



# A recyclable probe for highly selective and sensitive detection of cyanide anion in aqueous medium by fluorescent and colorimetric changes

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## ABSTRACT

In this work, a novel Schiff-Base (**Q1**) which based on 5-(4-nitrophenyl)-2-furan and naphtho[2,1-*b*]furan-2-carbohydrazide was designed to act efficiently in a chemodosimeter approach for the selective detection of cyanide in aqueous medium. The recognition progress occurred via deprotonating between the hydrazide moiety of **Q1** and cyanide. When exposed **Q1** to the low concentration solution of cyanide anion, there was a significant color change from yellow to orange in visible light and accompanied with a strong and broad red shift (from  $\lambda_{\text{max-ab}} = 400 \text{ nm}$  to  $\lambda_{\text{max-ab}} = 468 \text{ nm}$ ) in the UV–vis absorption spectrum. Meanwhile, a dramatically decrease almost 4 times of the emission maximum of **Q1** took place from 775 (a.u.) to 204 (a.u.), and the color of the solution changed from bright orange to dim red, which can be saw by naked-eyes under the UV lamp (365 nm). However, without any signal changes after the addition of other common anions, especially the basic anions such as  $\text{F}^-$ ,  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{SCN}^-$ . Notably, this probe can serve as a recyclable component in sensing materials. The corresponding experiment proved that this probe can be repeated use above 10 times. (Scheme 1) On the basis of these observations and supporting mechanistic analyses, it is concluded that the recyclable probe **Q1** must be a promising cyanide anion indicator that is attractive in terms of its selectivity, ease-of-use, rapid response (<3 s), and the low, naked-eye discernible cyanide detection limit it, also it will be regarded as an environmental friendly material which can sensing cyanide anion in aqueous medium and making great contribution to the development of cyanide anion sensors.

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## 1. Introduction

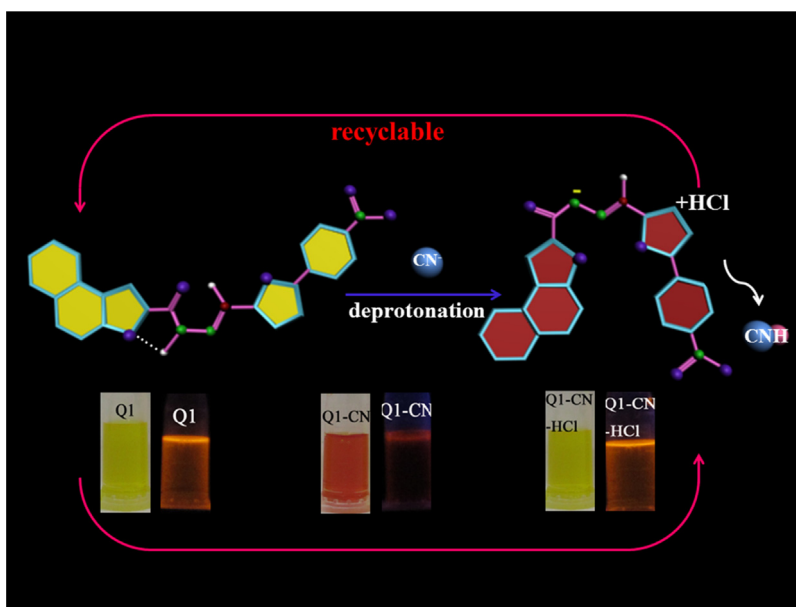
Anion recognition is an area of growing interest in supramolecular chemistry on account of its important role in a wide range of environmental, clinical, chemical, and biological applications [1–11], and considerable attention has been focused on the design of artificial receptors that are able to selectively recognize and sense anion species [12–16]. Cyanide is well-known as a hazardous chemical in biology and the environment, and is extremely toxic to mammals [17]. Cyanide poisoning can lead to vomiting, loss of consciousness, and eventual death. According to the World Health Organization, the maximum acceptable level of cyanide in drinking water is  $1.9 \mu\text{M}$  [18,19]. Despite safeguards and increasing

levels of monitoring and control, accidental releases of cyanide into the environment do occur. This can lead to disastrous consequences, as underscored by the large cyanide spill that took place in Tianjin city in 2015, an event that was considered to be a serious environmental disaster in China [20,21]. For the above reasons, there is considerable interest in selective detecting aqueous cyanide at sub-micromolar concentrations by using simple and visualized methods [22–24]. Indeed, considerable effort within the anion recognition community has been devoted to preparing such species. However, many of the cyanide anion receptors reported to date have relied on hydrogen-bonding motifs and, as a consequence, have generally displayed poor selectivity relative to other anions [25–30].

