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A benzimidazole functionalized NDI derivative for recyclable fluorescent detection of cyanide in water†

Qi Lin,^{ID}*^a Lu Liu,^a Feng Zheng,^a Peng-Peng Mao,^a Juan Liu,^{*b} You-Ming Zhang,^{ID}^a Hong Yao^a and Tai-Bao Wei^{ID}*^a

A fluorescent chemosensor (**L2**) has been designed and synthesized via a simple one step reaction through rationally combining benzimidazole and naphthalene diimide (NDI) moieties together. The structure of **L2** has been confirmed by single crystal X-ray diffraction. The sensor **L2** shows a highly selective and sensitive fluorescence response for CN^- . Upon the addition of a CN^- water solution into the DMSO solution of sensor **L2**, the solution of **L2** shows an instant fluorescence enhancement and other anions couldn't interfere in the CN^- detection process. The CN^- sensing process shows reversible properties by adding H^+ into the sensor **L2** solution treated by CN^- . The detection limit of the sensor towards CN^- is 8.32×10^{-7} M, which could be distinguished by the naked eye in a UV lamp. The sensor **L2** could serve as a practical and convenient recyclable test kit to detect CN^- .

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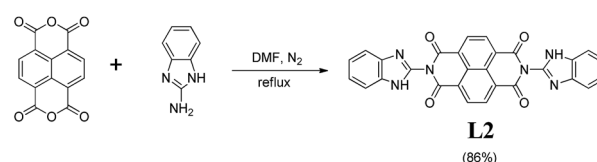
1. Introduction

As we all know, ions play a fundamental role in many chemical, biological, medical and technological processes.^{1–9} Cyanide ions (CN^-) are one of the most toxic anions, being extremely harmful to the environment and human health.^{10–12} When cyanide enters the body by oral, inhalation or dermal exposure, it exerts its acute effects by complexing with ferric iron atoms in metalloenzymes, resulting in histotoxic anoxia through inhibition of cytochrome c oxidase. The maximum permissive level of cyanide in drinking water is therefore set at as low as 1.9 mM by the World Health Organization (WHO).¹³ However, large quantities of cyanide salts are widely used in industrial settings such as metallurgy, electroplating, and the synthesis of fine chemicals. In addition, a higher level of cyanide can also be accumulated through the consumption of certain foods and plants.¹⁴ Therefore, much interest has been sparked in the design of new methods to monitor CN^- in biological and environmental samples.

Thanks to the enthusiastic efforts of scientists, a large number of good sensors for cyanide have been invented.^{15,16} Among the various sensors, fluorescent chemosensors present

numerous advantages, including high sensitivity, low cost, and easy operation.^{17–19} Several fluorescent chemosensor systems for CN^- detection reported to date are based on the mechanism of coordination,^{20–24} hydrogen-bonding interactions,^{25–27} nucleophilic addition reactions,^{28–36} Sonogashira cross-coupling reaction^{37–39} and so on. However, most of the CN^- sensors often employ sophisticated structures and require complicated synthetic steps and high temperature or a long reaction time for detection of CN^- . Thus, developments of simple and high efficiency fluorescent chemosensor for detecting CN^- are very necessary.

In view of these and as a part of our research interests in ion recognition,^{40–48} we attempt to develop an easy-to-make and efficient fluorescent chemosensor which can sense CN^- with specific selectivity and high sensitivity. Herein, we report a benzimidazole functionalized NDI-based⁴⁹ fluorescent chemosensor **L2** which could be obtained from an easy one step reaction (Scheme 1). The sensor **L2** could efficiently detect CN^- in water under mild conditions via a deprotonation and electric charge transferring mechanism, which could be used for highly selective and sensitive fluorescence enhancement detection of cyanide in aqueous media (Scheme 1).

Scheme 1 Synthesis of the sensor molecule **L2**.

