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## Fluorescence turn-on chemodosimetric sensing of cyanide by cyanovinylterpyridine modified phthalonitrile and subphthalocyanine

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### ABSTRACT

Terpyridine-attached phthalonitrile (Pn-TP) linked by cyanovinyl bond has been synthesized and employed for the preparation of subphthalocyanine (SubPc-TP) bearing conjugated terpyridine moieties. Both Pn-TP and SubPc-TP exhibited highly selective fluorescence turn-on in the presence of cyanide anions ( $\text{CN}^-$ ) based on chemodosimetric sensing mechanism. The conjugation of the Pn-TP molecule was interrupted by the addition of  $\text{CN}^-$  at the cyanovinyl bond, showing the ratiometric fluorescence turn-on behavior. This sensing mechanism was further supported by density functional theory calculation and nuclear magnetic resonance titration studies. Optical and photophysical responses of SubPc-TP towards  $\text{CN}^-$  were also investigated, in which similar fluorescence enhancement was observed due to the addition of  $\text{CN}^-$  at the reactive boron trimer. The detection limit was estimated to be 94 nM, much below the World Health Organization-allowed level (1.9  $\mu\text{M}$ ) of  $\text{CN}^-$  in water.

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### 1. Introduction

Cyanide has been considered highly toxic and harmful to the living things even in trace amounts [1]. It often caused the arrest of respiration and leads to death owing to strong binding affinity at the active site of the heme unit [2–4]. In spite of well-known toxicity, the usage in industries has been unavoidable, especially in metallurgy and organic chemicals, and synthetic polymers and fibers [5–7]. Thus, it should be essential to develop the method for detecting and monitoring the level of cyanide. Fluorescence chemosensors have been considered convenient in terms of expense, sensitivity and tenability compare to the other instrumental methods [8–12]. Numerous reports have been available for sensing the cyanide anion, in which most sensing mechanisms depended on the functional groups present in the organic molecules. Some of them involved hydrogen bonding [13], nucleophilic addition [14], excited state intramolecular proton transfer [15] and the activation of carbonyl group bonds [16,17]. Chemodosimetric mechanism is a unique method that based on the reaction of the analyte with organic molecules [18–20], which exhibited ratiometric changes in both absorbance and fluorescence intensities with high selectivity and quick response [21–24]. Sensing compounds with fluorescence quenching (turn-off) were not as attractive as those with enhancement (turn-on), hence developing a chemosensor with ratiometric turn-on response is highly required. Furthermore, extending the ability of detection of cyanide anion in water has been important [25,26], as many inorganic cyanide salts are well soluble in water. Thus, it is critically

necessary to develop the fluorescence turn-on and ratiometric chemosensor for cyanide in aqueous mediums.

