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# A Colorimetric and Fluorescent Probe Based on Michael Acceptor Type Diketopyrrolopyrrole for Cyanide Detection

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Abstract A new probe 1 was synthesized by incorporating an  $\alpha$ ,  $\beta$ -unsaturated ketone to a diketopyrrolopyrrole fluorophore. The probe exhibited a selective and sensitive response to cyanide against other anions. Addition of CN<sup>-</sup> aqueous solution to 1 resulted in a rapid color change from pink to light yellow together with a blue shift from 518 to 421 nm, while other anions did not induce any significant color change. Furthermore, the Michael addition of cyanide to 1 elicited 98% fluorescence quenching at 608 nm, which constituted the fluorescence signature for cyanide detection. The detection limit was 0.67  $\mu$ M using the fluorescence spectra changes, which was far lower than the WHO guideline of 1.9  $\mu$ M. Moreover, 1-based test strips could successfully detect CN<sup>-</sup> solutions.

**Keywords** Michael acceptor · Cyanide anion · Colorimetric · Diketopyrrolopyrrole

## Introduction

Anion recognition is an area of growing interest in supramolecular chemistry due to its crucial role in a wide range of chemical, biological and environmental processes. Among various anions, cyanide is well known as one of the most toxic species and is extremely harmful to mammals. Any accidental

Lingyun Wang lingyun@scut.edu.cn release of cyanide to the environment causes serious problems [1-3]. Therefore, the maximum permissive level of cyanide in drinking water is set at 1.9  $\mu$ M by the World Health Organization (WHO). 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.

Compared with detection approaches for cyanide based on hydrogen bonding or supramolecular interactions [4–7], 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 C = O, C = N, C = C, and so on [8–11]. The irreversible formation of chemical bonds can provide chemodosimetric information and develop ratiometric fluorescent probes. Unfortunately, none of these is ideal. Many of them suffer from the requirement of a long reaction time and elevated reaction temperature, the need for surfactant media and a slow response [12–20]. 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.

As brilliant red and strong fluorescent high performance pigments, diketopyrrolopyrrole (DPP) and its derivatives have gained wide attention in recent years due to its ease of synthetic modification, high fluorescence quantum yields and good light and thermal stability [21–25]. To date, only limited DPP-derived probes for reaction-based cyanide detection have been reported [26, 27]. In the present work, probe **1** for cyanide was designed and synthesized (Scheme 1), in which DPP was used as the fluorophore and an  $\alpha$ , $\beta$ -unsaturated ketone moiety was introduced as the cyanide receptor. The probe displays high selectivity and sensitivity for CN<sup>-</sup> over other anions with a fast response.

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Scheme 1 Synthesis of probe 1



## Experimental

#### **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). The THF solutions of anions ( $F^-$ ,  $CN^-$ ,  $CI^-$ ,  $Br^-$ ,  $\Gamma^-$ ,  $AcO^-$ ,  $HSO_4^-$ ,  $H_2PO_4^-$ ,  $NO_3^-$ ,  $CIO_4^-$ ) were prepared from their tetrabutylammonium salts with distilled tetrahydrofuran.

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 [28]. Compound 6 was synthesized according to the literature [29].

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.

## Synthesis of 1

111.0 mg (0.2 mmol) coumpond 6, 111.6 mg (0.6 mmol) 2,4-dinitrofluorobenzene and 1.00 g (7.25 mmol) K<sub>2</sub>CO<sub>3</sub> were mixed in 10 mL of N,N-dimethylformamide. After stirring overnight at room temperature, the resultant was neutralized with dilute HCl solution and extracted by methylene chloride. The solvent was evaporated under reduced pressure to get the crude product, which was further purified by column chromatography using hexane/dichloromethane/ethylacetate (10/60/1) as an eluent to obtain 120 mg pure compound 1 in 52% yield. m.p. 212-213 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ, ppm): 8.84 (d, J = 2.8 Hz, 2H), 8.31 (dd, J = 2.8 Hz, 2H), 7.87(t, J = 8.4 Hz, 6H), 7.73 (d, J = 8.4 Hz, 4H), 7.70–7.61 (m, 4H), 7.51 (t, J = 7.6 Hz, 2 H), 7.42 (d, J = 15.6 Hz, 2H), 7.21(d, J = 8 Hz, 2H), 6.93(d, J = 9.2 Hz, 2H), 3.77 (t, J = 7.6 Hz, 4H), 1.60 (t, J = 5.2 Hz, 4H), 1.21 (d,J = 6.4 Hz, 20H), 0.84 (t, J = 6.8 Hz, 6H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, δ, ppm): 190.05, 162.5, 155.96, 151.31, 147.66, 144.43, 141.7, 139.01, 136.74, 133.88, 132.59, 131.33, 130.21, 129.28, 129.03, 127.15, 126.24, 122.25, 121.82, 118.35, 110.66, 42.10, 31.69, 29.43, 29.07, 28.98, 26.69,22.57, 14.04. HRMS-ESI: m/z calcd (%) for  $C_{48}H_{52}N_{10}O_{10}$ : 1136.4066 [M + Na]<sup>+</sup>; Found: 1159.4060.