^aKey Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu, 730070, P. R. China. E-mail: linqi2004@126.com; weitaibao@126.com

^bCollege of Chemical Engineering, Northwest University for Nationalities, Lanzhou, 730000, P. R. China. E-mail: liujuan656@126.com

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2. Experimental

The fluorescent chemosensor **L2** was synthesized through a simple one-step reaction (Scheme 1). 1,4,5,8-naphthalenetetracarboxylic dianhydride (2.68 g, 10 mmol) and 2-amino-benzimidazole (2.66 g, 20 mmol) were mixed in DMF (25 mL) in a round-bottom flask (50 mL). The reaction mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was poured into H₂O (15 mL). The precipitate was collected by filtration, washed with ethanol (20 mL × 3), and then dried in vacuum, give a yellow powder compound **L2**. Yield: 4.43 g, 86%. mp > 300 °C. ¹H NMR (600 MHz, DMSO-*d*₆, Fig. S1†) δ 12.68 (s, 2H), 8.83 (s, 4H), 7.69 (dd, *J* = 12.0, 6.0 Hz, 4H), 7.33 (dd, *J* = 12.0, 6.0 Hz, 4H). ¹³C NMR (150 MHz, DMSO-*d*₆, Fig. S2†) ¹³C NMR (150 MHz, DMSO-*d*₆) δ 162.95, 142.27, 141.16, 134.38, 131.68, 127.59, 126.97, 123.70, 122.31, 119.85, 112.52. IR (KBr, Fig. S3†) ν: 1330 (–C=N–), 1681 (–C=O), 3509 (–NH) cm^{–1}. MS: ESI *m/z* for **L2** [C₂₈H₁₄N₆O₄ + H]⁺ found: 499.01, calcd: 499.11 (Fig. S4†).

The structure of the sensor was further confirmed by single-crystal X-ray diffraction. The single crystal (CCDC: 1553559) was obtained by slowly vaporizing the DMSO solution of **L2**. As shown in Fig. 1a, in the molecular of **L2**, the benzimidazole

moiety and the naphthalene diimide (NDI) moiety don't on one plan. The dihedral angle of benzimidazole group and naphthalene diimide (NDI) moiety is 99.1°. Moreover, as shown in Fig. 1b, the benzimidazole moiety of one molecular of **L2** shows parallel stacking with naphthalene diimide (NDI) moiety on adjacent molecular of **L2**. The distance between the two plan is 3.62 Å, which indicate that there are intermolecular π–π interaction⁵⁰ existing among the neighboring **L2** molecular. In addition, in the powder the X-ray diffraction (XRD) of **L2** (Fig. 2), we observed a sharp diffraction peak with *d*-spacing of 3.62 Å at 2θ = 24.42°, which suggested that π–π stacking exists between the between molecular of **L2**.

3. Results and discussion

In order to investigate the anion recognition abilities of the sensor **L2** in water, we carried out a series of host–guest recognition experiments. The recognition profiles of the chemosensor **L2** toward various anions, including F[–], Cl[–], Br[–], I[–], AcO[–], H₂PO₄[–], HSO₄[–], ClO₄[–] and CN[–], were primarily investigated using fluorescence spectroscopy. As shown in Fig. 3, in the fluorescence spectrum of **L2** DMSO solution, the maximum emission of **L2** appeared at 510 nm in water when excited at λ_{ex} = 455 nm. When 10 equiv. of CN[–] water solution was added to the DMSO solution of sensor **L2**, the fluorescence emission band at shifted to 550 nm and shows obvious enhancement. The apparent fluorescence emission change could be distinguished by the naked eye under UV lamp (Fig. 3). To validate the selectivity of sensor **L2**, the same tests were also conducted using F[–], Cl[–], Br[–], I[–], AcO[–], H₂PO₄[–], HSO₄[–], ClO₄[–] ions, and none of these anions induced any significant changes in the fluorescent spectrum of the sensor (Fig. 4). Therefore, the sensor **L2** could selectively sense CN[–] in water solution.

To further investigate the CN[–] detection property of the sensor **L2**, the fluorescence emission spectral variation of **L2** in DMSO/H₂O (9 : 1, v/v) HEPES buffered solution was monitored during titrations with different concentrations of CN[–] in water from 0 to 25 equivalents (Fig. 5). With an increasing amount of

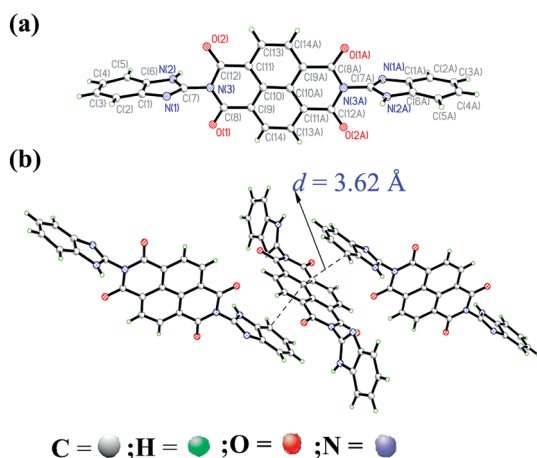


Fig. 1 Different perspectives of **L2**'s crystal structure.

