HIGHLY SELECTIVE COLORIMETRIC AND FLUORESCENT CHEMOSENSOR FOR CN^- BASED ON o-TOLIDINE

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A colorimetric and fluorescent chemical sensor N1 based on o-tolidine was designed and synthesized, which can be used as an efficient colorimetric and fluorescent sensor for CN^-. Compared to other common anions, the color of N1 solution was observed from yellow to colorless after the addition of CN^-, while under UV lamp the yellow fluorescence of N1 was clearly annihilated. In addition, the detection limit on fluorescence response of N1 for CN^- was down to $4.43 \cdot 10^{-7}$ M. ^{1}H NMR titration suggested that the ICT process occurred between N1 and CN^-, and the reaction ratio was 1:2. N1 was successfully used to detect cyanide content in bitter almonds, and N1-based test strips were also produced, which could more conveniently and effectively detect the CN^- in aqueous solution.

Keywords: *chemosensor, colorimetric, fluorescence, intramolecular charge transfer, CN^-, bitter almonds, test strip.*

ВЫСОКОСЕЛЕКТИВНЫЙ КОЛОРИМЕТРИЧЕСКИЙ И ФЛУОРЕСЦЕНТНЫЙ ХЕМОСЕНСОР НА ОСНОВЕ o-ТОЛИДИНА ДЛЯ ОБНАРУЖЕНИЯ CN^-

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Разработан колориметрический и флуоресцентный химический сенсор N1 на основе о-толидина, который может быть использован для обнаружения CN^-. По сравнению с другими распространенными анионами цвет раствора N1 изменялся от желтого до бесцветного после добавления CN^-, в то время как под УФ-лампой желтая флуоресценция N1 явно аннигилировалась. Предел обнаружения флуоресцентного отклика N1 для CN^- снижен до $4.43 \cdot 10^{-7}$ М. Титрование ^{1}H ЯМР показало, что процесс внутримолекулярного переноса заряда происходит между N1 и CN^-, соотношение реакций 1:2. N1 успешно использован для определения содержания цианида в горьком миндале, также изготовлены тест-полоски на основе N1, которые более удобно и эффективно обнаруживают CN^- в водном растворе.

Ключевые слова: *хемосенсор, колориметр, флуоресценция, внутримолекулярный перенос заряда, CN^-, горький миндаль, тест-полоска.*

Introduction. Since anions play an important role in environmental, clinical, chemical, and biological fields, anion sensors have received extensive attention in the field of supramolecular chemistry [1–5]. As we all know, CN^- as a highly toxic substance confers great harm to living organisms and the environment and has a serious impact on blood vessels, vision, and nerve centers of the human body [6–9]. Therefore, it is especially important to use a simple and efficient method to detect CN^-.

In the past few decades, many methods have been proposed to detect CN^-, but due to its expensive instrument, complicated operation, and lack of professional operators, its practical application was seriously

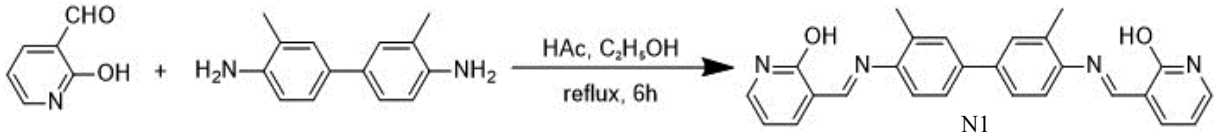
limited [10–16]. The CN^- sensor has become a focal center for scientists at this stage because of its low price, simple operation, and strong specificity [17–21].

Our research group has been engaged in ion recognition for many years [22–31]. Therefore, we designed and synthesized a novel sensor N1 with o-tolidine and 2-hydroxypyridine formaldehyde as raw materials and studied its anion recognition capability. The experimental results showed that the sensor N1 can selectively recognize CN^- in a DMSO solution with 30% water content. In addition, it was found in the anti-interference experiment that other ions do not interfere with the identification of CN^- ions. ^1H NMR, mass spectrometry, and other data indicate that the recognition mechanism was due to the deprotonation process. The sensor N1 was used to successfully identify the CN^- ions in bitter almond and was made into test strips for rapid detection of CN^- ions in water, which has certain application values.

