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A new sensitive and selective fluorescence probe for detection of cyanide

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ABSTRACT

A class of new fluorescence probe α-p-trifluoroacetamidophenyl-4-alkoxycinnamonitrile for detection of cyanide anion was synthesized by the trifluoroacetylation of the fluorophore α-p-aminophenyl-4-alkoxycinnamonitrile. It was found that the probe could selectively detect cyanide anions, even in the presence of hydrogen sulfite and dicarbonate anions which were reported to easily interfere with the detection. The concentration of the cyanide anions that could be detected was as low as 1.0 μM.

1. Introduction

Cyanide anion is one of most toxic compounds with a lethal dose of 0.5–3.5 mg/kg in human body and an lethal concentration of 23–26 μM in human blood [1,2], but it is still widely used in many industrial areas such as gold mining, electroplating, metallurgy, chemical products, and so on [3,4]. Therefore, to detect and analyze cyanide anions always attracts intensive interest [5–8]. Especially in recent several years, a large number of reports about the analysis methods of cyanide anion have been rapidly documented, including those based on gold nano-particles etching by cyanide [9–13], formation of Cu(II)-cyanide complexes [14–16] and B(III)-cyanide complexes [17,18], nucleophilic addition of unsaturated bond by cyanide anion [19–30], and so on. By the extensive effort, both selectivity and sensitivity for the detection of cyanide anions have been improved very much. For example, the method based on gold nano-particles etching could detect cyanide anions as low as 8.0×10^{-8} M in aqueous solution [12], which showed a very high sensitivity. However, gold nano-particles etching and Cu(II)-cyanide complex methods are obviously unsuitable for the solution containing thiols or sulfide anions which could form very stable complex with heavy metals. The method based on nucleophilic addition of unsaturated bond by cyanide anion, such as addition of trifluoroacetamide compounds [25–29], usually has high selectivity, but the sensitivity is not high. Other methods also have questions of sensitivity, selectivity or practicality. So that, to develop sensitive, selective and practical method for detection of cyanide anions is still a challenge. Here we report that a class of new fluorescence probe α-p-trifluoroacetamidophenyl-4-alkoxycinnamonitrile for cyanide anion was synthesized and could selectively detect cyanide anions, even in the presence of hydrogen sulfite and dicarbonate anions which were reported to easily interfere with the detection. The concentration of the cyanide anions that could be detected was as low as 1.0 μM.

2. Experimental

2.1. Materials and measurements

All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received unless otherwise indicated. ^1H NMR and ^{13}C NMR spectra were measured on a 400 MHz spectrometer at 298 K in DMSO-d_6 or acetone-d_6. Absorption spectra were recorded on a UV–vis spectrophotometer. Fluorescence spectra were collected on a fluorophotometer at 298 K with ex/em slits 5/5 or 5/10.

2.2. Synthesis of fluorescence probes

The synthetic route is shown in Scheme 1.

Synthesis of compound **3**: a solution of compound **2** [31] (1.85 g, 6.97 mmol) and $SnCl_2 \cdot 2H_2O$ (7.86 g, 34.85 mmol) in ethanol (95%, 40 mL) was refluxed for 5 h. After the reaction solution was cooled to about 0 °C in an iced bath, saturated K_2CO_3

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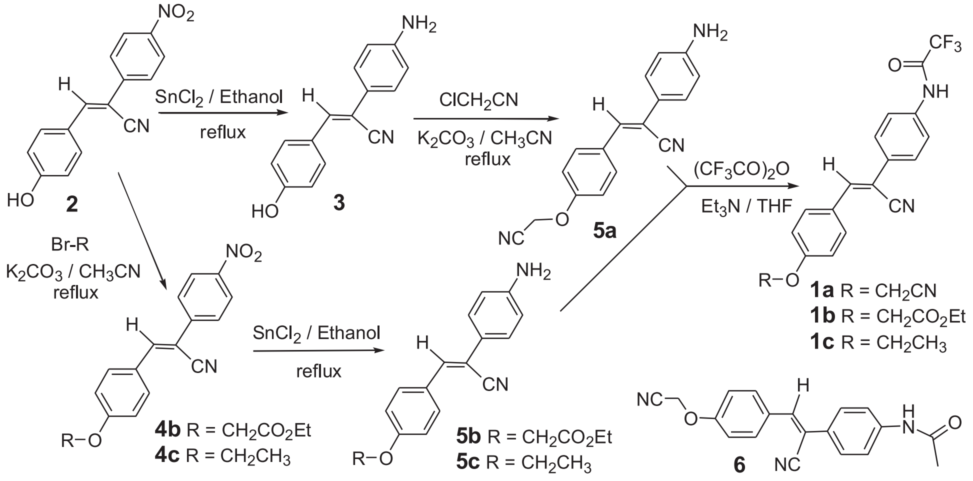


