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Simple benzothiazole chemosensor for detection of cyanide anions *via* nucleophilic addition

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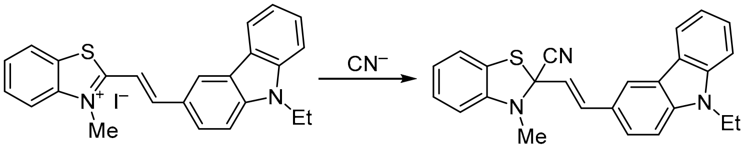


A benzothiazolium salt containing carbazole group has been synthesized in a good yield *via* simple condensation reaction. Its photophysical properties and affinity for cyanide anion (tetrabutylammonium cyanide) have been investigated. The compound exhibited quick and well visible UV/Vis absorption and fluorescence responses to cyanide anion in MeCN, as the yellow color faded and the orange fluorescence disappeared. The *in situ* analysis by ^{1}H NMR indicated that the cyanide anion was added to the C=N bond in the benzothiazolyl group.

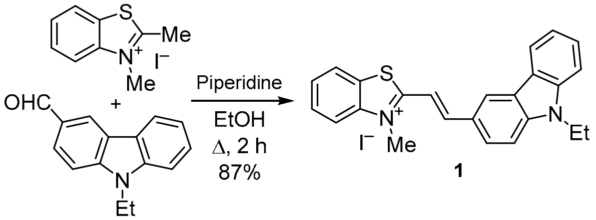
Keywords: benzothiazole, carbazole, cyanide, chemosensor, nucleophilic reaction.

Fluorescent chemosensors have been developed to identify important anions, with the aim of achieving high sensitivity and selectivity.[1–5] Among the numerous important anions, cyanide (CN^-) has attracted much attention because of its high toxicity. Cyanide traces can cause acute symptoms of poisoning, such as vomiting, convulsion, loss of consciousness, and even death.[6–8] Despite the toxicity, cyanides are important raw materials for the manufacturing of synthetic resins,[9] pharmaceuticals,[10] pesticides,[11] and in other industrial areas.[12–16] Meanwhile, cyanides are also used to dissolve gold and silver ores in the mining industry,[17] used in electroplating,[18] production of plastics,[19] and other industrial processes.[20] Thus, it has been an important task of chemists to develop highly selective chemosensors for cyanide anions.[21–25]

In our earlier work, series of fluorescent chemosensors for cyanide anions based on the ability of cyanide anion to undergo nucleophilic addition was reported.[26–31] Here we describe a structurally simple and easily synthesized benzothiazole-based chemosensor for the detection of CN^- based on nucleophilic addition. This chemosensor exhibits remarkable response to CN^- with obvious color and fluorescence changes, enabling simple visual detection.

The title compound **1** was synthesized by straightforward approach using a condensation reaction between *N*,2-dimethylbenzothiazolium iodide and *N*-ethylcarbazole-3-aldehyde (Scheme 1) with a yield of 87%. *N*,2-dimethylbenzothiazolium iodide was synthesized by the reaction between *N*,2-dimethylbenzothiazole and iodomethane with MeOH as solvent.[31]

Scheme 1



Linear absorption and steady-state fluorescence emission spectra of compound **1** in various solvents of different polarity are shown in Figure 1. The compound exhibited strong absorption in the blue region and strong orange fluorescence with high quantum yield (Φ 0.12 in MeCN). As shown in Figure 1, the UV/Vis absorption peaks showed little dependence on the solvent polarity, but the choice of solvents visibly affected the fluorescence emission intensity of compound **1**, which was clearly enhanced by increase in solvent polarity.