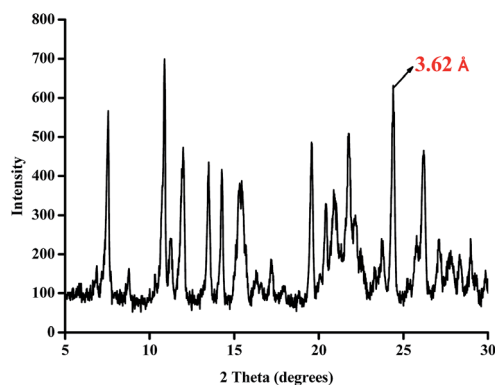


Fig. 2 XRD diagram of the sensor of **L2**.

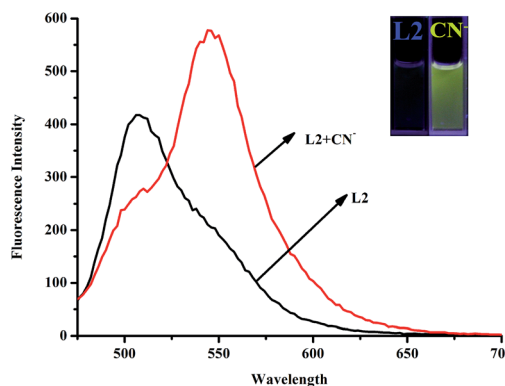


Fig. 3 Fluorescence spectra of **L2** (20 mM) upon excitation at 455 nm DMSO/H₂O (9 : 1, v/v) before and after addition of CN[–] (50 equiv.) water solution. Inset: Photographs showing the change in the fluorescence of **L2** after addition of CN[–] (10 equiv.) in DMSO/H₂O (9 : 1, v/v) HEPES buffered solution.



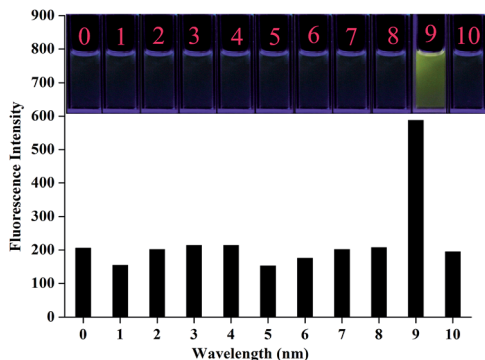


Fig. 4 Histogram of fluorescence emission of L2 ($c = 2 \times 10^{-5}$ M) in the presence of various anions (50 equiv., $\lambda_{\text{ex}} = 455$ nm) in DMSO/H₂O (9 : 1 v/v) HEPES buffered solution. Inset: Color changes observed for L2 upon the addition of various anions in water. From 0 to 10: L2, Cl[−], Br[−], I[−], H₂PO₄[−], F[−], AcO[−], HSO₄[−], ClO₄[−], CN[−], SCN[−].

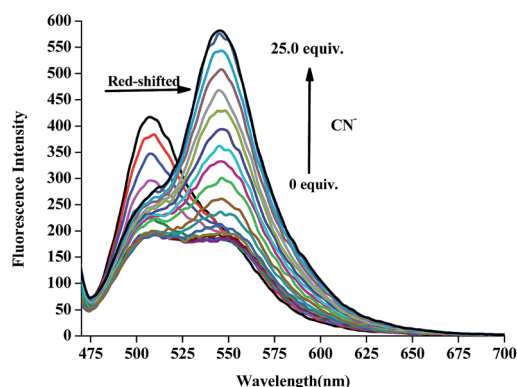


Fig. 5 Fluorescence spectra of L2 in the presence of different concentrations of CN[−] in DMSO/H₂O (9 : 1, v/v) HEPES buffered solution.