Experimental. The melting point was measured by X-4 digital melting point apparatus (Beijing Tektronix Instrument Co. Ltd.). The UV-vis absorption spectrum and fluorescence emission spectrum were respectively measured by UV-2550 ultraviolet visible absorption spectrometer and RF-5301 fluorescence spectrometer using a 1 cm quartz cell. A Varian Mercury-400BB nuclear magnetic resonance apparatus was used to record ^1H and ^{13}C NMR, and the mass spectrum was recorded using a ZAB-HS mass spectrometer.

All the anions except the sodium salt (CN^-, SCN^-) were analytically pure tetrabutylammonium salts (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-) and were dried before use. Other reagents and solvents are of commercially available analytical grade.

Synthesis of sensor N1. 2-Hydroxypyridinecarboxaldehyde (0.246 g, 2 mmol) and o-benzidine (0.218 g, 1 mmol) were added in a 50 mL round bottom flask, followed by addition of 20 mL of absolute ethanol and 0.5 mL of HAc (Scheme 1). The mixture was refluxed at 80℃ for 6 h, then cooled to room temperature and filtered to give yellow precipitates, which were recrystallized in anhydrous ethanol and dried to give the desired product N1 in 78% yield (m.p. 245-247°C). ^1H NMR (500 MHz, chloroform-d) δ: 13.42 (d, J = 2.5 Hz, 2H), 8.88 (d, J = 2.1 Hz, 2H), 8.30 – 8.28 (m, 2H), 7.55 (d, J = 8.1 Hz, 4H), 7.40 (s, 1H), 7.38 – 7.37 (m, 1H), 7.33 – 7.32 (m, 2H), 7.31 (s, 1H), 7.27 (s, 1H), 2.51 (d, J = 2.3 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-d) δ 206.91, 163.06, 158.50, 145.74, 141.40, 139.67, 137.53, 133.37, 129.43, 126.69, 125.77, 124.94, 118.20, 30.93, 18.48. ESI-MS calcd for $C_{26}H_{22}N_4O_2+H^+$ 423.49, found 423.2637.



Scheme 1. The synthesis process of N1.

In the UV-vis and fluorescence experiments, N1 and anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^-, and SCN^-) were prepared in DMSO solution. All the experiments were carried out in DMSO/H_2O (8:2, v/v) HEPES solution. Any changes in UV-vis and fluorescence spectra of the synthesized compound were recorded on addition of tetrabutylammonium salts while keeping the ligand concentration constant (2.0×10^{-5}M) in all experiments.

For ^1H NMR titrations, the solution of N1 and the solution of NaCN were prepared in DMSO-d_6, and the two solutions were mixed directly in the NMR tube. The experiments were carried out on a Varian Mercury-400BB type nuclear magnetic resonance apparatus.

Results and discussion. The UV-visible spectrum of the N1 (2.0×10^{-5} M) in DMSO/H_2O (7:3, v/v) solution was found to have a significant absorption peak at 390 nm. After the addition of 50 equiv. of anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^-, and SCN^-), only CN^- showed a new absorption peak at 310 nm. At the same time, the color of the N1 solution with CN^- changed from yellow to colorless. There were no significant changes in the other anions. The results showed that N1 could specifically identify CN^- (Fig. 1a).

The fluorescence spectrum showed that N1 in DMSO/H_2O (v/v, 7:3) solution exhibited a strong fluorescence emission peak at 530 nm under excitation of 437 nm. After the addition of CN^-, the fluorescence emission peak was significantly weakened, while the other anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^- and SCN^-) showed no significant change. The color change of N1 with added CN^- from yellow to colorless was distinguishable by the naked eye under the UV lamp, as shown in Fig 1b.

CN^- (0.01M) was gradually added to the DMSO/H_2O (v/v, 7:3) solution of N1, and the changes in UV-visible absorption spectrum and fluorescence spectrum were observed. When CN^- increased from 0 equiv. to 27.5 equiv., the absorption peak of N1 at 390 nm in UV-visible spectrum was continuously weakened, and the absorption peak at 310 nm was gradually enhanced (Fig. 2a). Figure 2b showed that when the concentration of CN^- increased from 0 to 24.5 equiv., the fluorescence intensity of the N1 gradually decreases at 437 nm.