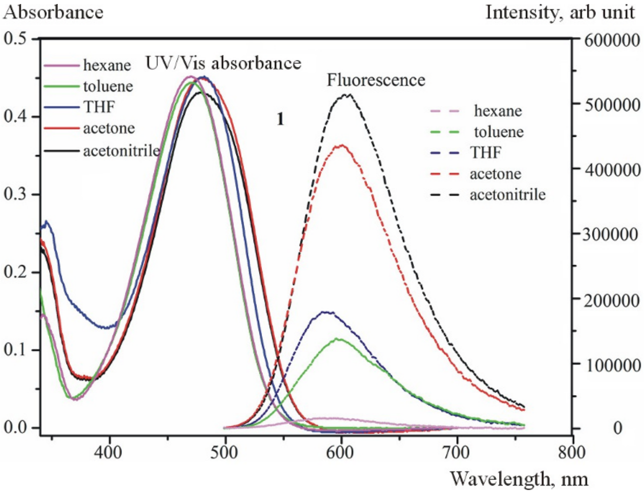


Figure 1. UV/Vis absorption and fluorescence emission spectra of compound **1** in various solvents.

First, the response of compound **1** to the presence of CN⁻ ions (tetrabutylammonium cyanide, TBACN) was measured as changes in UV/Vis absorption, which were fast (<5 s). Compound **1** showed one major absorption band at 469 nm, which was attributed to intramolecular charge transfer within the chemosensor from carbazolyl group to the benzothiazolium group. When cyanide anions were added, the absorption peak at 469 nm (ε 5.3 × 10^{-4} M^{-1} × cm^{-1}) gradually decreased and disappeared, while new absorption peaks appeared in the shorter wavelength region, with the isosbestic point at 326 nm. The color change is shown in the insert of Figure 2*a*. The changes in the absorption spectrum of solution were accompanied by disappearance of the yellow color, which allowed purely visual detection of CN⁻. Compound **1** also exhibited fluorescence spectral response to cyanide anions. As shown in Figure 2*b*, the fluorescence intensity at 600 nm decreased and orange fluorescence was nearly completely quenched when 3.5 equiv of cyanide anions were added. The color and fluorescence changes occurred immediately upon the addition of CN⁻. The reaction between compound **1** and CN⁻ was reversible, based on the fact that more than 1 equiv of cyanide anions were needed for complete absorption change and fluorescence quenching. The binding constant was calculated to be 7.53 × 10^5 M^{-1} based on absorbance titration data.[32] The detection limit of compound **1** for CN⁻ ions with the detection of fluorescence and absorbance were determined according to references.[33,34] The detection limits in MeCN were 4.6 × 10^{-5} μM (fluorescence) and 0.046 μM (absorbance), respectively. Compared to previous reports, this chemosensor possesses the following advantages. First, the synthesis and purification were very simple. Second, the response time was short (<5 s). Third, a visible color change from yellow to colourless with almost complete quenching of fluorescence was observed, which allowed visual detection of CN⁻.

The stoichiometry of the interaction between receptor **1** and cyanide anion was determined using UV/Vis absorption spectra. A maximum was observed in the Job plots (Fig. 3) at 0.5 fraction, indicating the formation of a 1:1 complex.

