN$^-$ ion to BCB leads to disruption of π-conjugation and block of ICT process, thus, resulting in the recovery of the fluorescence of benzothiazolyl carbazole moiety. As shown in Fig. 2a, two equivalents of cyanide reacted completely with BCB in ca. 2 min, indicating the high reactivity of the probe. Pseudo first-order kinetic was assumed and, by monitoring the increase at 424 nm over time, the rate of the reaction was calculated from ln((Fmax-Ft)/Fmax) versus time (Fig. 2b), where Fmax and Ft are fluorescence intensities at time t and end of the reaction, respectively. The rate constant of 0.027 s^{-1} was obtained from the slope of the straight line.[9]

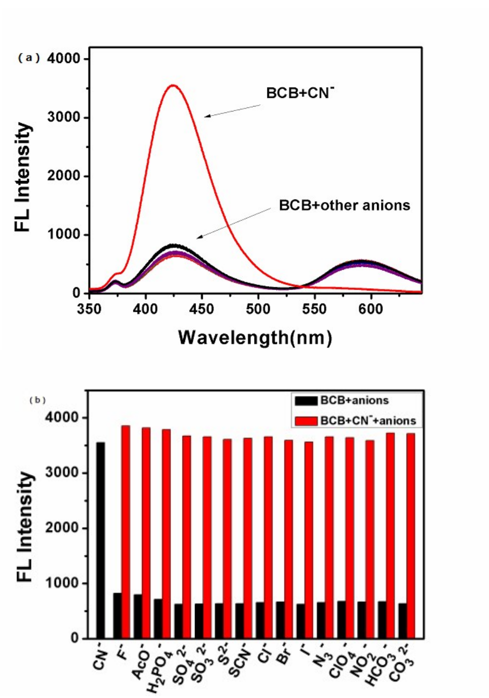


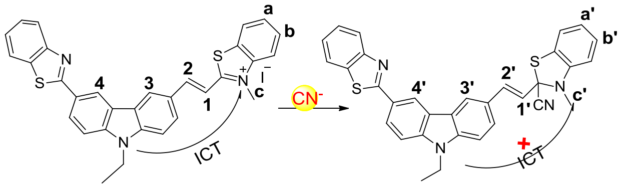
Fig.4 (a) Emission spectra of BCB upon addition of different anions and (b) Fluorescence intensities of BCB at 424 nm upon addition of CN$^-$ in the presence of interfered anions. $C_{BCB}= 10\times10^{-6}$ mol L^{-1}; $C_{CN^-} =10\times10^{-5}$ mol L^{-1}; $C_{anions} =10\times10^{-5}$ mol L^{-1}.

Selectivity in cyanide response

To examine the selectivity, BCB (10 μM) was treated with various anion species (100 μM). Among 15 different anions tested under identical conditions, including F$^-$, AcO$^-$, $H_2PO_4^-$, SO_4^{2-}, SO_3^{2-}, S^{2-}, SCN$^-$, Cl$^-$, Br$^-$, I$^-$, N_3^-, ClO_4^-, NO_2^-, HCO_3^- and CO_3^{2-}, only CN$^-$ responded to BCB with a large blue shift and a marked color change from orange-red to colorless (Fig. 3), manifesting a good chromogenic selectivity of the probe toward CN$^-$ ions in aqueous solution. Consistent with the results of the absorption spectra, no appreciable changes in the emission spectra were observed for the other interfering anions except for the cyanide anion (Fig. 4a). Further, competitive anions interaction studies show that the emission intensity of BCB + CN remained unaffected by the addition of other anions in excess (Fig. 4b). This establishes that BCB can be used to quantitatively detect cyanide presence with high selectivity.

The sensing mechanism and stoichiometry

The interaction mechanism was further confirmed by a combination of ^1H NMR spectroscopy and high-resolution



Scheme 2 A plausible mode of cyanide interaction with BCB

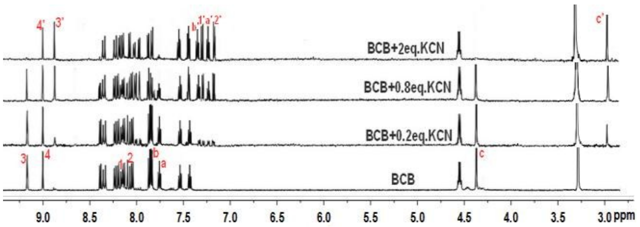


Fig.5 ^1H NMR spectral changes observed for BCB on addition of various amounts of cyanide in DMSO-d_6.