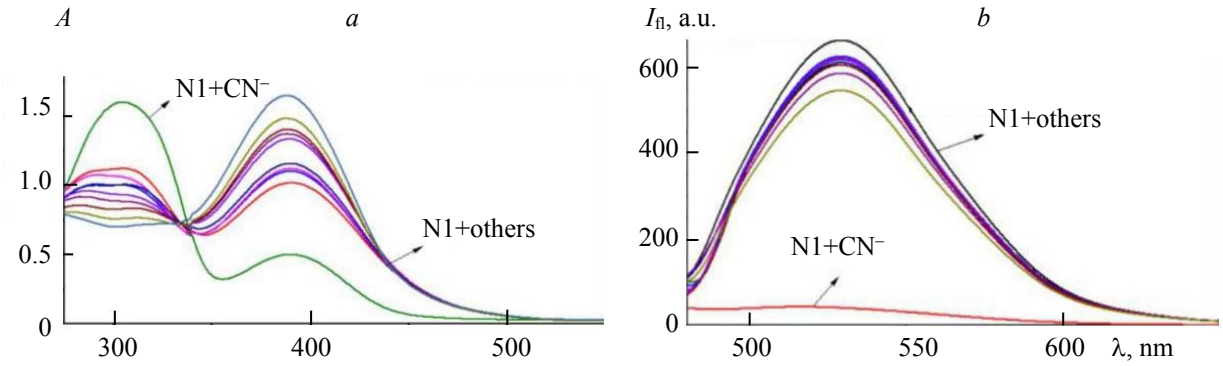


Fig. 1. UV-visible (a) and fluorescence spectrum (b) of 50 equiv. of different anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, CN^-, and SCN^-) added to N1 (2.0×10^{-5} M) in DMSO/H_2O (7:3, v/v) solution.

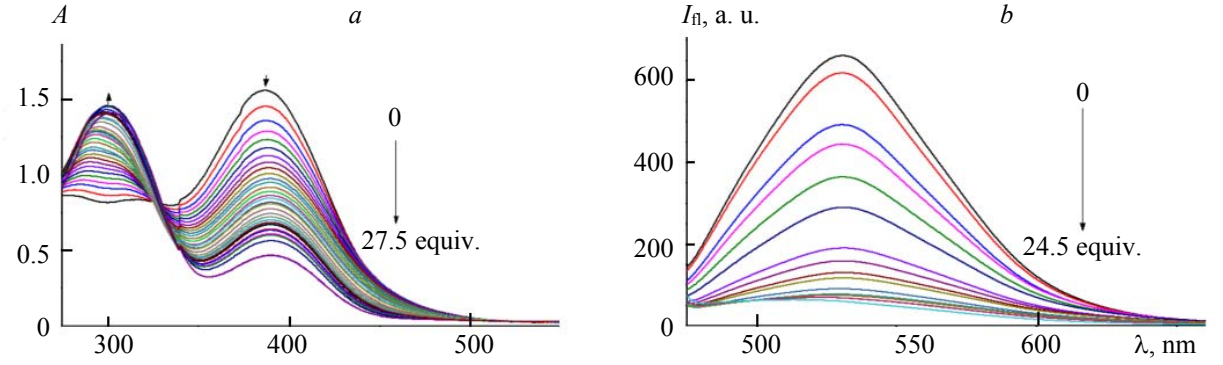
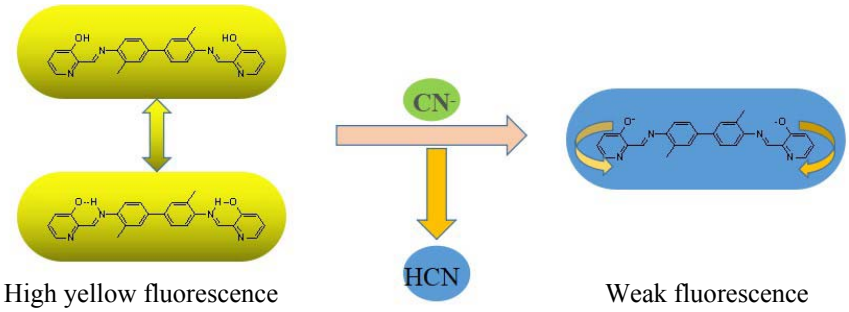


Fig. 2. Absorption (a) and fluorescence (b) spectra of N1 (2.0×10^{-5} M) in the presence of different concentrations of cyanide in DMSO/H_2O (7:3, v/v) solutions.

