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Selective fluorescent and colorimetric recognition of cyanide via altering hydrogen bonding interaction in aqueous solution and its application in bioimaging

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ABSTRACT

In this paper, we report a new pyrene imine derivative which bears a relatively rigid intramolecular hydrogen bonding pocket, for fluorescent and colorimetric sensing of cyanide. In CH_3CN solution, the chemosensor displayed distinct fluorescent and UV absorption changes towards CN^-, $CH_3CO_2^-$, F^-, and $H_2PO_4^-$. Notably, in an aqueous CH_3CN medium (10%, v/v), the selectivity towards cyanide over other various anions were observed with an obvious fluorescence enhancement and colorimetric change. Thus, we demonstrated that the selectivity of the pyrene based chemosensor towards anions can be optimized *via* controlling hydrogen bonding interactions in different solvent systems. Finally the application of the chemosensor in fluorescent imaging cellular cyanide variation was demonstrated with living HeLa cells.
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1. Introduction

Construction of novel detection methods capable of fluorescent and colorimetric recognition of anions have been active research targets in supramolecular chemistry, due to their importance in biology and the environment [1–5]. Among the various anions, cyanide is of particular interest due to its extreme toxicity. The best known effect of cyanide is as an inhibition of respiration, more specifically, the inhibition of the terminal oxidase (cytochrome oxidase) of the mitochondrial respiratory chain. The World Health Organization (WHO) has set an upper limit of 1.9 μM for cyanide in drinking water. In spite of the high toxicity of cyanide, cyanide salts are widely used in the chemical industry (1.5 million tons/year) and in gold mining [6,7].

Accordingly, it is very important to monitor or image cyanide ions by simple methods. Fluorescence and colorimetric detections of anions are the most convenient methods in this regard and have been successfully developed based on various mechanisms, such as intramolecular charge transfer (ICT), photo-induced electron transfer (PET), excited state intramolecular proton transfer (ESIPT), and metal-ligand charge transfer (MLCT) [8,9]. Among the various approaches, chemodosimeters and displacement based ensembles have shown quite successful results, which include Michael type addition, cyanohydrin reaction and displacement approach using high metal-cyanide affinity [10–38].

On the other hand, less examples of hydrogen bonding based chemosensors are available [33–38] since it is very challenging to get a high selectivity for cyanide through these conventional hydrogen bonding interactions. However, in the current study, we successfully demonstrated that a relatively simple and rigid hydrogen bonding pocket can generate sufficient selectivity for cyanide in combination with controlling solvent system. A new pyrene derivative **1** has been synthesized, in which a pyrene group with hydroxyl group and a nitrobenzene group bearing hydroxyl group, are connected via imine linkage. In CH_3CN solution, fluorescence enhancements as well as colorimetric changes were

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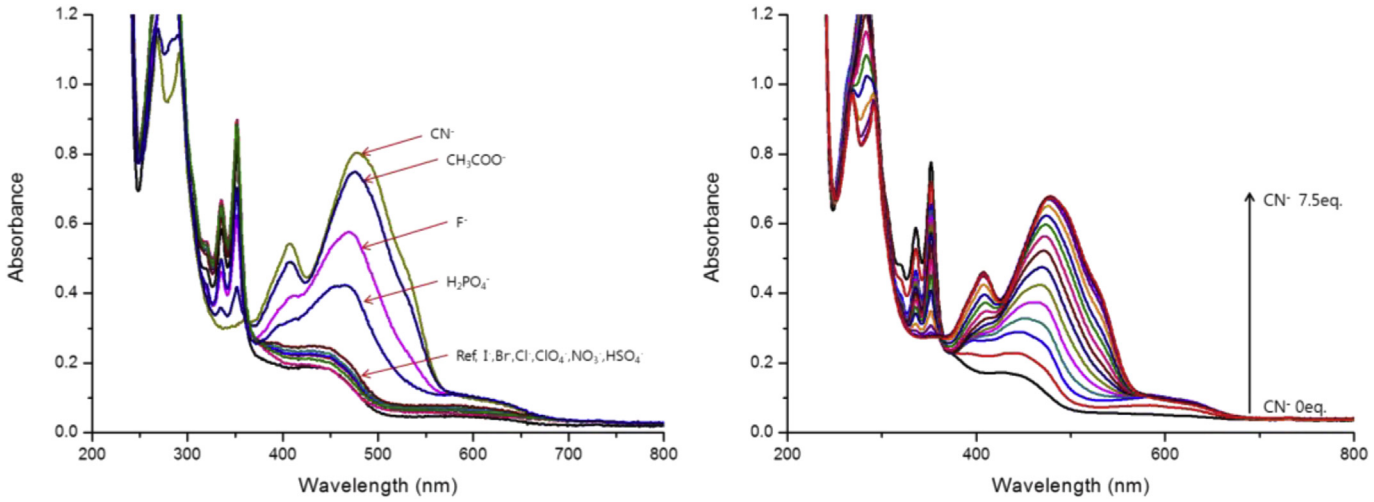

Fig. 1. Left: UV spectra of **1** (5 μM) with anions in CH_3CN solution upon addition of 10 equiv. of anions. Right: UV titration of **1** (5 μM) with CN^- in CH_3CN solution.

