



## Coumarinyl aldehyde as a Michael acceptor type of colorimetric and fluorescent probe for cyanide in water

Gun-Joong Kim, Hae-Jo Kim \*

Department of Chemistry, Hankuk University of Foreign Studies, Yongin 449-791, Republic of Korea

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### ABSTRACT

A simple aldehyde-functionalized coumarin (**1**) was utilized as a doubly activated Michael acceptor type of chemodosimeter for cyanide in water. The probe has shown a selective and sensitive response to the cyanide anion over other various anions through the Michael addition reaction of the cyanide to **1**. When cyanide anions were added, the prominent color changes as well as fluorescence changes of **1** were observed so that millimolar concentrations of cyanides were detectable by the naked eye.

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Cyanide is a hazardous chemical that damages by absorption through the lungs, gastrointestinal tract, and skin, and can kill mammals upon binding to a heme unit.<sup>1</sup> The process of cellular respiration in mammals is inhibited by the cyanide anion, which interacts strongly with the heme unit at the active site of cytochrome  $a_3$ .<sup>2</sup> Although cyanides have been found in many foods and plants, most environmental cyanides are released by industries involved in gold mining, electroplating, and metallurgy.<sup>3</sup> Humans may be exposed to cyanides from dietary, industrial, environmental, and other sources. Consequently, there is of considerable interest in detecting the presence of the toxic cyanides by using chemosensors.<sup>4</sup> There are, however, a few chemical probes<sup>5</sup> that are operating in water and show both the colorimetric and fluorescence changes upon the complexation of cyanide anions.<sup>6</sup>

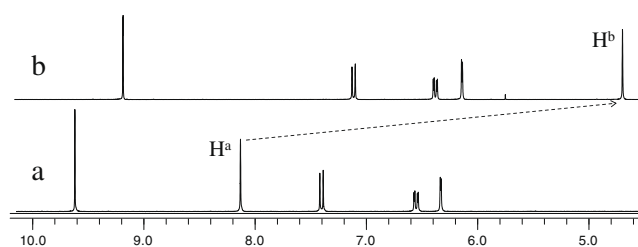
Recently, our group developed a doubly activated coumarin<sup>7</sup> as a cyanide probe and herein we report a new Michael acceptor type of colorimetric and fluorescent probe **1** for cyanide, which is operating in water.

Probe **1** has a doubly activated coumarin unit as a Michael acceptor toward the cyanide anion. The chemical reaction of **1** with the cyanide nucleophile through a conjugate addition will change the electronic structure of the coumarin fluorophore so that the fluorescence intensity of **1** can be significantly changed. For the aim, the chemodosimeter **1** was prepared according to the literature procedure.<sup>8</sup>

In order to get an insight into the reaction, we investigated <sup>1</sup>H NMR spectrum after adding cyanide anions to **1** and compared it

with that of the probe itself. Upon the addition of cyanides to **1**, a new set of <sup>1</sup>H NMR peaks appeared and the reaction was almost complete within 10 min. <sup>1</sup>H NMR spectral analysis showed that an aromatic proton at 8.15 ppm of **1** was highly upfield shifted to 4.68 ppm, while the other aromatic protons and an aldehyde proton are slightly upfield shifted (Fig. 1). These <sup>1</sup>H NMR spectra indicate that the cyanide anion was added to the aromatic region rather than the aldehyde group of **1**. <sup>13</sup>C NMR spectra have corroboratively shown that the cyanide anions were added to the aromatic region (Fig. S2), leading to the Michael addition product of **2**.

The chemical reaction in water could be monitored by UV–vis spectroscopy. Upon the addition of cyanide (1000 equiv) to **1** (10 μM in HEPES buffer), the absorption maximum at λ 446 nm decreased with an apparent rate constant of  $k = 6.4 \times 10^{-4} \text{ s}^{-1}$ , whereas a new maximum appeared around λ 282 nm with a pseudo-isosbestic point at λ 311 nm (Fig. 2). These spectral changes could be observed by the naked eye. The light green color of **1** turned to colorless as soon as cyanide ions were added.



**Figure 1.** Partial <sup>1</sup>H NMR spectra of **1** (20 mM) in DMSO- $d_6$ /D<sub>2</sub>O (100:1, v/v). (a) **1**, (b) **1** + 1.0 equiv of NaCN.

\* Corresponding author. Tel.: +82 31 330 4703; fax: +82 31 330 4566.  
E-mail address: [haejkim@hufs.ac.kr](mailto:haejkim@hufs.ac.kr) (H.-J. Kim).



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