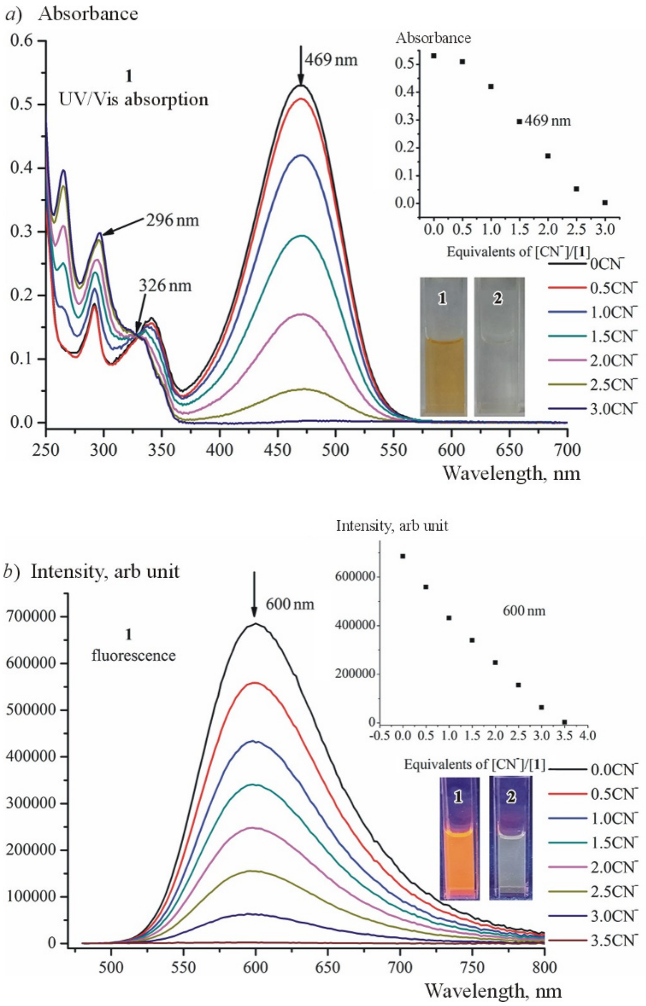


Figure 2. *a*) UV/Vis absorption and *b*) fluorescence emission spectra of compound **1** (*c* 1.0 × 10^{-5} M) in MeCN upon addition of different concentrations of CN⁻.

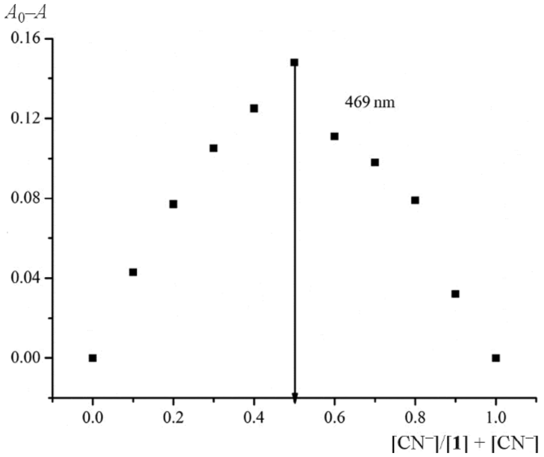


Figure 3. Job plots for the receptor-cyanide complex in MeCN upon the addition of CN⁻.

^1H NMR spectra of compound **1** before and after the addition of cyanide anions were investigated. As shown in Figure 4, after the addition of cyanide anions, the olefinic proton signals of compound **1** at 8.40 ppm (H_a, d, *J* = 15.6 Hz) and 8.04 ppm (H_b, d, *J* = 15.6 Hz) were shifted to 4.93 ppm

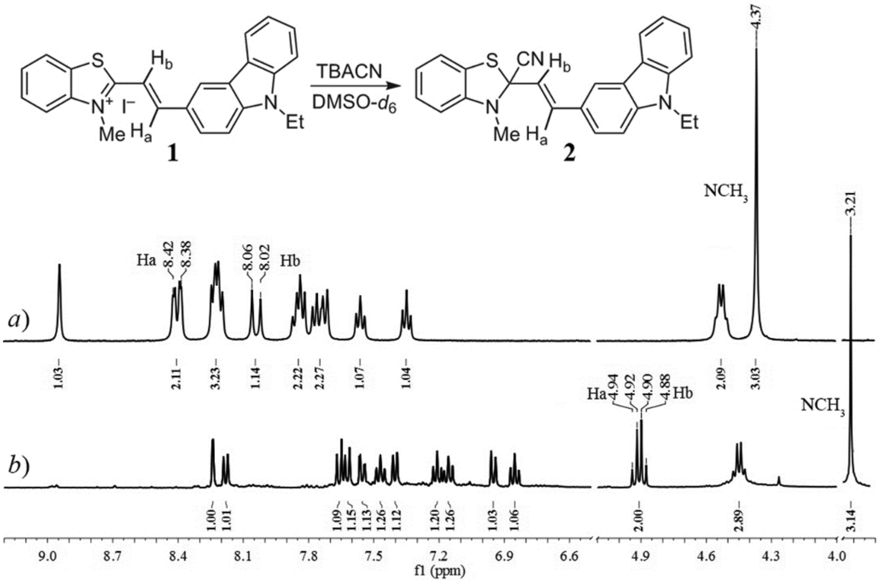


Figure 4. ^{1}H NMR spectra of compound **1** *a*) before and *b*) after the addition of cyanide anion in DMSO-d_6.