According to the fluorescence spectrum titration experiment, the detection limit of N1 to CN^- calculated by the formula $3S_B/L$ [32] was 4.43×10^{-7} M, as shown in Fig. 3a, which is far lower than the WHO standard (1.9×10^{-6} M). This indicated that N1 has potential applications in real life. To gain an insight into the stoichiometry between N1 and CN^-, a Job's plot experiment was performed to study the identification mechanism of CN^--N1. As shown in Fig. 3b, the molar ratio of [N1]/[N1+CN^-] was 0.7, indicating that the stoichiometry of N1-cyanide was 1:2.

To examine the effect of pH (2-12) on N1, CN^- was added to different pH values of N1 buffer solutions for pH experiments. It was found that N1 works well in the pH range of 2-9, while in the range of 10-12, the fluorescence of N1 was quenched. After adding CN^- to N1, the fluorescence of solution was quenched in the pH range of 7-12, which indicated that the recognition of CN^- by N1 was affected by pH (Fig. 3c). In addition, by alternately adding CN^- and H^+, the reversibility of N1 could be observed. The results showed that the process of N1 recognizing CN^- could be repeated more than five times, indicating that N1 was a recyclable CN^- ion sensor (Fig. 4).

The mechanism of recognition of N1 with CN^- was studied by ^1H NMR titration experiments (Fig. 5). The results showed that when CN^- was added to N1, the -OH peak of N1 at 13.9 ppm disappeared, and the proton of the benzene ring was observed to upshift to the high field, indicating that deprotonation caused intramolecular charge transfer (ICT) in N1. Based on these experimental results, we proposed a possible identification mechanism, as shown in Scheme 2.



Scheme 2. Possible reaction mechanism of N1 with CN^-.

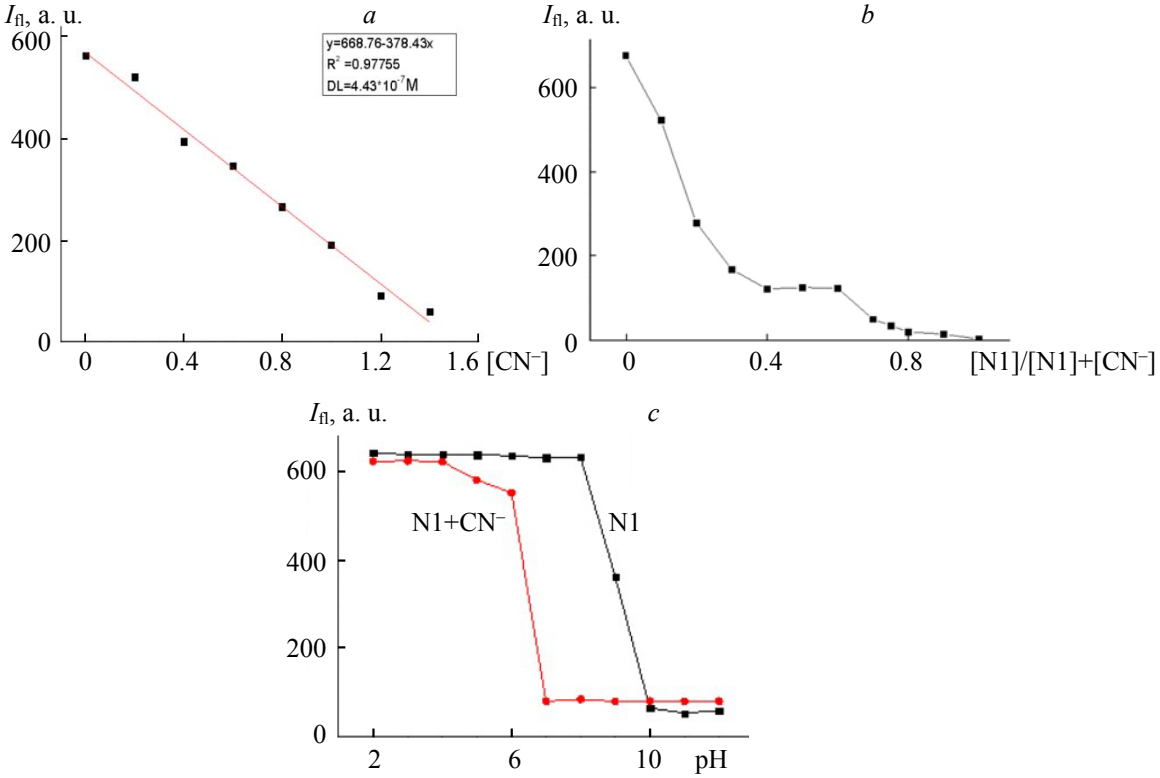


Fig. 3. Fluorescence detection limit (a), job plot (b) of N1 towards CN^-, and corresponding fluorescence intensity of N1 to CN^- under different pH conditions (c).