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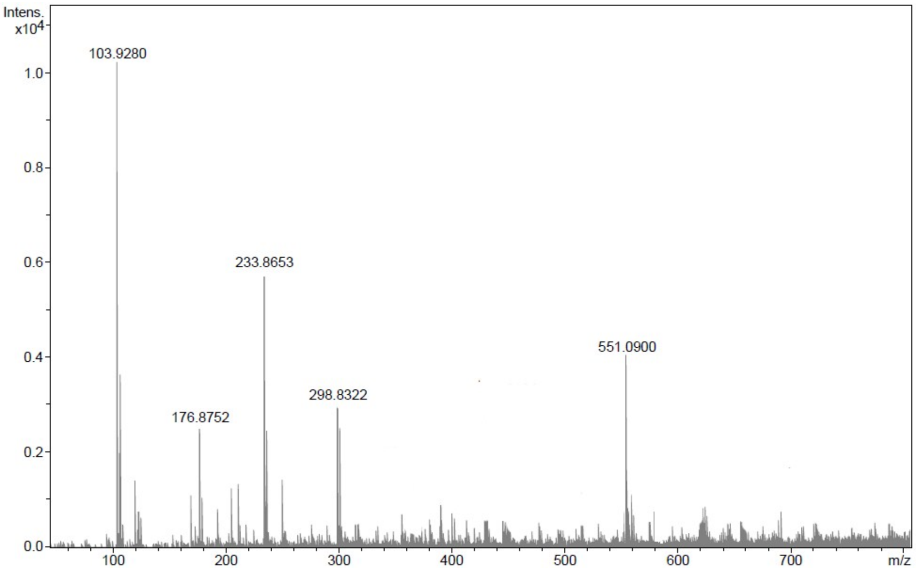

Fig.6 The HRMS of product obtained by reaction between BCB and CN^-.

mass spectrometry. A solution of BCB in DMSO-d_6 was monitored by ^1H NMR spectroscopy with the gradual addition of KCN. As shown in Fig. 5 and scheme 2, significant upfield shifts for most protons of BCB occurred upon CN^- addition, indicating that the CN^- functions as a nucleophile. The δ value of methyl protons (H_c) adjacent to quaternary nitrogen dramatically shifted upfield from 4.37 ppm to 2.97 ppm. The vinyl protons at δ 8.38 (H_1) and 8.10 (H_2) ppm shifted upfield toward δ 7.26 and 7.19 ppm, respectively, indicating that the electron withdrawing effect of the benzothiazolium quaternary N atom decreased. Also, the aromatic protons (H_a, H_b and H_3) participated in electronic delocalization showed an upfield shift due to the removal of electron-withdrawing effect originating from the benzothiazolium moiety. All these observations are in accordance with the nucleophilic addition of cyanide to the iminium carbon in BCB. High-resolution ESI-MS analysis also identified a peak for the BCB-CN adduct: calcd for $C_{27}H_{35}N_4O_3$ [BCB-CN+Na], 551.1340; found, 551.0900 (Fig.6).

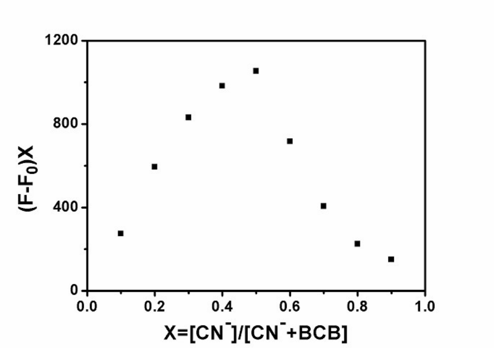

Fig.7 Job's plot between BCB and cyanide anion in HEPES buffer (DMSO/H_2O =1:9, v/v, pH = 7.4).

Finally, the analysis of a Jobs plot for BCB, derived from fluorimetric titration, confirmed the formation of a 1:1 adduct with the cyanide (Fig.7).