Scheme 1. The synthetic route of fluorescence probes and structure of acetamide compound **6**.

solution was slowly added under stirring until the pH 8–9. Then the mixture was extracted three times with ethyl acetate, and the combined organic layer was washed by saturated brine and dried over anhydrous Na_2SO_4. Solvents were evaporated under reduced pressure, and the obtained solid was recrystallized with ethanol to afford yellow powder (1.6 g, yield 97%). *Mp* 218–219 °C; IR (KBr) v 3485, 3389, 3336, 3028, 2212, 1896, 1603, 1584, 1514, 1457, 1393, 1350, 1279, 1248, 1173, 1110, and 829 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d$_6$) δ 8.91 (s, 1H), 7.83 (d, 2H, J=8.4 Hz), 7.49 (s, 1H), 7.44 (d, 2H, J=8.4 Hz), 6.95 (d, 2H, J=8.8 Hz), 6.75 (d, 2H, J=8.8 Hz), 5.0 (s, 2H); ^{13}C NMR (100 MHz, acetone-d$_6$) δ 158.9, 149.3, 137.3, 130.8, 126.6, 126.4, 123.1, 118.7, 115.8, 114.4, and 108.1.

Synthesis of compound **5a**: to the solution of chloroacetonitrile (2 mL, 23.6 mmol) in acetonitrile (10 mL) compound **3** (0.5 g, 2.1 mmol) and K_2CO_3 (0.44 g, 3.2 mmol) was added. The mixture was refluxed for 30 min and acetonitrile was removed under reduced pressure. Ethyl acetate was added and the resultant mixture was washed by saturated brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The obtained solid was recrystallized with THF and ethanol to give pale yellow powder (0.50 g, 86%). *Mp* 197–199 °C; IR (KBr) v 3288, 3201, 3131, 3087, 2226, 1714, 1606, 1549, 1516, 1446, 1422, 1359, 1310, 1281, 1254, 1229, 1209, 1187, 1157, 1050, 903, and 833 cm^{-1}. ^{1}H NMR (400 MHz, acetone-d$_6$) δ 10.41 (s, 1H), 8.09–8.05 (m, 2H), 7.89 (d, 3H, J=8 Hz), 7.84–7.81 (m, 2H), 7.29–7.25 (m, 2H), 5.24 (s, 2H); ^{13}C NMR (100 MHz, acetone-d$_6$) δ 158.4, 155.1, 154.7, 141.3, 137.2, 131.8, 131.3, 128.6, 126.5, 121.2, 117.8, 115.6, 115.2, 108.8, and 53.4.

Synthesis of compound **1a**: a solution of compound **5a** (0.45 g, 1.63 mmol) and triethylamine (0.68 mL, 4.9 mmol) in dry THF (5 mL) was cooled to 0 °C in an iced bath. To this solution at 0 °C, another solution of trifluoroacetic anhydride (0.58 mL, 4.08 mmol) in dry THF (2 mL) was slowly dropped over 20 min. The reaction mixture was raised to room temperature and continued to stir over night. After THF was evaporated under reduced pressure, ethyl acetate was added. The solution was washed by saturated brine, dried over anhydrous Na_2SO_4, and evaporated to dryness. The obtained solid was recrystallized with ethanol and THF to afford white powder (0.48 g, 77%). *Mp* 204–206 °C; IR (KBr) v 3444, 3357, 3217, 3040, 2972, 2205, 1625, 1601, 15147, 1436, 1356, 1289, 1258, 1221, 1178 , 1134, 1118, 1046, and 834 cm^{-1}.^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.89 (d, 2H, J=8.88 Hz), 7.66 (s, 1H), 7.42 (d, 2H, J=8.6 Hz), 7.22–7.18 (m, 2H), 6.65 (d, 2H, J=8.6 Hz), 5.59 (s, 2H), 5.25 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 157.5, 150.4, 136.5, 130.9, 129.3, 127.1, 121.4, 119.0, 116.9, 115.6, 114.4, 109.9, and 54.0.