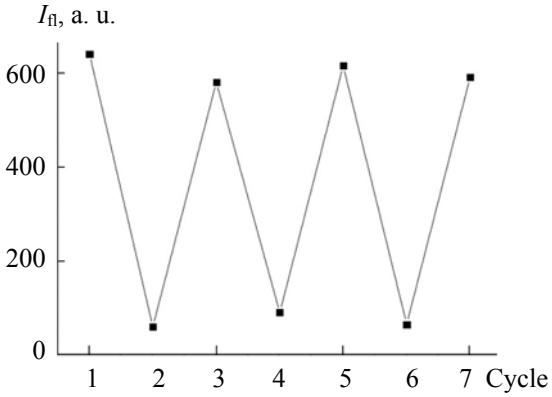


Fig. 4. Reversible switching cycles of fluorescence intensity by alternate addition of CN^- ions and H^+ in N1.

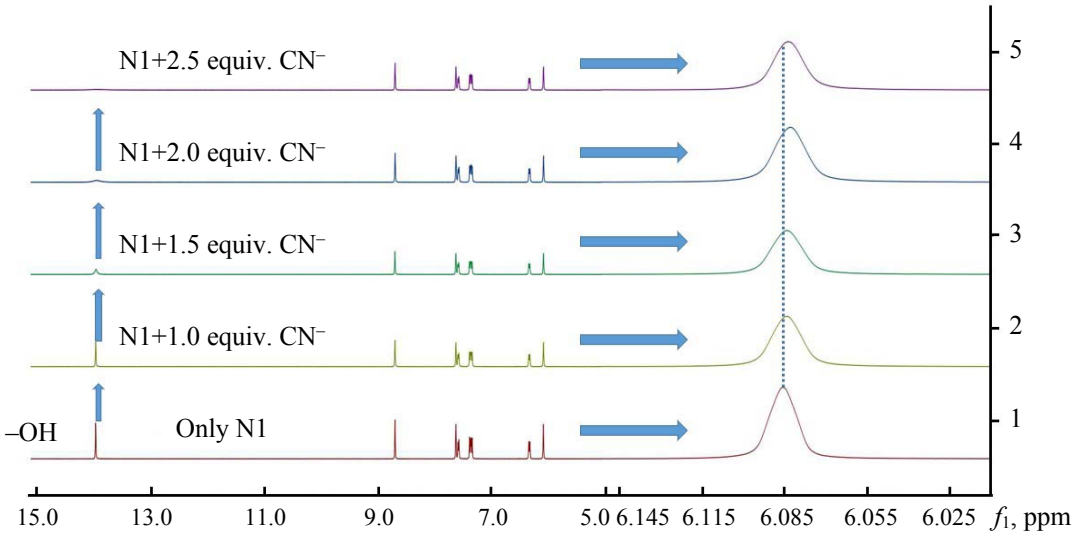


Fig. 5. ^{1}H NMR titration spectra of N1 and in the presence of varying amounts of CN^- in DMSO-d_6.

In order to better confirm the proposed mechanism of N1 with CN^-, DFT calculations were performed at the B3LYP/6-311g(2*d*, *p*) level [33]. Based on the N1 and N1 complexes, we calculated the spatial distribution of the electron cloud and the orbital energy of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). As shown in Fig. 6, when N1 interacted with CN^-, the occupied molecular orbitals HOMO and LUMO are transferred from the benzene ring to the pyridine ring, and the energy gap (ΔE) of the N1 and N1-CN^- system was 0.134 and 0.112 a.u., respectively, which showed that the mechanism of N1 with CN^- was theoretically possible.