The practical applications

Since BCB showed a selective and sensitive response to CN^- in 90% aqueous solution, we utilized it to detect CN^- in tap water samples. The water sample was found to be free from cyanide and so the sample was prepared by adding known amounts of cyanide to sample. With a given amount of CN^- spiked in water samples, recovery yields were determined using the calibration curve and listed in table 1. As shown in table 1, the probe was able to measure the concentrations of spiked CN^- with good recovery, suggesting that the method could potentially be used for detecting CN^- in real samples.

Table **1**. Determination of CN^- in water samples.

Samples	CN^- added (μM)	CN^- found (μM)	Recovery (%)	R.S.D.[a] (%)
Tap Water 1	0	-	-	-
Tap Water 2	2	1.98	99.0%	0.81%
Tap Water 3	6	6.04	100.1%	0.96%
Tap Water 4	10	10.21	102.1%	0.52%
Tap Water 5	14	14.16	101.1%	0.83%

[a] RSD: relative standard deviation, n = 5.

Probe BCB was further examined to detect cyanide in living HeLa cells. The Hela cells were treated with BCB (10 μ M) for 30 min at 37℃, and then washed with phosphate-buffered saline (PBS, 10 mM, pH 7.4) for three times. The cells showed no detectable fluorescence upon incubation only with BCB (Fig. 8b). After the treatment with KCN (20 μ M) for 10 min and further incubated with BCB (10 μ M) for 30 min, however, a bright blue fluorescence was

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observed (Fig. 8e). Thus, probe BCB showed the potential to detect CN$^-$ in vitro cellular system.

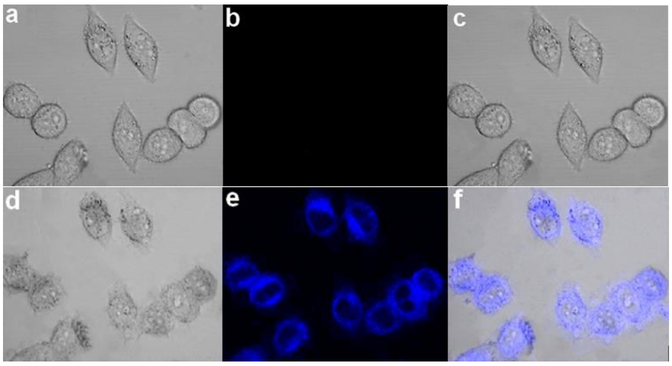

Fig.8 Confocal laser fluorescence images of Hela cells treated with BCB (a-c) and with both BCB and CN$^-$ (d-f). (Left) bright field image; (Middle) fluorescence image; (right) merged image.

Experimental

Materials and instrumentation

3-formyl-N-ethylcarbazole (99%), o-aminothiophenol (96%) and 2-methylbenzothiazole (98%) were purchased from Aladdin Reagent Co. (shanghai, China). All the other chemical reagents were of analytical grade and used as received without further purification. All the anions were supplied from their corresponding sodium or potassium salts. Stock solution of BCB was prepared in DMSO at 2.0×10^{-3} mol L^{-1}. Anion stock solutions (2.0×10^{-3} mol L^{-1}) were prepared by dissolving appropriate amounts of sodium or potassium salts in water. Double distilled water was used throughout.

UV-vis absorption spectra were recorded on an Agilent 8453 UV-vis spectrophotometer (Lakewood, NJ). Fluorescence spectra were taken on Hitachi F-7000 fluorescence spectrometer. The samples were excited at 330 nm. The excitation and emission slits were both set at 5 nm. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 600 and 400 MHz at 298 K, using tetramethylsilane (TMS) as internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra were obtained on a Bruker micrOTOF-Q Ⅱ mass spectrometer. Melting points were measured on a RD-Ⅱ digital melting point apparatus and were uncorrected.

Synthesis of probe molecule BCB

Compound 1 (BCB) was synthesized by the protocol as shown in scheme 1.

