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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.

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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. ^{1}H 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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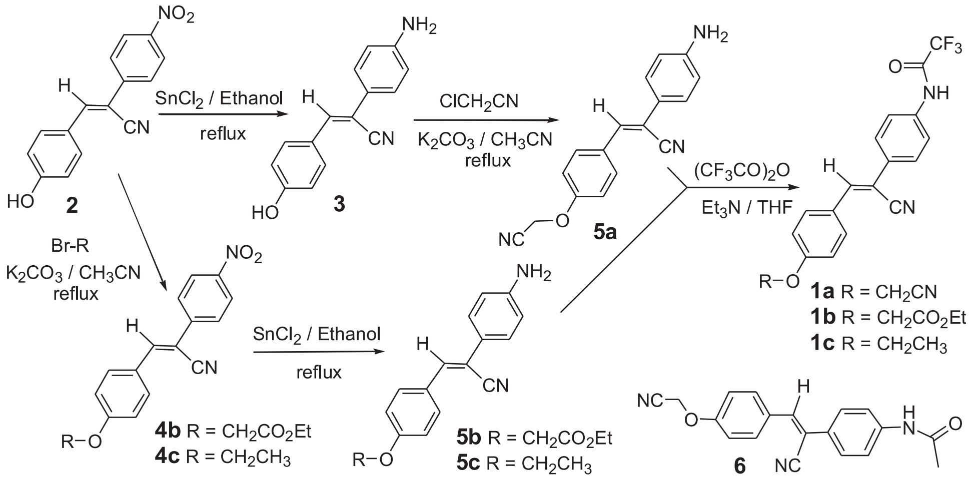

Scheme 1. The synthetic route of fluorescence probes and structure of acetamide compound **6**.

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$_2$SO$_4$. 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) ν 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$_2$CO$_3$ (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$_2$SO$_4$, 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) ν 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$_2$SO$_4$, 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) ν 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$_2$CO$_3$ (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$_2$SO$_4$, 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) ν 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) ν 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$2H$_2$O (7.86 g, 34.85 mmol) in ethanol (95%, 40 mL) was refluxed for 5 h. After the solution was cooled to about 0 °C in an iced bath, saturated K$_2$CO$_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$_2$SO$_4$. 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) ν 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) ν 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),

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