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Michael addition-based colorimetric and fluorescence chemodosimeters for the nanomolar-level tracking of cyanide ions in aqueous-organic media

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ABSTRACT

Two new naphthalimide-based chemodosimeters, **R1** and **R2**, for CN^- anions were designed and synthesized. For the sensing event, the dicyanovinyl group and ethyl cyanoacrylate groups acted as the recognition sites in conjunction with the electron-withdrawing naphthalimide fluorophore group. Both receptors exhibited high sensitivity and selectivity, with apparent response signals that could be observed by the naked eye, even in the presence of various other interference anions. We used electronic and fluorescent spectroscopic techniques, NMR titration measurements and HRMS techniques to rationalize the sensing mechanisms of these two receptors. Upon the addition of CN^-, the fluorescence of **R1** and **R2** was distinctly enhanced. Specifically, compared with **R2**, **R1** exhibited a higher affinity and a higher sensitivity (detection limit of 9.69 nM) toward CN^- in THF- H_2O (3:7, v/v) mixture.

1. Introduction

Recently, considerable effort has been devoted to the design chemosensors for anions. The reason for this intensive interest is the importance of the detection of anions in disciplines such as biology and environmental science [1]. The ease of production and extreme toxicity of anions underscores the need to detect these odorless and colorless chemicals. Among anions, CN^- is extremely toxic to mammals in small amounts, and it can affect many functions, including those of the vascular, visual, central nervous, cardiac, endocrine and metabolic systems [2]. Moreover, even very small amounts of CN^- are extremely toxic to living creatures because it binds to cytochrome c oxidase and inhibits the mitochondrial electron transport chain [3], which also leads to environmental contamination. According to the World Health Organization (WHO), the threshold limit of CN^- in drinking water is 1.9×10^{-6} M [4]. Nevertheless, CN^- has been produced in large quantities and is used in various industrial processes, such as the manufacture of synthetic fibers, resins, and herbicides and in gold mining, electroplating and metallurgy [5,6].

Thus, the development of CN^--selective colorimetric and fluorescent sensors is urgently needed, and a large number of chemosensors for CN^- have been reported [7–11]. Most of the traditional sensors for CN^- are based on supramolecular approaches that depend on hydrogen-bonding motifs; however, the main disadvantage of such an approach is a lack of selectivity. Other anions, e.g., fluoride, acetate and phosphate ions, often interfere with such assays [12–14]. To overcome this limitation, many other detection methods for CN^- involve the chemical reaction of CN^- with metal-coordinated sensors [15–17]. Recently, more attention has been devoted to the design of chemodosimeters for selective recognition of the CN^- ion [18]; this reaction-based approach is usually irreversible and relies on the strong nucleophilicity of CN^- [19], which has been successfully utilized by the reaction between an organic host and a CN^- guest [20–42]. The literature contains only a few studies involving the Michael addition of CN^- to doubly activate acceptors, where two electron-withdrawing groups are necessarily attached to the C=C [43–49].

Photo-induced electron transfer (PET) has become one of the most frequently used concepts in the field of molecular recognition since its introduction by Silva et al. in 1997 [50]. Generally, PET-based probes are composed of three units: a fluorophore, spacer and a receptor unit. PET is the most commonly exploited mechanism for the development of fluorescent sensors, which are essentially three-component systems that comprise a fluorophore

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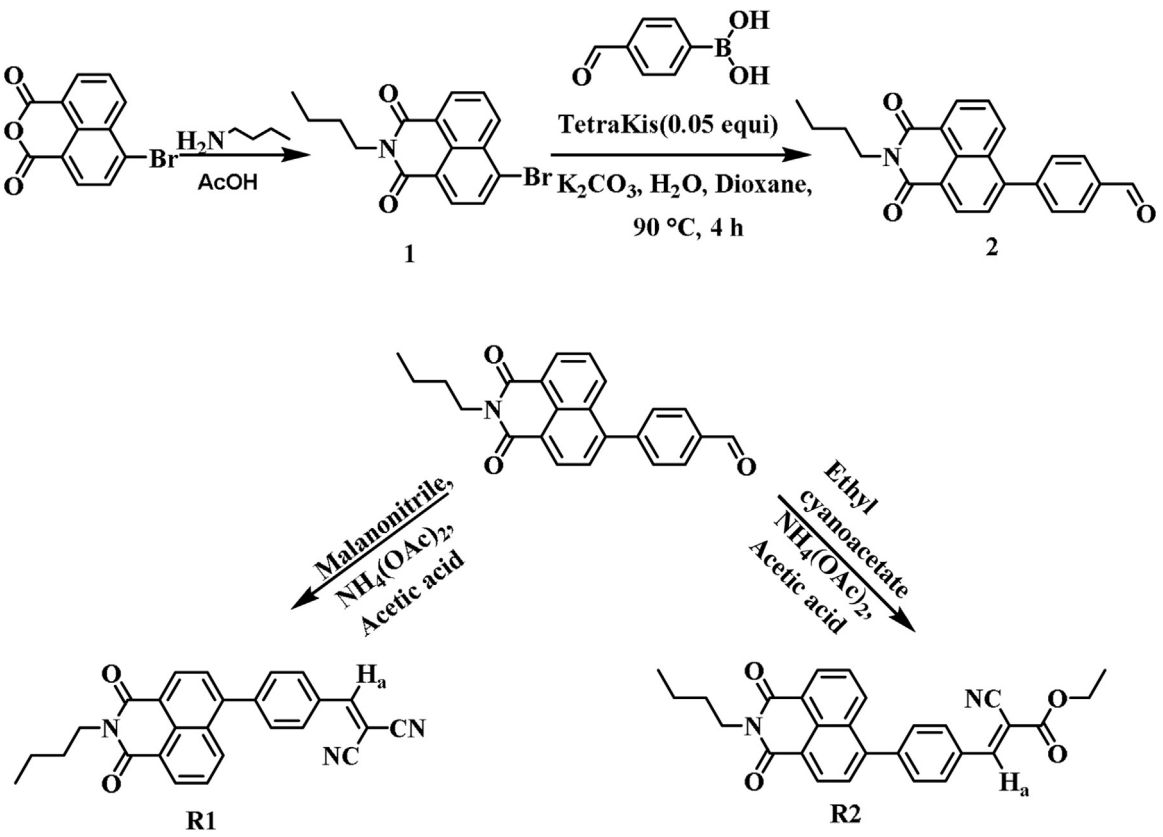