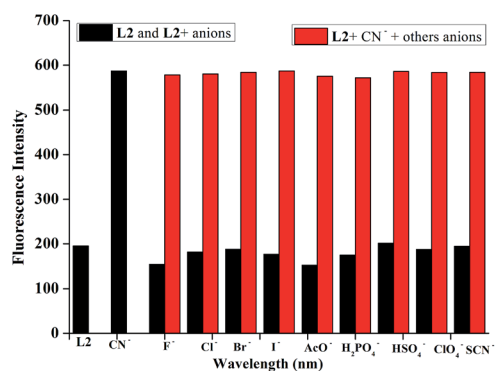


Fig. 6 Fluorescence intensity at 587 nm of L2 ($c = 2 \times 10^{-5}$ M) exposed to 50 equiv. various anions and to the mixture of 10 equiv. CN[−] with other 50 equiv. ions in DMSO/H₂O (9 : 1, v/v) HEPES buffered solution.

CN[−], the emission peak at 510 nm gradually shows a bathochromic effect, however, the emission peak at 550 nm increased. The scatter plot indicated that the reaction basic

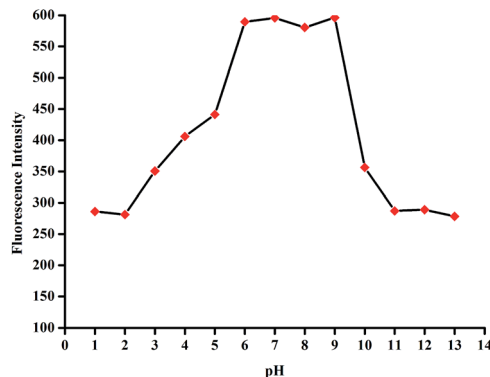


Fig. 7 Influence of pH on the fluorescence of L2–CN[−] ($c = 2.0 \times 10^{-5}$ M) in HEPES buffered solution in DMSO/H₂O (9 : 1, v/v) HEPES buffered solution. ($c = 0.01$ M, $\lambda_{\text{ex}} = 455$).

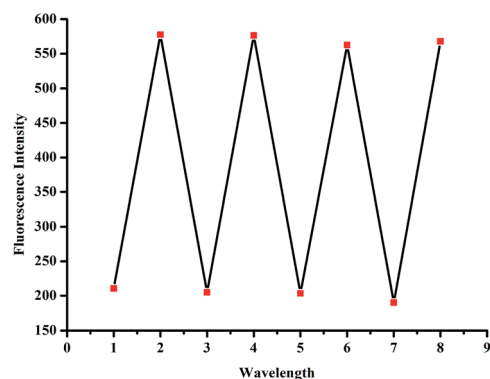


Fig. 8 Fluorescence switching cycles of L2 ($c = 2.0 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 455$ nm), controlled by alternating the addition of CN[−] and HClO₄.

achieved balance when the concentration of CN[−] ions increased to 25.0 equivalent. Furthermore, as shown in Fig. S5,[†] the detection limit of the fluorescent spectrum changes calculated on the basis of $3\delta/s$ (ref. 51) is 8.82×10^{-7} mol L^{−1} for CN[−], which is far lower than the WHO guideline of 1.9 $\mu\text{mol L}^{-1}$ cyanide.¹³

To further exploit the utility of the chemosensor L2 as an anion-selective sensor for CN[−], competitive experiments were carried out in the presence of 10 equiv. of CN[−] and 50 equiv. of various anions in DMSO/H₂O (9 : 1, v/v) HEPES buffered solution. As shown in Fig. 6, none of the competing anions interfered in the detection of CN[−]. This result displays the highly selectivity of the chemosensor L2 toward CN[−] over the other anions analytes mentioned above.

The selectivity of L2 to CN[−] was also examined over the range of pH values. The detection of CN[−] can work well in the pH range of 6.0–9.0 in HEPES buffered solution in DMSO/H₂O (9 : 1, v/v) (Fig. 7).

Moreover, the recyclability is very important for chemosensors. Therefore, we carefully investigated the reversibility of the CN[−] recognition properties by adding H⁺ into the solution of CN[−] treated sensor L2. As a result, by alternating the addition of CN[−] and HClO₄, the fluorescence of the sensor shows “off–



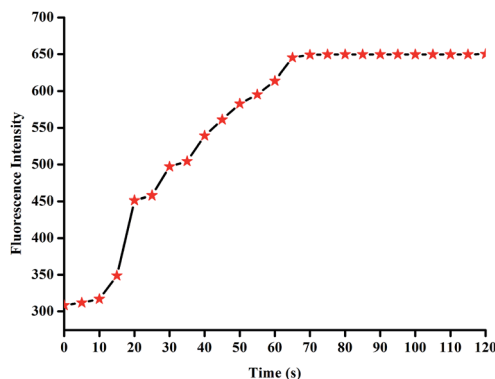


Fig. 9 Fluorescence intensity of a solution of **L2** ($c = 2.0 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 455$ nm, $\lambda_{\text{em}} = 550$ nm) in DMSO/H₂O (9 : 1, v/v) HEPES buffered solution after addition of 50 equivalents CN[−] in water.