Synthesis of compound **4b**: compound **2** (1.0 g, 3.75 mmol), K_2CO_3 (0.62 g, 4.50 mmol), acetonitrile (10 mL), and ethyl bromoacetate (1.25 g, 7.5 mmol) were mixed in a flask. After the mixture was refluxed for 3 h, acetonitrile was evaporated under reduced pressure and ethyl acetate was added. The organic layer was washed by saturated brine, dried over anhydrous Na_2SO_4, and evaporated to dryness. The obtained solid was recrystallized with ethanol to give yellow powder (0.98 g, 74%). *Mp* 168–169 °C; IR (KBr) v 3107, 3082, 2920, 2446, 2216, 1754, 1583, 1512, 1479, 1458, 1440, 1375, 1339, 1309, 1267, 1218, 1180, 1112, 1077, 1019, and 852 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, 2H, J=8.8 Hz), 7.96 (d, 2H, J=8.8 Hz), 7.82 (d, 2H, J=9.2 Hz), 7.61 (s, 1H), 7.01(d, 2H, J=8.8 Hz), 4.71 (s, 2H), 4.30 (m, 2H), 1.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 160.4, 147.6, 144.7, 140.9, 131.9, 126.6, 124.4, 117.6, 115.3, 107.0, 65.2, 61.7, and 14.2.

Synthesis of compound **4c**: the synthesis method was similar with that of compound **4b**. Yellow powder (1.0 g, 90%). *Mp* 184–185 °C; IR (KBr) v 2983, 2206, 1575, 1509, 1395, 1375, 1336, 1308, 1264, 1176, 1105, 1039, and 852 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, 2H, J=8.8 Hz), 7.94 (d, 2H, J=8.8 Hz), 7.81 (d, 2H, J=9.2 Hz), 7.60 (s, 1H), 6.99 (d, 2H, J=8.8 Hz), 4.12 (m, 2H), 1.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 147.5, 145.1, 141.2, 132.0, 126.3, 125.5, 124.3, 117.8, 115.1, 105.9, 63.9, and 14.7.

Synthesis of compound **5b**: a solution of compound **4b** (2.45 g, 6.97 mmol) and $SnCl_2 \cdot 2H_2O$ (7.86 g, 34.85 mmol) in ethanol (95%, 40 mL) was refluxed for 5 h. After the solution was cooled to about 0 °C in an iced bath, saturated K_2CO_3 solution was slowly added under stirring until the pH 8–9. Then the mixture was extracted three times with ethyl acetate, and the combined organic layer was washed by saturated brine and dried over anhydrous Na_2SO_4. Solvents were evaporated under reduced pressure, and the obtained solid was recrystallized with ethanol to afford yellow powder (2.0 g, yield 88%). *Mp* 159–162 °C; IR (KBr) v 3446, 3359, 3235, 3029, 2983, 2910, 2213, 1749, 1715, 1636, 1602, 1513, 1466, 1433, 1382, 1300, 1254, 1220, 1176, 1079, and 830 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d$_6$) δ 7.90 (d, 2H, J=8.8), 7.54 (s, 1H), 7.47–7.45 (m, 2H), 7.05 (d, 2H, J=8.84 Hz), 6.75 (d, 2H, J=8.64), 5.06 (s, 2H), 4.81 (s, 2H), 4.26–4.20 (m, 2H), 1.28–1.24 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 168.9, 159.0, 150.3, 136.8, 130.7, 128.1, 127.0, 121.5, 119.2, 115.4, 114.4, 109.0, 65.1, 61.2, and 14.5.

Synthesis of compound **5c**: the synthesis method was similar with that of compound **5b**. Yellow powder (1.6 g, yield 87%). *Mp* 150–152 °C; IR (KBr) v 3459, 3367, 3215, 2979, 2206, 1601, 1511, 1441, 1298, 1243, 1175, 1118, 1087, 1042, and 833 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 7.83 (d, 2H, J=8.84 Hz), 7.61 (s, 1H), 7.40 (d, 2H, J=8.6 Hz), 7.04 (d, 2H, J=8.84 Hz), 6.64 (d, 2H, J=8.64), 5.54 (s, 2H), 4.12–4.07 (m, 2H), 1.37–1.33 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 160.0, 150.2, 137.1, 130.8, 127.3, 126.9, 121.7, 119.25, 115.2, 114.4, 108.4, 63.8, and 15.0.

Synthesis of compound **1b**: the synthesis method was similar with that of compound **1a**. Pale yellow powder (yield 80 %). *Mp* 119–121 °C; IR (KBr) v 3274, 3186, 3120, 3073, 3002, 2946, 2911, 2216, 1732, 1592, 1518, 1414, 1370, 1288, 1266, 1186, 1075, 1028, and 832 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d$_6$) δ 10.40 (s, 1H), 8.00 (d, 2H, J=0.80 Hz), 7.89–7.80 (m, 5H), 7.12 (d, 2H, J=8.88 Hz), 4.86 (s, 2H), 4.28–4.22 (m, 2H), 1.30–1.26 (m, 3H); ^{13}C NMR (100 MHz, acetone-d$_6$) δ 170.8, 162.7, 139.7, 134.7, 133.8, 130.0, 129.0, 123.8, 123.7, 120.6, 120.1, 117.7, 117.2, 110.4, 67.5, and 63.4.