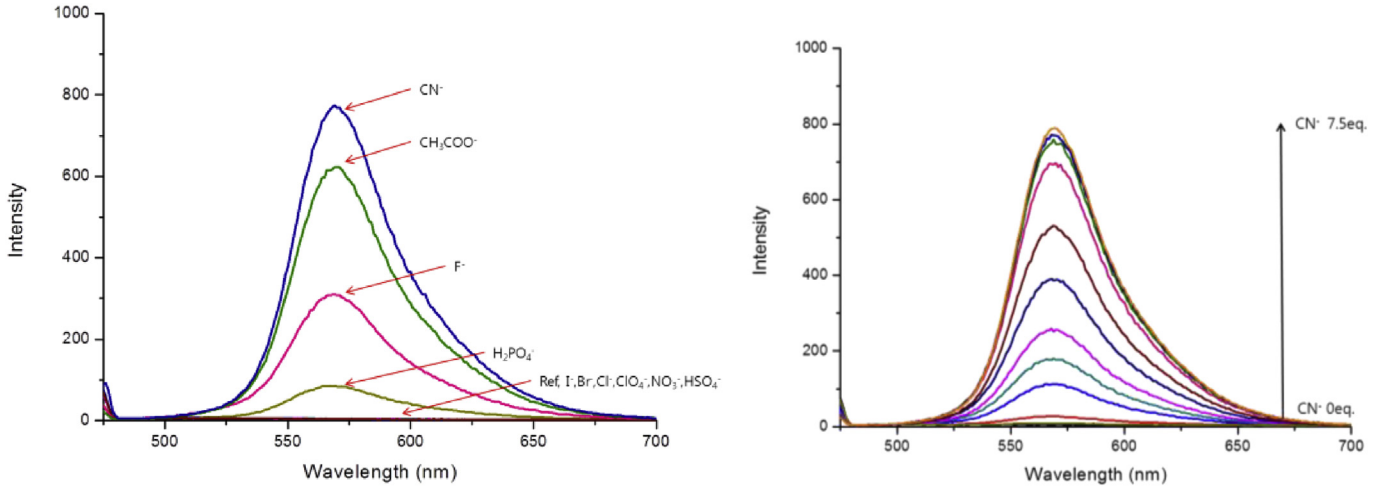

Fig. 2. Left: Fluorescence spectra of **1** (5 μM) upon the addition of 10 equiv. of various in CH_3CN solution. Right: Fluorescence titrations of **1** (5 μM) with CN^- in CH_3CN solution (Excitation wavelength: 470 nm) (Slit: 3 × 5 nm).

observed with CN^-, $CH_3CO_2^-$, F^- and $H_2PO_4^-$. On the other hand, in CH_3CN–H_2O medium (10%, v/v), a selective fluorescence enhancement with cyanide among the various anions, which can be attributed to the favorable interaction between other anions and water compared to that of CN^-. A fluorescent chemosensor **1** contains relatively rigid hydrogen binding pocket and unique and different selectivity was obtained by controlling solvent systems.

2. Experimental

2.1. Synthesis

2.1.1. Materials and methods

Materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel (230–400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded using 300 MHz and 75 MHz. Chemical shifts were expressed in ppm and coupling constants (J) in Hz.

2.1.2. Synthesis of *1*

A stirred solution of 1-hydroxypyrene-2-carbaldehyde **2** (0.30 g, 1.22 mmol) and 2-amino-4-nitrophenol (0.19 g, 1.22 mmol) in ethanol (60 mL) was heated under reflux overnight under a nitrogen atmosphere. The mixture was cooled to room temperature and a dark blue colored solid was separated and filtered, washed thoroughly with ethanol, and dried in vacuum yielded 0.42 g (90%) of **1**: mp 348 °C; IR (KBr,cm^{-1}):1614($V_{C=N}$), 1527,1332, (V_{NO2}), 887, 839, 817, 761, 682($V_{C=C}$).^1H NMR (DMSO-d_6) δ 14.85 (s, 1H), 11.57 (s, 1H), 9.58 (s, 1H), 8.46 (s, 1H), 8.45 (s, 1H), 8.43 (d, 1H, J = 10.5 Hz), 8.13 (d, 1H, J = 7.5 Hz), 8.10 (d, 1H, J = 4.5 Hz), 8.08 (t, 1H, J = 4.5 Hz), 8.06 (d, 1H, J = 3.6 Hz), 8.01 (d, 1H, J = 1.5 Hz), 7.96 (d, 1H, J = 7.5 Hz), 7.87 (d, 1H, J = 9 Hz), 7.14 (d, 1H, J = 9 Hz); ^{13}C NMR (DMSO-d_6) δ 165.26, 158.24, 156.87, 140.45, 135.00, 132.69, 132.47, 129.39, 127.98, 127.54, 126.87, 125.27, 124.88, 124.81, 124.68, 124.54, 123.44, 121.84, 119.48, 118.50, 116.92, 116.41, 115.81; HRMS (FAB) m/z = 383.1005 $(M)^+$, calc. for = $C_{23}H_{15}N_2O_4$ 383.1026.

2.2. Preparation of anion solutions for fluorescent study or UV absorption study

Stock solutions (10 mM) of the tetrabutylammonium salts of $CH_3CO_2^-$, F^-, Cl^-, ClO_4^-, CN^-, NO_3^-, Br^-, I^-, $H_2PO_4^-$ and HSO_4^- in CH_3CN were prepared. Stock solution of **1** (1 mM) was prepared in DMSO. Test solutions were prepared by placing 30 μL of the

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