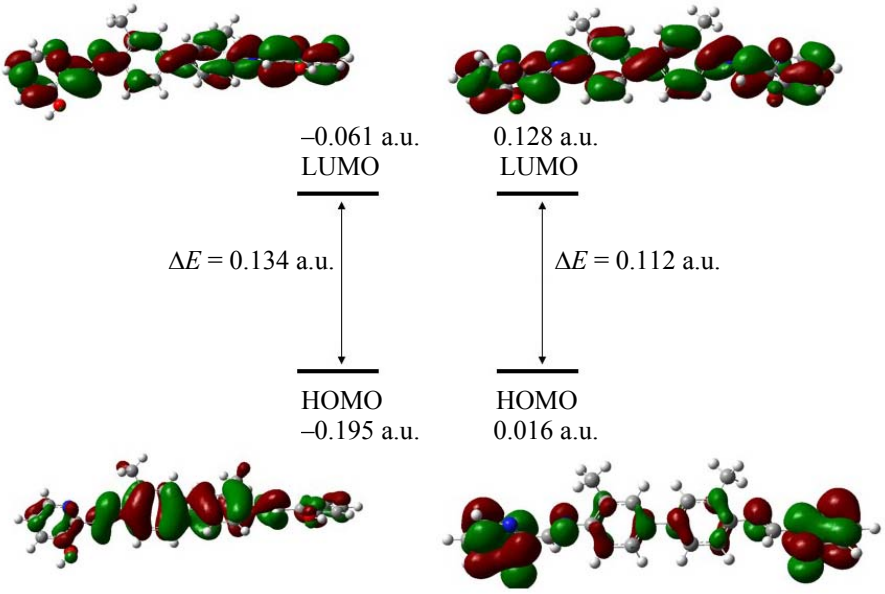


Fig. 6. The DFT calculations of LUMO, HOMO, and energy gaps of the N1 and N1-CN^- system.

To facilitate the detection of CN^- using N1, test strips were prepared by dipping the filter paper into a binary solution of N1 in DMSO/H_2O (v/v, 7:3) and then drying them. After the aqueous solution of CN^- was added to the test strips, the color changes from dark yellow to colorless under visible light, while under UV light, the yellow fluorescence was quenched. It is indicated that the test strips containing N1 can quickly and easily detect the CN^- in the aqueous solution.

To further investigate the utility of N1 in our life, bitter almonds were chosen for the following experiments: 100 grams of crushed bitter almonds, 300 mL water, and 0.5 g NaOH were placed in a beaker; then the pH of the solution was adjusted to 8. After stirring evenly, 2 mL of filtrate was added 1ml of N1. As shown in Fig. 7, the fluorescence of mixture was obviously weakened, indicating that the sensor can be applied to the qualitative detection of cyanide in bitter almond.

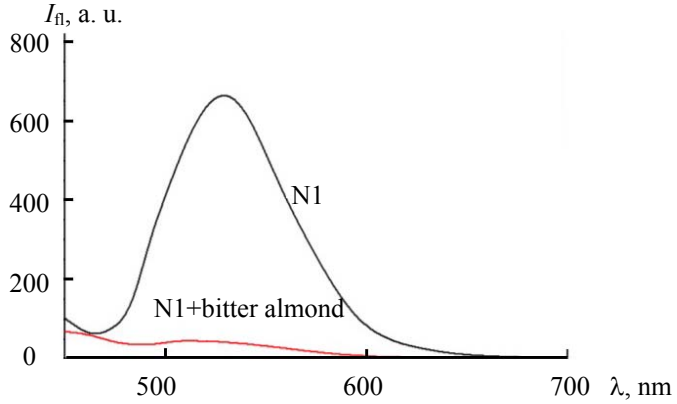


Fig. 7. Detection of cyanide in bitter almonds by N1.

Conclusions. We have synthesized a simple and efficient dual-channel chemical sensor N1. N1 in DMSO/H_2O (v/v, 7:3) exhibited high selectivity, sensitivity, and specificity for UV-vis and fluorescence recognition to CN^-. In addition, the fluorescence detection limit of the sensor to CN^- was 4.43×10^{-7} M. The proposed mechanism for detection of CN^- was based on ICT, and the stoichiometric ratio of N1 to CN^- was 1:2. The sensor successfully detected cyanide in bitter almonds and was used to produce test strips for easy and rapid detection of CN^- in aqueous solution. We believe that the sensor N1 has certain potential practical applications in real life.

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