Synthesis of compound **1c**: the synthesis method was similar with that of compound **1a**. White powder (yield 79%). *Mp* 190–193 °C; IR (KBr) v 3277, 3198, 3130, 2983, 2937, 2224, 2215, 1713, 1606, 1548, 1516, 1418, 1299, 1254, 1204, 1186, 1168, 1153, 1120, 1048, 837, and 823 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 11.44 (s, 1H), 7.93 (d, 3H, J=8.4 Hz), 7.823–7.759 (m, 4H), 7.09 (d, 2H, J=8.8 Hz), 4.13–4.113 (m, 2H), 1.377–1.342 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 161.0, 155.2, 154.8, 142.7, 137.2, 131.7, 131.6, 126.6, 126.5, 121.8, 120.5, 118.8, 117.6, 115.4, 114.7, 106.6, and 63.9.

Synthesis of compound **6**: the synthesis method was similar with that of compound **1a**. White powder (yield 80%). *Mp* 244–246 °C; IR (KBr) v 3300, 3256, 3186, 3116, 2214, 1667, 1600, 1514, 1408, 1373, 1325, 1293, 1259, 1224, 1177, 1052, and 836 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.20 (s, 1H), 7.97 (d, 2H, J=9.2 Hz), 7.91 (s, 1H), 7.70 (m, 4H), 7.24 (d, 2H, J=8.8 Hz), 5.27 (s, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 169.0, 158.1, 140.8, 140.6, 131.4, 128.8, 128.7, 126.7, 119.6, 118.6, 116.9, 115.7, 108.8, 54.0, and 24.5.

3. Results and discussion

3.1. Synthesis and fluorescence mechanism of probes

As shown in Scheme 1, fluorescence probes, α-p-trifluoroacetamidophenyl-4-alkoxycinnamonitrile **1a**–**1c**, could be synthesized from starting compound α-p-nitrophenyl-4-hydroxycinnamonitrile **2**, which was easily prepared according to the synthetic procedure in literature [31] from commercially available p-nitrophenylacetonitrile and p-hydroxybenzaldehyde. All compounds including **2**–**6** prepared in Scheme 1 could be purified just by recrystallization, so that the synthesis of the fluorescence probes could be easily prepared on a large scale.

Quantum yields of all the synthesized compounds were measured using quinine bisulfate in 1 N H_2SO_4 as the standard (Table 1). Quantum yield of nitro compounds **2**, **4b** and **4c** was 0.51, 1.37 and 0.33%, respectively, which was smaller than that of the corresponding amino compound **3** (1.61%), **5b** (8.82%) and **5c** (2.65%). This indicated that the nitro group, which is strong electron-withdrawing, enhanced electron transfer of oxygen atom of hydroxyl or alkoxy group onto aromatic rings, while the amino group, which is strong electron-donating, inhibited the electron transfer. It is well known that photo-induced electron transfer (PET) generally leads to weakened emission or fluorescence quench [32,33]. For nitro compounds **2**, **4b** and **4c**, the PET from oxygen atom of hydroxyl or alkoxy group to aromatic rings would also easily occur due to the strong electron-withdrawing effect of nitro groups, which resulted in weakened fluorescence. But in amino compounds **3**, **5b** and **5c**, the PET was inhibited because of the strong electron-donating effect of amino groups, and a strong fluorescence was observed (Scheme 2). Furthermore, compared with ethyl group of **5c**, which was electron-donating, the cyanomethyl group of **5a** and ethoxycarbonylmethyl group of **5b** were electron-withdrawing and could reduce the electron transfer of oxygen atom, therefore, they had larger quantum yield (25.05 and 8.82%, respectively) than **5c** (2.65%). After amino group is connected with trifluoroacetyl group, the resultant trifluoroacetamide group is electron-withdrawing rather than electron-donating due to strong electron-withdrawing of trifluoroacetyl group, which will facilitate the PET process and make the fluorescence weakened. Therefore, the trifluoroacetamide compounds **1a**, **1b** and **1c** had a very low quantum yield of 0.34, 0.22 and 0.25%, respectively. For further demonstrating the effect of PET on the fluorescence of the probes, acetamide compound **6** bearing acetyl group instead of trifluoroacetyl group was synthesized. Obviously, acetyl group has a weaker electron-withdrawing effect than trifluoroacetyl group, which will reduce the electron transfer of oxygen atom onto phenyl rings and make a stronger fluorescence emission. It was true that acetamide **6** had a larger quantum yield (1.02%) than the corresponding trifluoroacetamides **1a**, **1b** and **1c**. It is known that the trifluoroacetamide group is easily converted into cyanohydrin anion by nucleophilic addition of cyanide anion [25–29], which will lead to strong fluorescence due to electron-donating effect of cyanohydrin anion (Scheme 2). This phenomenon could be exploited to detect cyanide anion.