Scheme 1. Synthesis method for the chemodosimeters **R1** and **R2**.

– spacer – receptor system. The components are selected such that the PET between the fluorophore and the receptor quenches the fluorescence of the system. In the presence of a guest, the PET communication between the receptor and the fluorophore is disrupted and the fluorescence of the system is recovered. Thus, the presence of a guest is signaled by the fluorescence enhancement (FE) of the system. A large number of fluorescent sensors based on the PET process have been developed for protons and metals [51,52]. In contrast, the number of probes for biologically important anions remains limited.

The first example of a fluorescent anion sensing system that utilizes the PET process was described by Czarnik et al. [53]. They reported that anthrylpolyamines can be used in aqueous solution at a pH of 6–7 to detect anions such as phosphate and pyrophosphate. Later, various authors developed fluorogenic sensors that contain thioureas [54,55] and bisimidazolium [56] as the binding functionalities because of their hydrogen-bond donor properties. Moieties such as acridinedione [57], naphthilimide, and anthracene [58–60] have been used as the fluorophore units in these sensors. A survey of the literature reveals that numerous attempts have been made to increase the H-bond donor property of the receptor moiety in thiourea-based sensors. Unfortunately, all of these available PET-based fluorophores sense more than two anions, such as F^-, $H_2PO_4^-$, CH_3COO^-, etc., and the main drawback to this design is the quenching of the fluorescence of the fluorophore in the presence of guest species. These limitations can be circumvented by using the chemodosimeter approach, which is less prone to such selectivity problems. Still, most of the currently available PET probes follow the quenching strategy because anions bind with receptors that enhance the electron-donating character and, thus, strengthen the conjugation [59]. Unlike many PET sensors for anions, the fluorescence of many sensors for cations are “switched on” rather than “switched off” upon cation recognition because of their electron-withdrawing nature and reduced conjugation [60,61]. Building upon this prior work, we here report two novel chemodosimeters, **R1** and **R2**, that were developed according to a new strategy for the development of color/fluorescent CN^--ion sensors based on the PET signaling mechanism, where 1,8-naphthalimide (Naph) was used as the fluorophore and a cyanovinyl group was used as the receptor (i.e., the CN^- binding site). These two moieties are linked covalently in a conjugated manner that drains the electronic communication between the receptor unit and fluorophore moiety. This design incorporates several important structural properties that are vital to the success of the new strategy. The CN^- binds to the receptor units (C=C) and enhances their electron-withdrawing character, which results in an enhancement of both absorption and emission. To our knowledge, these chemodosimeters are the first examples of charge-neutral fluorescent PET sensors that exhibit ideal PET behavior for the CN^- anion in an aqueous medium.

2. Experimental section

2.1. Chemicals and apparatus

All of the reagents for the synthesis of chemodosimeters **R1** and **R2** were obtained commercially and were used without further purification. Spectroscopic-grade solvents were used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer operated at 300 and 75 MHz, respectively, using tetramethylsilane as the internal standard. The chemical shifts in the ^1H NMR spectra are expressed in units of ppm (normalized integration, multiplicity and the value of *J* in Hz). FAB-MS spectra were obtained using a JEOL JMS 700 mass spectrometer. High-resolution mass spectra were recorded on a micrOTOF-QII (Bruker, Daltonik, Germany) mass spectrometer. UV–Vis spectra were recorded using an Agilent 8453 spectrophotometer (1 cm quartz cell) at 25 °C.