(H$_a$, d, J = 8.8 Hz) and 4.89 ppm (H$_b$, d, J = 8.8 Hz), respectively. The signal corresponding to NMe protons was shifted upfield from 4.37 to 3.21 ppm. Based on the small coupling constants of olefinic protons (J = 8.8 Hz), it is probable that compound **2** assumes a *cis* configuration upon the addition of cyanide anions.[35]

The electrophilicity of sp^2 carbon atoms toward CN$^-$ can be enhanced by the presence of positively charged nitrogen atom in the benzothiazolium unit.[36] The addition of cyanide disrupted the intramolecular charge transfer chain in the compound and resulted in a change of color and fluorescence emission. The obtained ^{1}H NMR spectrum and literature data related to analogous compounds[36] together allowed us to propose the mechanism for nucleophilic addition of cyanide ion to the positively polarized carbon atom in benzothiazole group.

The selectivity and competitive binding experiments of compound **1** to other anions and some small peptides as glutathione (GSH) and amino acids such as cysteine (Cys) and homocysteine (Hcy) were carried out. The addition of other anions such as SO_4^{2-}, SO_3^{2-}, SCN$^-$, F$^-$, Cl$^-$, Br$^-$, I$^-$, $H_2PO_4^-$, HS$^-$, and GSH, Cys, and Hcy caused only slight changes in UV/Vis absorption and fluorescence spectra (Fig. 5), which indicates good selectivity of compound **1** to CN$^-$. The aforementioned competing anions and molecules also did not interfere with the recognition reaction between compound **1** and CN$^-$.

In conclusion, a new fluorescent chemosensor with high selectivity and sensitivity for CN$^-$ ion was synthesized. The sensing mechanism may be typical nucleophilic addition reaction. This chemosensor possesses short responding time. Visible color change from yellow to colourless with almost complete fluorescence quenching is observed. We expect this chemosensor to be useful for detection of cyanide ion in a range of chemical industry and environmental samples.