Synthesis of compound 3: A mixture of compound 2 (2.23 g, 10 mmol) and o-aminothiophenol (1.37 g, 11 mmol) in DMSO (20 mL) was stirred at 195℃ for 6h under N_2 atmosphere. After completion of the reaction, it was cooled to room temperature and poured into 300 mL of water. The precipitate was filtered by vacuum filtration and was chromatographed (silica, petroleum: ethyl acetate=10:1, v/v) to give white solid (2.65g, 81%). m.p. 142-145℃. ^{1}H NMR(600 MHz, DMSO-d_6) δ (ppm): 8.92(s, 1H), 8.38(d, *J*=12Hz, 1H), 8.21(d, *J*=6Hz, 1H), 8.13(d, *J*=12Hz, 1H), 8.05(d, *J*=12Hz, 1H), 7.78(d, *J*=12Hz, 1H), 7.68(d, *J*=6Hz, 1H), 7.54(d, *J*=6Hz, 2H), 7.44(t, *J*=6Hz, 1H), 7.29(t, *J*=6Hz, 1H), 4.51(q, *J*=6Hz, 2H), 1.36(t, *J*=6Hz, 3H); ^{13}C NMR (400 MHz, DMSO-d_6) δ (ppm):167.90, 153.27, 140.64, 139.66, 133.73, 125.89, 124.26, 123.35, 122.09, 121.57, 120.41, 119.04, 108.99, 36.64, 13.12; HRMS(ESI): calcd. for $C_{21}H_{16}N_2S$ 328.1034(M), found:328.0948.

Synthesis of compound 4: DMF (25 mL) were placed in a 100 mL round bottom flask cooled in an ice-water bath. $POCl_3$ (7.70 g, 50 mmol) was added dropwise to the flask. After stirring for another 30 min, the mixture was raised to room temperature and continued to stir for 1 h. To this solution, compound 3 (3.28g, 10mmol) in 1,2-dichloroethane (20 mL) was added in dropwise fashion, and the mixture was stirred at 90℃for 12h. The resulting mixture was poured into 100ml ice water. The solution was then brought to pH = 7 by the addition of 1M NaOH and was extracted with CH_2Cl_2 (3×50 mL). The combined organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was distilled off and the residue material was chromatographed (silica, petroleum: ethyl acetate=5:1, v/v) to give yellow solid (1.24g, 35%). m.p. 171-173℃. ^{1}H NMR(600 MHz, DMSO-d_6) δ (ppm): 10.10(s, 1H), 9.06(s, 1H), 8.01(s, 1H), 8.29(d, *J*=12Hz, 1H), 8.15(t, *J*=12Hz, 1H), 8.06(d, *J*=6Hz, 2H), 7.86(t, 12Hz, 2H), 7.55 (t, *J*=12Hz, 1H), 7.45(t, *J*=12Hz, 1H), 4.57(q, *J*=6Hz, 2H), 1.39(t, *J*=12Hz, 3H); ^{13}C NMR(400 MHz, $CDCl_3$) δ (ppm): 191.43, 144.17, 142.44, 129.33, 127.55, 126.51, 125.11, 124.71, 123.56, 123.14, 122.63, 121.63, 120.62, 109.63, 109.31, 38.31, 19.93; HRMS(ESI): calcd. for $C_{22}H_{16}N_2O_S$ 356.0983(M), found:357.1062.

Synthesis of compound 6: Compound 6 was synthesized according to literature methods.[10] Yellow powder (1.6g, 87%). ^{1}H NMR(600 MHz, D_2O) δ (ppm): 8.09(d, *J*=12Hz, 1H), 8.00(d, *J*=12Hz, 1H), 7.77(t, *J*=12Hz, 1H), 7.70(t, *J*=12Hz, 1H), 4.14(s, 3H), 3.06(s, 3H).

Synthesis of compound 1: to the stirred EtOH solution of compound 4 (3.56g, 10mmol) and compound 6 (2.91g, 10mmol) was added 1-3 drops of piperidine. The mixture was refluxed for 12 h under stirring. Then the reaction mixture was allowed to cool to the room temperature, filtered, washed thoroughly with EtOH and dried under vacuum to give the product as a red solid (1.6g, 87%). ^{1}H NMR (600MHz, DMSO-d_6) δ (ppm): 9.16(s, 1H), 8.99(s, 1H), 8.38(d, *J*=6Hz, 1H), 8.33(d, *J*=12Hz, 1H), 8.22(d, *J*=6Hz, 1H), 8.19(d, *J*=6Hz, 1H), 8.15(d, *J*=12Hz, 1H), 8.13(d, *J*=6Hz, 1H), 8.07(d, *J*=18Hz, 1H), 8.04(d, *J*=6Hz, 1H), 7.84(m, 3H), 7.75(t, *J*=6Hz, 1H), 7.53(t, *J*=6Hz, 1H), 7.43(t, *J*=6Hz, 1H), 4.55(q, *J*=6Hz, 2H), 4.37(s, 3H), 1.39(t, *J*=6Hz, 3H); ^{13}C NMR(400Hz, DMSO-d_6) δ (ppm): 172.27, 168.42, 154.19, 150.49, 143.26, 142.46, 142.36, 134.76, 129.95, 128.51,