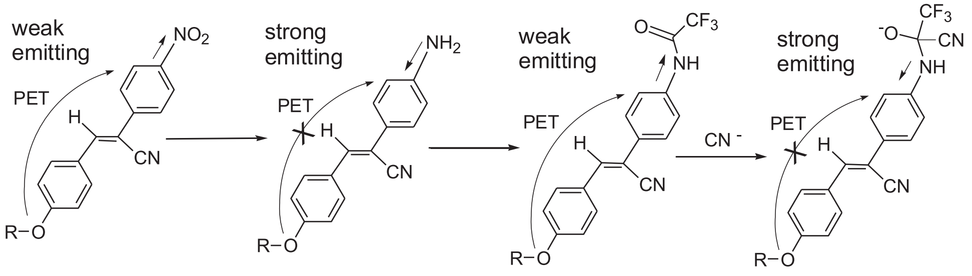
Table 1
Quantum yields (Φ%) of compounds.

	2	**3**	**4b**	**4c**	**6**	
Φ%	0.51	1.61	1.37	0.33	1.02	
	5a	**5b**	**5c**	**1a**	**1b**	**1c**
Φ%	25.05	8.82	2.65	0.34	0.22	0.25

Measured using quinine bisulfate in 1 N H_2SO_4 as the standard.

3.2. Sensitivity and selectivity of fluorescence probes for detection of cyanide anion

By addition of cyanide anions, trifluoroacetamide **1a**, **1b** or **1c** truly exhibited stronger fluorescence (Fig. 1). While the solution of **1a** in a mixed solvent of water and THF (v/v, 7:3) had a weak emission at a emission maximum wavelength λ_{max} of 420 nm, the



Scheme 2. Schematic illustration for the photo-induced electron transfer (PET) of oxygen atom onto phenyl rings which determined the fluorescence intensity.

addition of cyanide anion (6.0×10^{-5} M) led to a strong emission of the solution at emission $\lambda_{\max}$ of 506 nm. Not only did the fluorescence intensity increase, but also the emission wavelength had a bathochromic shift of up to 86 nm, indicating that the nucleophilic addition of trifluoroacetamide group by cyanide anion occurred. At the emission $\lambda_{\max}$ of 506 nm, the fluorescence intensity of **1a** was 18.7 but that of the mixture of **1a** and cyanide anion was 389, which gave a fluorescence intensity ratio up to 21 for mixture of **1a** and cyanide ion vs. **1a**. By addition of cyanide anion, both the fluorescence intensity and the emission wavelength $\lambda_{\max}$ of **1b** or **1c** increased, but the change was much less than that of **1a**. The bathochromic shift was 68 and 59 nm, and fluorescence intensity ratio was 16 and 10 for **1b** and **1c**, respectively, in the solutions with and without cyanide anions. The fluorescence intensity ratio of **1a**, **1b** and **1c** aroused by cyanide anion was 21, 16 and 10, respectively, having an order of **1a** > **1b** > **1c**. From Table 1, the quantum yield ratio of amino compounds **5a**, **5b** and **5c** vs. corresponding trifluoroacetamides **1a, 1b** and **1c** was 74, 40 and 11, respectively, showing a similar order to the fluorescence intensity ratio. This result further indicated that the electron-withdrawing trifluoroacetamide groups in **1a**, **1b** and **1c** had been converted into electron-donating ones just like amino group.

Because the fluorescence intensity change of **1a** aroused by cyanide anion was much larger than that of **1b** and **1c**, it was chosen to test as fluorescence probe for cyanide anion. As shown in Fig. 2A, fluorescence intensity of **1a** at a concentration of 1.0×10^{-4} M increased when the concentration of cyanide anion gradually increased from 1.0×10^{-5} M to 5.0×10^{-4} M in the mixed solvent of water and THF (v/v 7:3). Even the concentration of cyanide anions was in the range of larger than that of **1a**, the fluorescence was also gradually elevated, indicating that **1a** could detect cyanide anions in a relatively wide range of concentrations. When the concentration of cyanide anions changed in the range of very small concentration from 1.0×10^{-6} M to 5.0×10^{-5} M, the fluorescence intensity of **1a** also gradually increased. Even in the presence of 1.0×10^{-6} M cyanide anion, the fluorescence intensity of **1a** at about 506 nm also had an obvious increase compared with that of **1a** without cyanide anion. This meant that **1a** could detect cyanide anion at a concentration as low as 1.0 μM.

