



A colorimetric and fluorescent probe containing diketopyrrolopyrrole and 1,3-indanedione for cyanide detection based on exciplex signaling mechanism



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ABSTRACT

A new fluorescent probe **1** comprising diketopyrrolopyrrole and indanedione-based Michael receptor, which recognized cyanide anion with high selectivity was designed and synthesized. Addition of CN^- aqueous solution to **1** in THF resulted in a rapid color change from purple to yellow together with a large blue shift from 553 to 480 nm, while other anions did not induce any significant color change. Furthermore, the Michael addition of cyanide to **1** elicited 3.11 and 6.13-fold PL enhancements at 484 and 572 nm, respectively, which constituted the fluorescence signature for cyanide detection. The mechanism of exciplex formation was proposed for this interesting observation. The detection limits were 0.36 μM using the fluorescence spectra changes, which was far lower than the WHO guideline of 1.9 μM . The results indicated **1** can act as dual-channel, high selective, immediacy and sensitive optical probe for CN^- .

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1. Introduction

Cyanide is well known as one of the most toxic species and is extremely harmful to mammals. Any accidental release of cyanide to the environment causes serious problems. Nevertheless, cyanide salts are still widely used as industrial materials in gold mining, electroplating, plastics production and other fields. Therefore, it is highly desirable to develop sensitive, selective and quick detection methods for toxic cyanide anions.

Traditionally, hydrogen bonding or supramolecular interactions have been used in the detection of low concentrations of cyanide in solution [1–3]. These approaches, however, usually result in poor selectivity over other common anions [4]. The burgeoning field of reaction-based indicators has made progress in this area because of the unique reactivity of CN^- toward a variety of organic functional groups including $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}=\text{C}$, and so on [5]. Unfortunately, none of these is ideal. More importantly, there are practical limitations to their use. For instance, the cationic borane receptor was very promising in that reaction with cyanide took place in water, but failed to produce a color change, a shortcoming that restricted its utility [5k]. Likewise, the oxazine-based indicators required specific

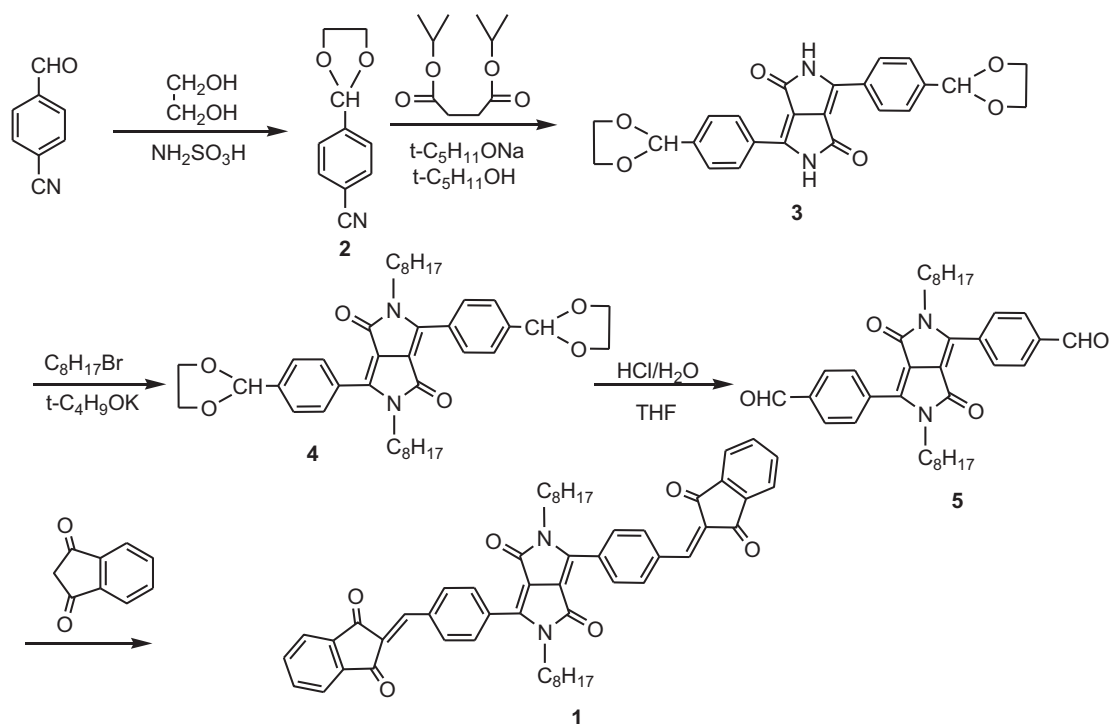
biphasic conditions [5q,5r], while the acridinium salts required an elevated reaction temperature [5s]. There thus remains a need for yet-improved reaction-based cyanide indicator systems.