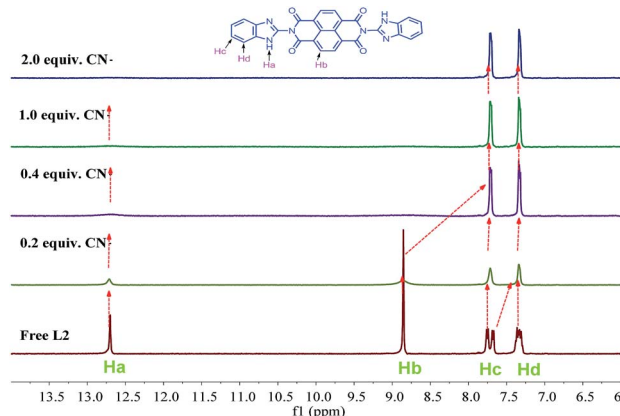
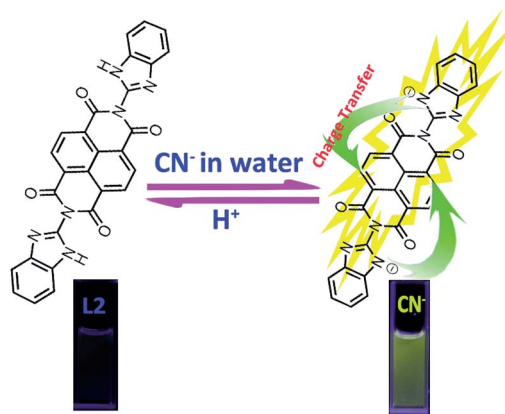


Fig. 10 ¹H NMR spectra (400 MHz, DMSO-*d*₆) of free **L2** and in the presence of CN[−].

on-off" changes several cycles with little loss of fluorescence efficiency (Fig. 8). These properties made sensor **L2** act as recyclable CN[−] sensor as well as a fluorescent switch.

In addition, it is well known that reaction-based chemosensors always have had the problem of a long response time. In our case, the detection of CN[−] using **L2** was found to be relatively rapid (Fig. 9). After adding the cyanide anion, the fluorescence emission intensity of **L2** increased and reached the plateau region in less than 1 min, suggesting that the whole process of the CN[−] detection might be completed rapidly.

In order to further explore the sensing mechanism of sensor **L2** to CN[−], the ¹H NMR titrations were investigated. As shown in Fig. 10, before the addition of cyanide ion, the ¹H NMR chemical shifts of the Ha (−NH), Hb, Hc, Hd protons on **L2** were at 12.71, 8.86, 7.72 and 7.33 ppm, respectively. Upon the addition of 0.2–2.0 equivalents of cyanide ion, the signal Ha (−NH) was disappeared and the Hb, Hc protons shifted upfield. These observations obviously indicate that the sensor **L2** were deprotonated by excess amounts of CN[−], which resulted in intramolecular charge transfer. The FT-IR spectroscopy (Fig. S6†) was also support the proposed mechanism. In the FT-IR spectroscopy of **L2**, a −NH vibration peak appeared at 3509 cm^{−1},



Scheme 2 The possible sensing mechanism of **L2** reaction with CN[−].

while, upon the addition of 2.0 equiv. CN[−], −NH vibration peak disappeared, which indicated that the deprotonation occurred. A possible mechanism for the formation of **L2**–CN[−] is proposed in Scheme 2.

4. Conclusions

In summary, a fluorescent chemosensor **L2** has been designed and synthesized by an one-step reaction. The sensor **L2** for could rapidly detect CN[−] with high selectivity and sensitivity *via* a deprotonation and intramolecular charge transfer mechanism. The detection limit of the chemosensor **L2** toward CN[−] was 8.32×10^{-7} mol L^{−1}, other anions couldn't interfere in the CN[−] detection process. The detection of CN[−] can work well in the pH range of 6.0–9.0. Moreover, the CN[−] sensing process shows reversible properties by adding H⁺ into the sensor **L2** solution treated by CN[−]. The sensor **L2** could act as a convenient recyclable test kits to CN[−].

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