Upon addition of other convenient anions, including F^-, Cl^-, Br^-, I^-, SO_4^{2-}, HSO_4^-, NO_3^-, NO_2^-, H_2PO_4-, Ac^-, and N_3^-, the fluorescence spectrum of **1a** did not display any change. As shown in Fig. 3, **1a** showed no emission at 506 nm in the presence of other anions with a concentration of 2×10^{-4} M, but it had strong fluorescence after mixed with 5×10^{-5} M CN^-. Even a mixture of all the other anions did not turn on the fluorescence of **1a**, but it emitted strong fluorescence at 506 nm as long as the cyanide anion was added into the mixture (Fig. 4). This result demonstrated that **1a** was a highly selective fluorescence probe for cyanide anion.

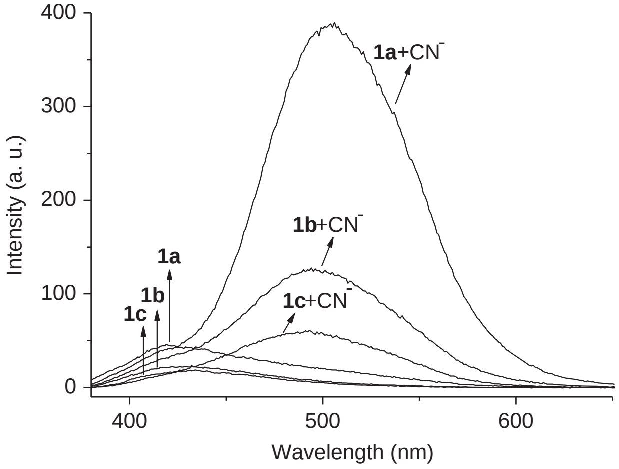


Fig. 1. Fluorescence spectra of **1a**, **1b** or **1c** with and without potassium cyanide in the mixed solvent of water and THF (v/v 7:3). $[CN^-]=6.0\times10^{-5}$ M, $[\mathbf{1a}]=[\mathbf{1b}]=[\mathbf{1c}]=1.0\times10^{-4}$ M; $\lambda_{ex}=365$ nm, ex/em slits=5/5.

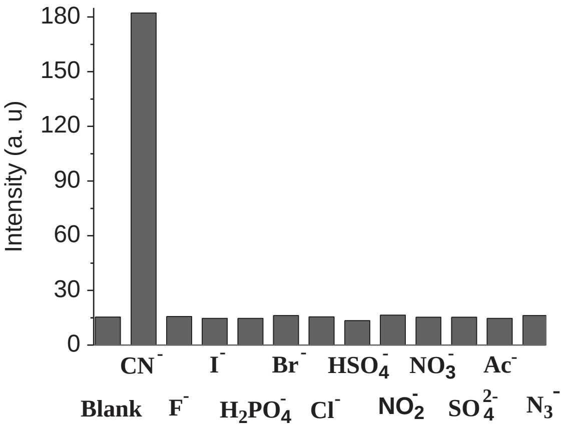


Fig. 3. Fluorescence intensity of **1a** at 505 nm after addition of CN^-, F^-, Cl^-, Br^-, I^-, SO_4^{2-}, HSO_4^-, NO_3^-, NO_2^-, $H_2PO_4^-$, Ac^-, or N_3^-. $[\mathbf{1a}]=1.0\times10^{-4}$ M, [other anion]$=5.0\times10^{-4}$ M, $[CN^-]=5.0\times10^{-5}$ M, $\lambda_{ex}=365$ nm, ex/em slits=5/5.

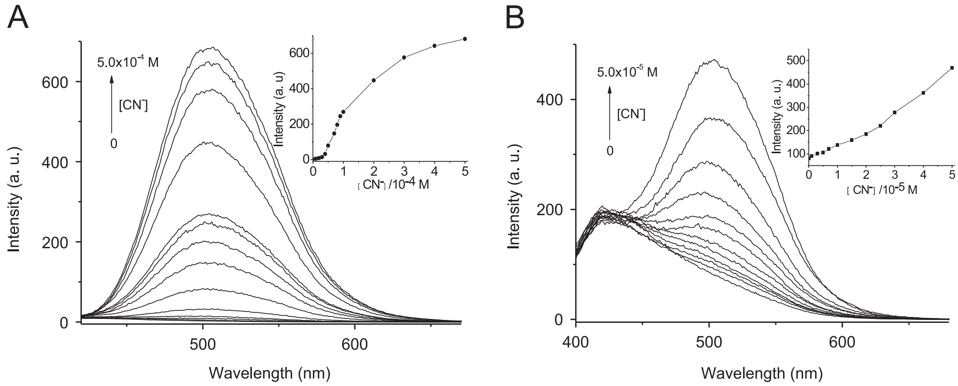


Fig. 2. Change of fluorescence spectrum of **1a** with concentration of cyanide anion in a mixed solvent of water and THF (v/v 7:3). A) $[CN^-]=0$, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, $50/10^{-5}$ M. B) $[CN^-]=0$, 0.1, 0.3, 0.5, 0.7, 1, 1.5, 2, 2.5, 3, 4, $5/10^{-5}$ M. $[\mathbf{1a}]=1.0\times10^{-4}$ M; $\lambda_{ex}=365$ nm. Inset, curve of fluorescence intensity of **1a** with concentration of cyanide anion.