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127.86, 127.05, 126.65, 126.39, 125.64, 125.55, 124.52, 123.77, 123.40, 123.24, 122.83, 122.69, 120.07, 116.91, 111.24, 111.01, 110.86, 38.24, 36.65, 14.39; HRMS(ESI): calcd. for $C_{31}H_{24}N_3S_2$ 502.1406(M), found:502.1390.

UV-vis and fluorescence titrations

UV-vis and fluorescence titrations were carried out in 10-mm quartz cuvettes at 25 °C. The procedure was as follows: into a DMSO: H_2O (1:9, v/v, HEPES buffer, pH 7.4) solution, containing 10 μ M BCB, a CN^- sample was gradually titrated. At the same time, any changes in the fluorescence intensity were monitored using a fluorescence spectrometer.

Conclusions

In conclusion, we have successfully devised a novel carbazole based fluorescent probe BCB for selective detection of cyanide ion in aqueous media. Upon reaction with CN^- functioning as a nucleophile, BCB displays substantial dual changes in both its ratiometric emission and absorption spectra. The significant changes in color, attributed to a restricted ICT due to the formation of a stable BCB + CN adduct, could be observed directly with the naked eye. The detection limit of BCB was estimated to be 0.09 μ M, which is lower than the maximum permissive level in drinking water according to the World Health Organization (WHO). Moreover, the application of BCB for imaging of CN^- in living cells was also successfully achieved.

Acknowledgements

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Abstract Graphic

The Ttitle:

A colorimetric and ratiometric fluorescent probe for selective detection of cyanide anions in aqueous media and living cells

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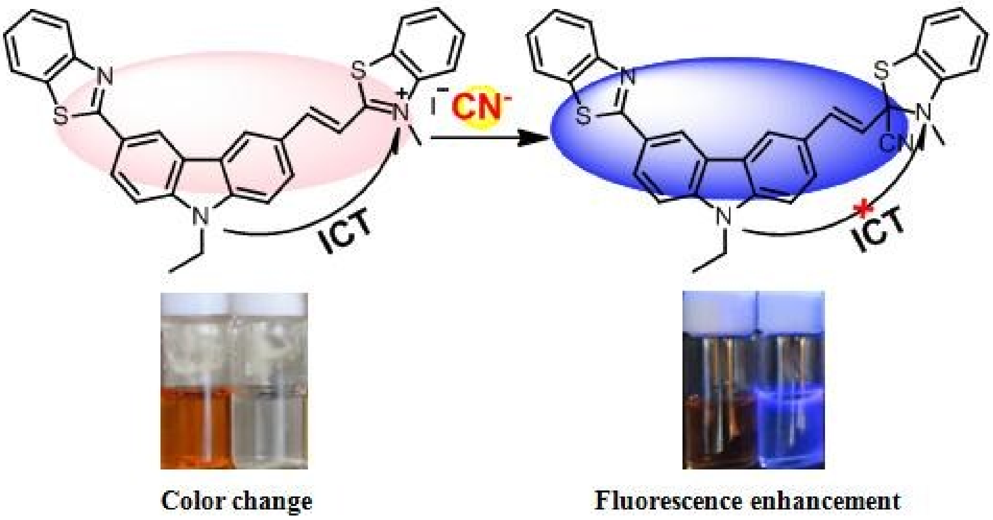

Based on the internal charge transfer (ICT) mechanism, a novel colorimetric and ratiometric fluorescent probe was developed for highly selective and sensitive detection of cyanide ion in aqueous media. The probe was successfully applied for the detection of CN^- in natural water samples as well as in live HeLa cells.