#### **Results and Discussions**

### Spectral Characteristics of 1 with CN

To get insight into sensing behavior of 1 with CN<sup>-</sup>, the absorption spectra of 1 in THF upon titration with CN<sup>-</sup> solution were recorded. As shown in Fig. 1a, free 1 showed two major absorption peaks at 336 and 518 nm. Upon addition of CN<sup>-</sup>, the absorption peaks of 1 at 336 and 518 nm gradually decreased following the formation of two new bands centered at 370 and 421 nm. Meanwhile, two isosbestic points at 358 and 476 nm were observed, which implied new species with less conjugation were formed. Notably, the ratios of A<sub>370</sub>/A<sub>518</sub> and A<sub>421</sub>/A<sub>518</sub> increased over 18.8 and 46.8-fold in presence of 30 equiv. CN<sup>-</sup>, respectively. The corresponding color changes of 1 with the increasing concentrations of cyanide anion are shown in Fig. 1c, resulting in a rapid color change from pink to light yellow.

The CN<sup>-</sup> sensing property was further examined through fluorescent titration studies in detail. As shown in Fig. 2a, 1

Fig. 1 a, b UV-Vis spectral changes and c color changes of 1 in THF (10  $\mu$ M) with increasing concentrations of cyanide anion

showed a major emission peak at 608 nm. Upon addition of  $CN^-$  aqueous solution to **1**, the PL intensity at 608 nm was decreased gradually and blue-shifted to 572 nm. A single crossover point at 570 nm was observed at low concentration of cyanide ion (0–10 equiv). A plateau with the addition of 30 equiv. of  $CN^-$  with 98% fluorescence quenching at 608 nm was achieved. Fig. 2c showed the emission color photographs of **1** in the presence of  $CN^-$  under excitation at 365 nm, where strong red emission was absent.

To exploit its sensing behavior, we examined the time dependent changes in the absorption spectra of 1 (10  $\mu$ M) upon reaction with CN<sup>-</sup> at room temperature. Generally, reaction-based chemosensors suffer from a long response time. In our case, the response of 1 to CN<sup>-</sup> was found to be very fast. The absorption increase around 421 nm reached maximum at 4 and 1 min in presence of 10 and 30 equiv. CN<sup>-</sup>, respectively, indicating nucleophilic addition reaction between the vinyl group and CN<sup>-</sup> was completed (Fig. 3). It is well known that the nucleophilicity of anions is greatly decreased in water due to hydrogen bond formation between the anions and water









**Fig. 3** Time-dependent UV-vis absorption strength of probe 1 (10  $\mu$ M) in THF at 421 nm in the presence of CN<sup>-</sup> (10 equiv.  $\blacktriangle$  in *green*, 30 equiv. • in *red*) at room temperature

molecules. For instance, Guo's group reported that the reaction of anthracene-indanedione Michael receptor and cyanide could be completed within 2 min at an elevated temperature of 50 °C in 9:1 CH<sub>3</sub>CN-water, and 10 equiv. of cyanide was required to reach the spectral saturation [30]. Herein, in the presence of 10 equiv. of cyanide, the nucleophilic CN<sup>-</sup> addition to 1 occurred very rapidly (within 4 min), indicating high reactivity was the unique feature of 1, which was impressive as many reported cyanide probes require high equivalents of cyanide and long reaction time to reach a maximal spectral signal [31–41].

#### Selectivity of 1 with CN<sup>-</sup>

For the purpose of evaluating selectivity of **1** to cyanide, the absorption spectral change of **1** upon addition of other anions

Fig. 4 a UV-vis absorption spectra and b color changes of 1 in THF (10  $\mu$ M) upon addition of 10 equiv. of each anion



was also investigated. Dramatic change of the absorption spectrum induced by  $CN^-$  was observed, while almost no changes could be found in presence of other anions, including  $F^-$ ,  $CN^-$ ,  $C\Gamma^-$ ,  $Br^-$ ,  $\Gamma^-$ ,  $AcO^-$ ,  $HSO_4^-$ ,  $H_2PO_4^-$ ,  $NO_3^-$ ,  $CIO_4^-$  (Fig. 4a). More importantly, the color change from pink to light yellow can be clearly observed by the naked eye in

presence of  $CN^-$ , while other anions did not induce any significant color change, which suggested that naked-eye selective detection of  $CN^-$  became possible (Fig. 4b).