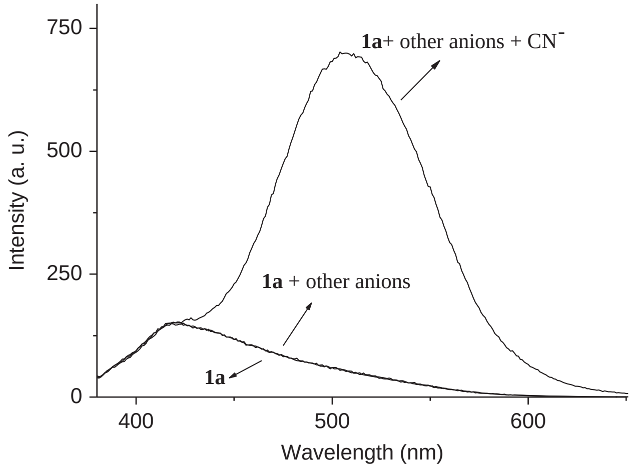


Fig. 4. Fluorescence spectra of **1a** in the mixture of other anions including F^-, Cl^-, Br^-, I^-, SO_4^{2-}, HSO_4^-, NO_3^-, NO_2^-, $H_2PO_4^-$, Ac^-, and N_3^- with and without CN^-. [**1a**]$=1.0\times10^{-4}$ M, [each other anion]$=1.0\times10^{-4}$ M, [CN^-]$=1.0\times10^{-4}$ M, $\lambda_{ex}=365$ nm, ex/em slits=5/10.

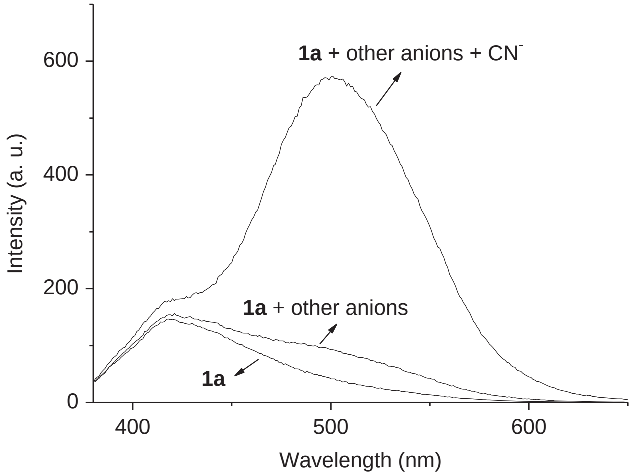


Fig. 6. Fluorescence spectrum of **1a** in the mixture of HS^-, HCO_3^-, HPO_4^{2-}, F^-, Cl^-, Br^-, I^-, SO_4^{2-}, SO_3^{2-}, NO_3^-, NO_2^-, Ac^-, $C_2O_4^-$$SCN^-$ and N_3^- with and without CN^-. [**1a**]$=1.0\times10^{-4}$ M, [each anion]=[CN^-]$=5\times10^{-5}$ M, $\lambda_{ex}=365$ nm, ex/em slits=5/10.

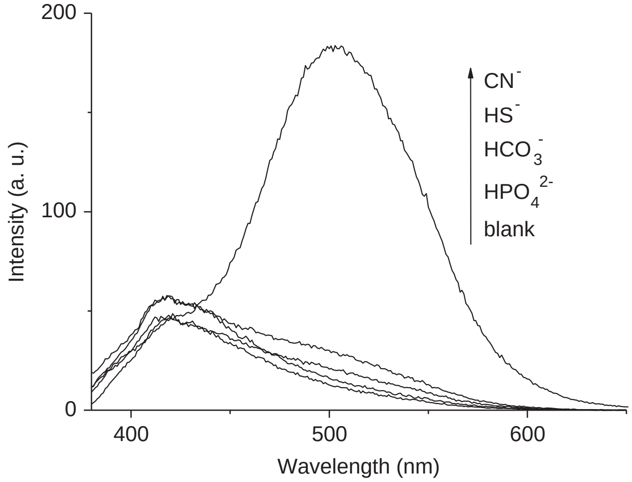


Fig. 5. Fluorescence spectrum of **1a** after addition of CN^-, HS^-, HCO_3^-, or HPO_4^{2-}. [**1a**]$=1.0\times10^{-4}$ M, [anion]$=5.0\times10^{-5}$ M, $\lambda_{ex}=365$ nm, ex/em slits=5/5.