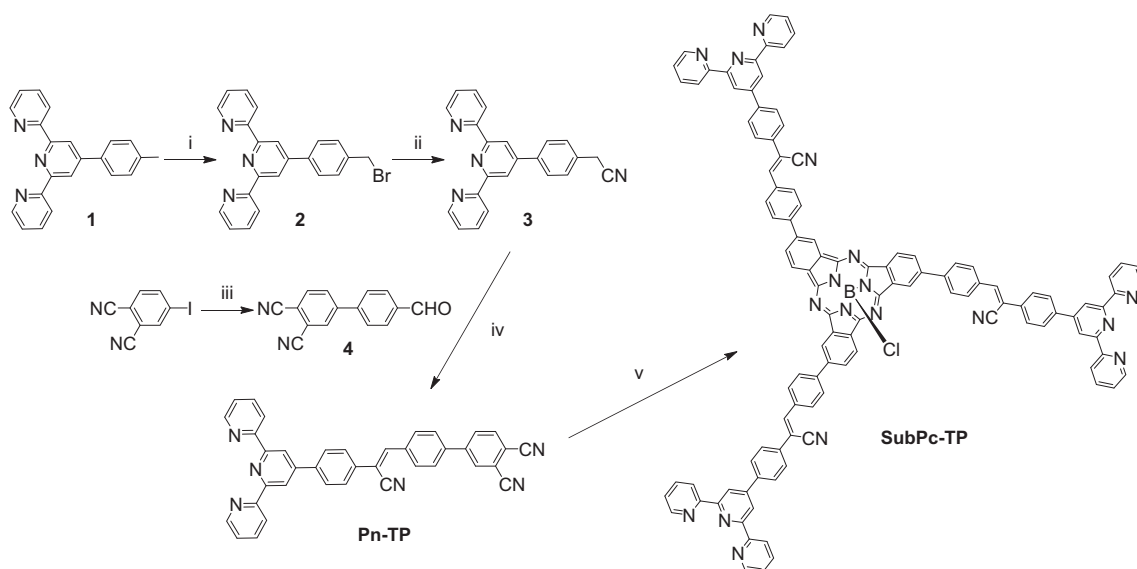
Here we have synthesized a new terpyridine-attached phthalonitrile (Pn-TP) linked by cyanovinyl bond and further prepared subphthalocyanine (SubPc-TP) bearing conjugated terpyridine moieties. Since phthalonitrile and terpyridine are both strong acceptors, their fluorescent natures were diminished when the bond rotation was restricted by the cyanovinyl linkage [27–29]. When  $\text{CN}^-$  was added, the cyanovinyl bond was set free to rotate, and, consequently, both terpyridine and phthalonitrile regained their original fluorescence. Another attractive aspect of Pn-TP is the utility as a precursor to form complex and hierarchical chromophoric architectures [30–32]. Indeed, a subphthalocyanine tethered with conjugated terpyridine moieties (SubPc-TP) was successfully prepared, which showed immediate color bleaching and dramatic fluorescence enhancement towards  $\text{CN}^-$ . In this case, the absorption and fluorescence responses are attributed to the concurrent addition of  $\text{CN}^-$  at the SubPc core and the cyanovinyl bond. Current responses, accompanying a significant fluorescence increase, can be distinguished from previous reports based on fluorescence quenching. In addition, both Pn-TP and SubPc-TP can be applied in aqueous media to recognize  $\text{CN}^-$  selectively and rapidly, based on chromo-fluorogenic and ratiometric responses.

### 2. Results and Discussion

Overall synthetic procedures of Pn-TP and SubPc-TP were shown in Scheme 1. Briefly, terpyridine intermediates **2** and **3** were successively synthesized as per literature procedure [33]. Suzuki coupling reaction was carried out to synthesize compound **4** from 4-iodo-phthalonitrile

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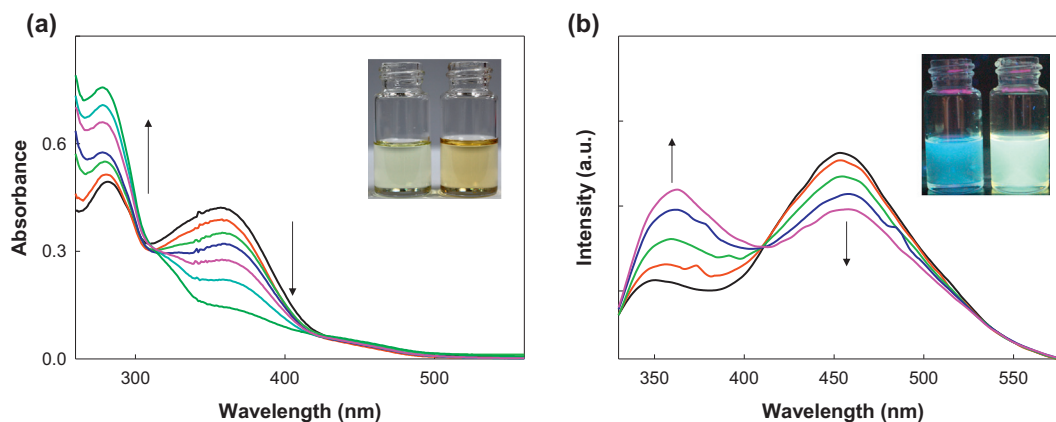
**Scheme 1.** Synthetic procedures: (i) NBS, *O*-DCB, 80 °C, (ii) NaCN, DMSO, 25 °C, (iii) 4-formyl phenyl boronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, (iv) NaOEt, Ethanol, 80 °C, (v) BCl<sub>3</sub>·DCM, DMSO, 160 °C.

to 4-formyl phenyl boronic acid. The Pn-TP was obtained by condensation reaction between **3** and **4**. The chemical structure of Pn-TP was confirmed by nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy.