Meanwhile, only CN<sup>-</sup> rendered a remarkable "Turn-Off" fluorescence response, whereas all other anions revealed a negligible change in the fluorescent spectra of **1** (Fig. 5a). In

Fig. 5 a Fluorescence and b emisson color changes of 1 in THF (10  $\mu$ M) upon addition of 10 equiv. of each anion aqueous solution







Fig. 6 Selectivity of 1. The *black bars* represent fluorescence intensity at 601 nm of 1 (10  $\mu$ M) in THF in the presence of other anions (300  $\mu$ M)

the presence of 30 equivalents of  $CN^-$ , an emission peak at 601 nm with 98% fluorescence quenching was observed. Fig. 5b showed the photographs of 1 in the presence of different anions under excitation at 365 nm using a portable UV lamp. The disappearance of intense red color of the solution upon interaction of 1 with  $CN^-$  was present. However, other anions did not induce any significant emission color change.

Another important feature of **1** is its high selectivity toward the  $CN^-$  in presence of other competitive anions. Changes of fluorescence spectra of **1** (10  $\mu$ M) caused by  $CN^-$  (30 equiv) and miscellaneous competing species (30 equiv) were recorded in Fig. 6. As can be seen, these competitive species, did not lead to any significant interference. In the presence of these ions, the  $CN^-$  still



Fig. 7 Job's plot for the evolution of binding stoichiometry between 1 and cyanide ions in THF solution. The total concentration of cyanide ions and 1 was 10  $\mu$ M



Fig. 8 Benesi-Hildebrand plot of 1 (10  $\mu$ M) using 1:2 stoichiometry for association between 1 and cyanide ions

produced similar optical spectral changes. These results showed that the selectivity of sensor 1 toward  $CN^-$  was not affected by the presence of other anions.

For determination of stoichiometry between 1 and CN<sup>-</sup>, Job's plot analyses were used. The method is that keeping total concentration of 1 and CN<sup>-</sup> at 10.0  $\mu$ M, and changing the molar ratio of CN<sup>-</sup> (X<sub>M</sub>; X<sub>M</sub> = [CN<sup>-</sup>]/{[1] + [CN<sup>-</sup>]}) from 0.1 to 0.9. From Fig. 7, when molar fraction of CN<sup>-</sup> was 0.3, the I<sub>0</sub>-I value got to maximum, indicating that forming a 1:2 complex between 1 and CN<sup>-</sup>.

Moreover, the binding stoichiometry and the binding constant to CN<sup>-</sup> were determined by Benesi–Hildebrand double reciprocal method following Eq. (1). Here  $I_0$  and  $I_{min}$  are the fluorescence intensities at zero and the maximum concentrations of CN<sup>-</sup>, [CN<sup>-</sup>] is the total CN<sup>-</sup> concentration,  $K_b$  is the binding constants for 1:2 binding mode. For receptor 1, a good linear fit could be obtained by Eq. (1), indicative of the binding stoichiometry of 1:2,



Fig. 9 The linear relation for concentration of  $CN^-$  vs fluorescence intensity of 1

**Fig. 10** a Color and b emission changes of 1-based test strips before and after addition of CN<sup>-</sup>



which conformed to the presence of two a,b-unsaturated ketone moiety in receptor 1 (Fig. 8). The binding constant was found to be  $1.24 \times 10^8$  M<sup>-2</sup>.

$$\frac{1}{I_0 - I} = \frac{1}{K(I_0 - I_{\min})[CN^-]^2} + \frac{1}{I_0 - I_{\min}}$$
(1)

The detection limit of **1** for CN<sup>-</sup> was calculated based on the fluorescence titration data according to a reported method [42]. Under optimal conditions, calibration graphs for the determination of CN<sup>-</sup> were constructed. The decreased fluorescence intensity of the system showed a good linear relationship ( $R^2 = 0.998$ ), as shown in Fig. 9. The detection limit for CN<sup>-</sup> was determined as 0.67 µM based on S/N = 3, which was far lower than the WHO guideline of 1.9 µM cyanide [43–47].

#### **Practical Application**

Active materials-based test strips represent a group of convenient probing substrate for practical utilization. 1based test strip was thus fabricated by immersing filter paper into the THF solution of 1  $(1.0 \times 10^{-3} \text{ M})$  and drying in air, which was energy- and cost-effective. The corresponding probing experiments were carried out subsequently. The results indicated that this protocol really took effect. The obvious color change from pink to yellow was observed by immersing this test strips in aqueous solutions of CN<sup>-</sup>, exhibiting colorimetric changes differentiable to naked eyes (Fig. 10a). As shown in Fig.10b, when the 1-exposed test strip was immersed into aqueous solutions of CN<sup>-</sup> (0.01 M), strong red fluorescence disappeared and easily distinguished. Since the color change was rapidly and clearly detected, the test strips could conveniently detect CN<sup>-</sup> in water solutions.

## Conclusions

In summary, we developed a new type of DPP-based "Turn-Off" fluorescence chemodosimeter, which displayed high selectivity and sensitivity for the detection of cyanide. Addition of  $CN^-$  aqueous solution to 1 in THF resulted in a rapid color change from pink to light yellow, while other anions did not induce any significant color change, suggesting naked-eye selective detection of  $CN^-$  using 1 became possible. In the presence of  $CN^-$ , the strong red emission of 1 was completely quenched. Test strips for use in practical applications are successfully realized.

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