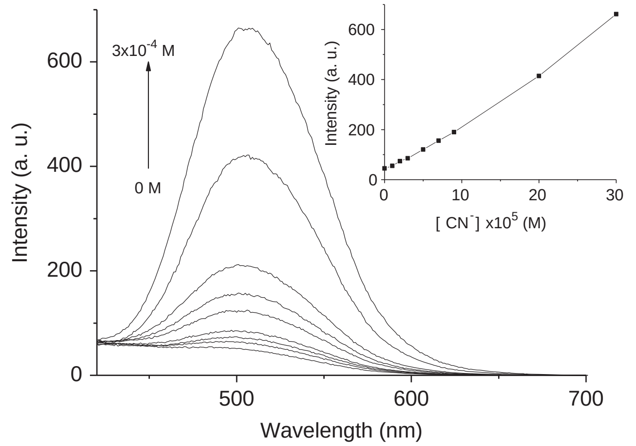


Fig. 7. Change of fluorescence spectrum of **1a** with concentration of cyanide anion in a mixed solvent of Yangzi River water and THF (v/v 7:3) with 1.5×10^{-4} M phosphate buffer saline (pH 7.0). [CN^-]=0, 1, 2, 3, 5, 7, 9, 20, 30/10^{-5} M; [**1a**]$=1.0\times10^{-4}$ M; $\lambda_{ex}=365$ nm, ex/em slits=5/5. Inset, curve of fluorescence intensity of **1a** with concentration of cyanide anion.

From reported literatures, effect of anions HS^-, HCO_3^-, and HPO_4^{2-} on the detection of cyanide is rarely mentioned when selectivity of a fluorescence probe for cyanide anion is assessed. However, these three anions are also very common, especially as a metabolite of living beings. Furthermore, a water sample was easily contaminated by HCO_3^- when it adsorbed carbon dioxide from atmosphere. Many fluorescence probes based on gold nanoparticles or copper complexes for cyanide anion are obvious to be interfered with anions containing sulfur atom which could form stable complex with heavy metal ions. Considering the fact that these three anions are ignored by literatures, Li and coworkers tested the response of them to N-2-anthracenyl trifluoroacetamide fluorescence probe for cyanide anion [25], and found that these three anions led to obvious fluorescence increase, especially, HCO_3^- and HS^- almost leading to same fluorescence intensity when they compared with cyanide anion in equal molar amount. Here, with **1a** as probe, upon addition of these three anions, the fluorescence spectrum of **1a** changed very little. As shown in Fig. 5, 5.0×10^{-5} M of these three anions only led to an intensity of 27 while the same concentration of cyanide anion resulted in an intensity of 182, which had a difference of more than six fold. Even in the mixture of HS^-, HCO_3^-, HPO_4^{2-}, F^-, Cl^-, Br^-, I^-· SO_4^{2-}, SO_3^{2-}, NO_3^-, NO_2^-, $C_2O_4^-$, Ac^-, SCN^- and N_3^-, **1a** could also detect the cyanide anion (Fig. 6), indicating the HS^- and HCO_3^- had very little interference with the analysis of the cyanide anion.

To study the applicability of the fluorescent probe **1a** for natural systems, real water samples including river water, lake water and tap water were tested. The river water and lake water were taken from Yangzi River and East Lake in Wuhan, respectively. As shown in Fig. 7, after the distilled water in the mixed solvent of water and THF (v/v 7:3) was replaced by Yangzi River water, fluorescence intensity of **1a** increased with concentration of cyanide anion, indicating this fluorescence probe could be used to detect cyanide anion in river water. Due to being not neutral, the river water was adjusted to pH 7.0 by phosphate buffer saline. In similar way, the cyanide anion in lake water and tap water could be also detected by this probe (Figs. S31–S32).

4. Conclusions

In conclusion, a new fluorescence probe based on trifluoroacetamide for cyanide anion was synthesized and the electronic effect of substituent groups played a key role on the fluorescence of the probe. It was found that the probe could selectively detect cyanide anions even in the presence of hydrogen sulfite and dicarbonate anions which were reported to easily interfere with the detection, and the concentration of cyanide anion that could be detected was as low as 1.0 μM, displaying a high sensitivity and selectivity for detection of cyanide anion. The research for using this class of new fluorescence probes for analysis of other analytes is in progress.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.01.048.

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