Most of the cyanide receptors are electrophilic organic reagents which undergo C–C bond forming reactions with cyanide. Some of these reactions necessitate basic pH and their reversibility is not always well documented [31]. Addition of cyanide to an activated

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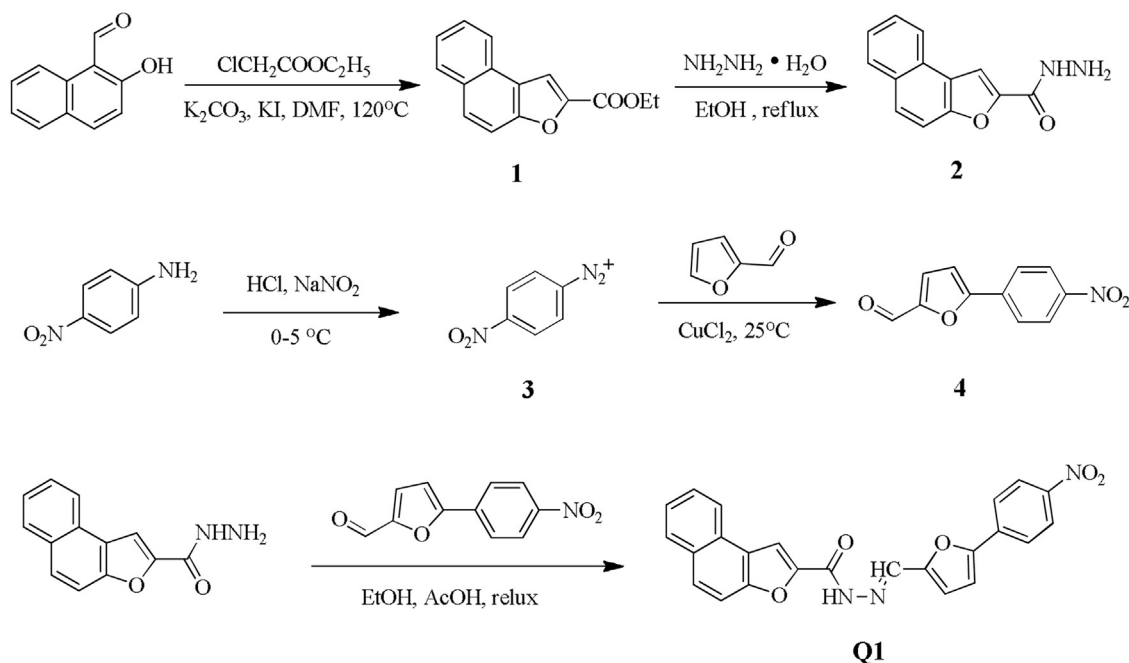
E-mail address: [zhangnmnu@126.com](mailto:zhangnmnu@126.com) (Y.-M. Zhang).



**Scheme 1.** Chemical structures and cartoon representations of **Q1** and cyanide in DMSO/H<sub>2</sub>O (9:1, v/v) solutions.

imine group is one of the important strategies that are selective to cyanide only. Schiff–base structure constructed by a simple synthetic method can provide highly diverse  $\pi$ -conjugated systems. Such high diversity of their structures may provide a big advantage as colorimetric and fluorescence materials [32,33]. In addition, naphthofuran derivatives, which have dramatic fluorescent emissions, have been synthesized for a long time, but they were seldom been used in ion recognition field. In view of this and as a longstanding interested in molecular recognition of our group [34–36]. Herein, we designed and synthesized a simple probe (**Q1**) based on naphthofuran derivatives for cyanide, which utilized to monitor cyanide anions by colorimetric and fluorescent method at room temperature. One of the most important advantages of this probe based on the deprotonation was that they could

be operable in aqueous medium. There was a deprotonation process between the probe molecule and cyanide, which increased the ability of intramolecular charge transfer which enlarge the conjugate system of the probe and then gave rise to large changes in the absorption spectra (from  $\lambda_{\text{max-ab}} = 400 \text{ nm}$  to  $\lambda_{\text{max-ab}} = 468 \text{ nm}$ , and the color change from yellow to bright orange) and the fluorescent spectra (the emission maximum from 775 (a.u.) to 204 (a.u.) at  $\lambda_{\text{max-em}} = 564 \text{ nm}$ , and the color change from bright orange to dim red). Meanwhile, other common anions had no influence on the response of cyanide. Differently from the previous reports, here, we considered whether recyclable project could be achieved by adding of the hydrochloric acid to affect the intramolecular charge transfer of the molecular and induce naked-eye color changes. After the addition of hydrochloric acid, **Q1-CN** shows an immediate



**Scheme 2.** Synthesis of the sensor molecule **Q1**.

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