Reaction-based cyanide indicators form the irreversible formation of chemical bonds that can provide chemodosimetric information and develop ratiometric fluorescent probes. However, up to now, only a limited number of Michael addition type probes for the ratiometric fluorescent detection of cyanide have been reported in literatures [5d,5f,5q]. There is an ever-present need to develop new reaction-based CN^- sensors, as these can help overcome lingering obstacles in its detection, such as selectivity, sensitivity, response times, sensor stability, reaction conditions, etc.

The signaling mechanisms of fluorescent chemosensor are generally based on photoinduced electron transfer, metal-ligand charge transfer, excimer formation, and intramolecular charge transfer, etc. However, exciplex formation, to the best of our knowledge, is not usually used as a signaling mechanism for anion recognition, though it has been documented previously [6]. We wished to explore this mechanism of achieving detectable optical response upon interaction of CN^- with probe. One design element was a CN^- -induced conformational change of probe, which subsequently triggered a fluorescence alteration. Zhou et al. have previously shown the viability of such this approach [7].

Considering our objectives, we designed probe **1** (Scheme 1) keeping in mind the following. (1) The probe should be

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Scheme 1. Synthesis of probe 1.

conformationally rigid before the interaction with CN^- . This would inhibit intramolecular interactions. (2) Interaction of such a probe with a CN^- should disrupt rigid structure and therefore, make the probe's frame work more flexible, which is easy to fold yielding π -stacking exciplex. (3) The signal reporting of probe derives from more reactive indandione-derived vinyl moiety which could selectively react and enhance the sensitivity of the nucleophilic addition reaction between the vinyl group and CN^- . (4) Electron-deficient diketopyrrolopyrrole (DPP) is selected as chromophore considering its many advantageous features including its enhanced vinyl moiety reactivity with CN^- , strong fluorescence as well as its distinct rigid ring structure. Herein, we report a DPP-indandione conjugate (**1**) as doubly activated Michael addition type probe for the colorimetric fluorescent detection of cyanide. The probe displays high selectivity and sensitivity for CN^- over other anions with a fast response.

2. Experimental

2.1. Chemicals and instruments

Nuclear magnetic resonance spectra were recorded on Bruker Avance III 400 MHz and chemical shifts are expressed in ppm using TMS as an internal standard. The UV-vis absorption spectra were recorded using a Helios Alpha UV-Vis scanning spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 FL spectrophotometer with quartz cuvette (path length = 1 cm).

N-Methyl-2-pyrrolidone (NMP) was dried with CaH_2 and distilled under nitrogen atmosphere. Other solvents were obtained from commercially available resources without further purification. 2,5-Dioctyl-3,6-bis(4'-formylphenyl)pyrrolo[3,4-c] pyrrole-1,4-dione (compound **5**) was synthesized according to our published literature [8].

The recognition between **1** and different anions was investigated by UV-vis and fluorescence spectroscopy in THF solution at room temperature. The stock solution of **1** and anions was at a concentration of 10.0 mM. After the **1** and anions with desired

concentrations were mixed, they were measured by UV-vis and fluorescence spectroscopy.

2.2. Synthesis of compound 1

A mixture of **5** (56.8 mg, 0.10 mmol), 1,3-indandione (86 mg, 0.60 mmol) and Al_2O_3 in dry CH_2Cl_2 (20 mL) was mixed at room temperature. After 24 h, the reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The purification by silica gel column chromatography (petroleum ether/dichloromethane/THF = 100/100/1, v/v/v) yielded the desired compound **1** (29.8 mg, 35%) as a dark red solid.

^1H NMR (CDCl_3 , 400 MHz, δ): 8.60 (d, 2H), 8.07–7.98 (m, 8H), 7.89–7.85 (m, 8H), 3.81 (t, 4H), 1.61–0.86 (m, 30H).

3. Results and discussions

3.1. Synthesis and structural characterization

Compared with the general Michael acceptors, the doubly activated acceptors, in which two electron-withdrawing groups are attached to the $\text{C}=\text{C}$ group [9,10], are more reactive [11–14], and allow the Michael addition reaction to occur under mild condition. Clearly, to improve the sensitivity, it is necessary to enhance the reactivity of the probe to cyanide. We reasoned that this could be accomplished by increasing the electrophilicity of the β -carbon. With this in mind, we decided to introduce electron withdrawing 1,3-indandione and electron-deficient DPP moiety to afford probe **1**. Thus, it is anticipated that probe **1** should be highly reactivity to CN^- .

2,5-Dioctyl-3,6-bis(4'-formylphenyl)pyrrolo[3,4-c] pyrrole-1,4-dione (compound **5**) was prepared from *p*-cyanobenzaldehyde as a starting material, in four steps following Scheme 1. Probe **1** was obtained by a straightforward aldol-type condensation reaction of 1,3-indandione with compound **5** in 35% yield as a purple solid.

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