The pristine Pn-TP was reddish orange in color. In UV-visible spectrum, a broad absorption band around 300–400 nm was observed with a weak tailing at 400–500 nm. Typical absorbance of terpyridine moiety was also observed at 280 nm. Pn-TP selectively recognize the CN<sup>−</sup> anion by the decrease in the absorbance of the band at 300–400 nm and enhancement in the band at 280 nm. In contrast, when other anions, such as F<sup>−</sup>, AcO<sup>−</sup>, H<sub>2</sub>PO<sub>4</sub><sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>, and NO<sub>3</sub><sup>−</sup>, were added in concentrations of up to 100 M equivalents, no noticeable changes were observed in the UV-vis spectrum (Fig. S1). In the titration of CN<sup>−</sup> to Pn-TP, the peak intensity at 300–400 nm was gradually decreased as that at 280 nm was enhanced, and the solution color also changed from light green to yellow (Fig. 1a). The remarkable changes upon CN<sup>−</sup> titration were attributed to the addition of CN<sup>−</sup> at the cyanovinyl bond linking phthalonitrile and terpyridine. Subsequently, the conjugation between the phthalonitrile and terpyridine was broken, permitting free rotation of the bond, which caused the spectral change. The selective detection of cyanide anion over other anions are attributed to strong nucleophilic nature CN<sup>−</sup>, which can attack the activated vinyl bond by nucleophilic addition reaction.

When excited at 320 nm, Pn-TP exhibited fluorescence maximum at 450 nm with a shoulder band at 360 nm, which were attributed to the ICT effect and terpyridine moiety, respectively. After adding CN<sup>−</sup>, the fluorescence intensity at 360 nm was enhanced with the concomitant reduction in the intensity of CT transition at 450 nm (Fig. S2). As a result, the bluish-green fluorescence of Pn-TP in the solution state turned to an intense yellow after the addition of CN<sup>−</sup>, when examined under UV 365 nm illumination (Fig. 1b). This fluorogenic sensing of Pn-TP to CN<sup>−</sup> matched well the proposed mechanism for the sensing and switching nature of Pn-TP being the conjugation breakage to the acceptor and the resulting free terpyridine moiety shown enhanced fluorescence at 360 nm. Based on the fluorescence change for Pn-TP to cyanide, detection limit was determined to be 12.0 × 10<sup>−8</sup> mol L<sup>−1</sup> by 3 σ/K (Fig. S4) [34].

For structural clarification, we performed the <sup>1</sup>H NMR titration experiment (Fig. 2). The peak at 8.2 ppm representing the H<sub>a</sub> proton at the cyanovinyl bond disappeared after adding CN<sup>−</sup>. A new peak for the proton H<sub>b</sub> was observed at 5.7 ppm, since the carbon became saturated due to the conjugation breakage after adding CN<sup>−</sup>. With the loss of conjugation, the protons from terpyridine and phthalonitrile moieties were shifted to their pre-conjugation positions. Since the cyanide addition involves the change in hybridization of vinyl carbon, we carried out



**Fig. 1.** (a) UV-Vis spectra of Pn-TP (10 μM) upon addition of 0–12 equivalents of KCN in 8:2 DMSO:water. The inset shows a color change of Pn-TP from pale green to yellow with the addition of CN<sup>−</sup> anion. (b) The change in fluorescence intensity of Pn-TP (10 μM) by the addition of 0–12 equivalents of KCN in 8:2 DMSO:water. The inset shows photo-images taken under 365 nm UV light. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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