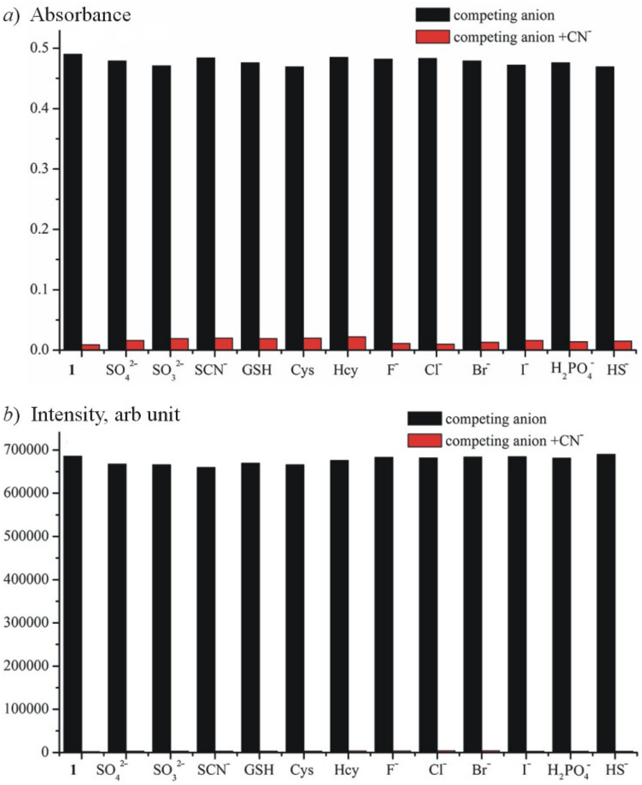


Figure 5. The changes of UV/Vis absorption (*a*, 469 nm) and fluorescence (*b*, 600 nm) of compound **1** (c 1.0 × 10^{-5} M) in the presence of various anions in response to CN$^-$ ions in MeCN.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 and 100 MHz, respectively) in DMSO-d_6 at room temperature with TMS as internal standard. ^{1}H NMR of compound **1** before and after the addition of cyanide anions in DMSO-d_6 was carried out. Firstly, ^{1}H NMR spectrum of compound **1** in DMSO-d_6 was measured. After 3 equiv TBACN were added, ^{1}H NMR spectrum of the solution was measured again. UV/Vis absorption and fluorescence spectra of compound **1** in MeCN were recorded at room temperature on a Shimadzu UV2550 spectrophotometer and a Horiba FluoroMax-4 fluorescence spectrometer with c 1.0 × 10^{-5} M. Fluorescence quantum yields were measured by using a standard method with rhodamine 6G as the standard.[37] The spectral changes were monitored with the addition of a solution of tetrabutylammonium cyanide as CN^- source in MeCN at room temperature. Mass spectrum was recorded on an Agilent Q-TOF6510 spectrometer with method of ionization being electrospray ionization. Elemental analyses were carried out on a Perkin Elmer 2400 elemental analyzer.

N,2-Dimethylbenzothiazole, *N*-ethylcarbazole-3-aldehyde, iodomethane, and piperidine used as starting materials were obtained from Aladdin industrial corporation. Solvents were obtained from Tianjin Fuyu industrial corporation and used without further purification.

2-[(*E*)-2-(9-Ethyl-9*H*-carbazol-3-yl)ethenyl]-3-methyl-1,3-benzothiazol-3-ium iodide (1). To a solution of *N*-ethylcarbazole-3-aldehyde (0.22 g, 0.01 mol) and *N*,2-dimethylbenzothiazolium iodide (0.29 g, 0.01 mol) in EtOH (30 ml), a few drops of piperidine were added and the mixture was refluxed for 5 h. After cooling to room temperature, the precipitate was filtered and washed with CH_2Cl_2 to afford the desired compound **1**. Yield 0.43 g (87%), light yellow-red amorphous powdered solid, mp 265–267°C. ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.36 (3H, t, J = 7.2, $CH_2C\underline{H}_3$); 4.37 (3H, s, $NC\underline{H}_3$); 4.53 (2H, q, J = 7.2, $C\underline{H}_2CH_3$); 7.35 (1H, t, J = 7.2, H Cbz); 7.56 (1H, t, J = 7.2, H Cbz); 7.72 (1H, d, J = 8.4, H Cbz); 7.76 (1H, t, J = 7.6, H Cbz); 7.82 (1H, d, J = 8.4, H-11 Cbz); 7.85 (1H, t, J = 7.2, H Ar); 8.04 (1H, d, J = 15.6, CH=); 8.19–8.24 (3H, m, H Ar); 8.39 (1H, d, J = 8.4, H-10 Cbz); 8.40 (1H, d, J = 15.6, CH=); 8.94 (1H, s, H-4 Cbz). ^{13}C NMR spectrum, δ, ppm: 13.8; 36.2; 37.4; 110.0; 116.4; 120.2; 120.6; 122.2; 122.9; 123.7; 124.0; 125.1; 126.8; 127.3; 127.9; 128.1; 129.1; 140.3; 141.9; 142.2; 150.5; 171.9. Found, m/z: 369.1400 $[M]^+$. $C_{24}H_{21}N_2S$. Calculated, m/z: 369.1425. Found, %: C 57.88; H 4.25; N 5.63. $C_{24}H_{21}IN_2S$. Calculated, %: C 58.07; H 4.26; N 5.64.

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