A simple chemosensor for naked-eye and fluorogenic detection of cyanide

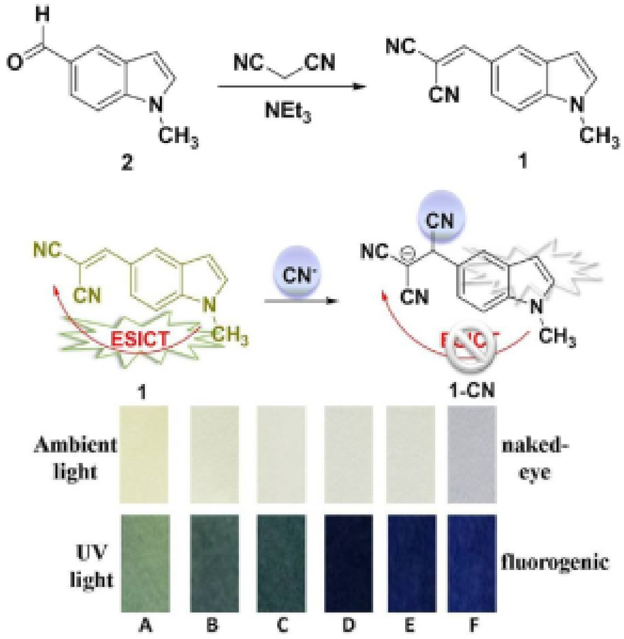

Fig.1. Synthetic route of sensor 1 and the reaction mechanism of 1 with the cyanide anion for forming 1-CN (top). Photographs of test strips of 1 at various concentrations of CN? (10?5 M) under ambient and UV light : (A) 0; (B) 0.5; (C) 1.0; (D) 1.5; (E) 2.0; and (F) 2.5 (bottom).

Cyanide ($CN^{?}$) is one of the most lethally toxic chemicals to the living environment. However, $CN^{?}$ is widespread in industrial processes, such as gold mining, metallurgy, electroplating, and the synthesis of nylon, fibers, and resins Thus, it is highly desirable to create simple, low-cost, selective, sensitive, colorimetric, and fluorometric chemosensors for detecting $CN^{?}$.
Optical sensors for $CN^{?}$, in which a change in the absorption and/or fluorescence spectra is monitored, have been intensively investigated due to their desirable features including simplicity, high sensitivity, and potential for *in vivo* imaging. We therefore developed a simple low-cost 1-methylindole-malononitrile conjugate, **1** (Fig. 1), as a colorimetric and ratiometric fluorescent probe, which could sense $CN^{?}$ with specific selectivity and high sensitivity in aqueous media based on excited-state intramolecular charge transfer (ESICT). The high yield synthesis of **1** was readily prepared through a condensation of aldehyde **2** with malononitrile in the presence of triethylamine.

We examined the sensing properties of sensor **1** in THF/H_2O solutions (9:1 (v/v), containing 0.01 M HEPES, pH = 7.3) by the addition of the tetrabutylammonium salt of various anions, including $F^{?}$, $Cl^{?}$, $Br^{?}$, $SCN^{?}$, $AcO^{?}$, $NO_3^{?}$, $BzO^{?}$, $H_2PO_4^{?}$, $HSO_4^{?}$, $NO_2^{?}$, $CO_3^{2?}$, and $S_2^{?}$, with and without $CN^{?}$ (Fig. 2). Upon the addition of 25 equivalents (equiv.) of various anions—except for cyanide ion—the absorption and emission spectra of **1** did not show any significant change. However, in the presence of $\mathrm{CN}^{?}$, the absorption and emission bands at 369 and 533 nm completely disappeared (Fig. 2a and 2b); as a result, a distinct color (fluorescence) change from yellow to colorless (blue) was clearly observed (Fig. 2c and 2d). The detection limit of the fluorescence spectrum changes calculated on the basis of 3?/*m* is 1.1 ?M for $\mathrm{CN}^{?}$, which is comparable to other cyanide-selective chemosensors and slightly lower than the maximum level of cyanide in drinking water (1.9 ?M) that the World Health Organization permits.

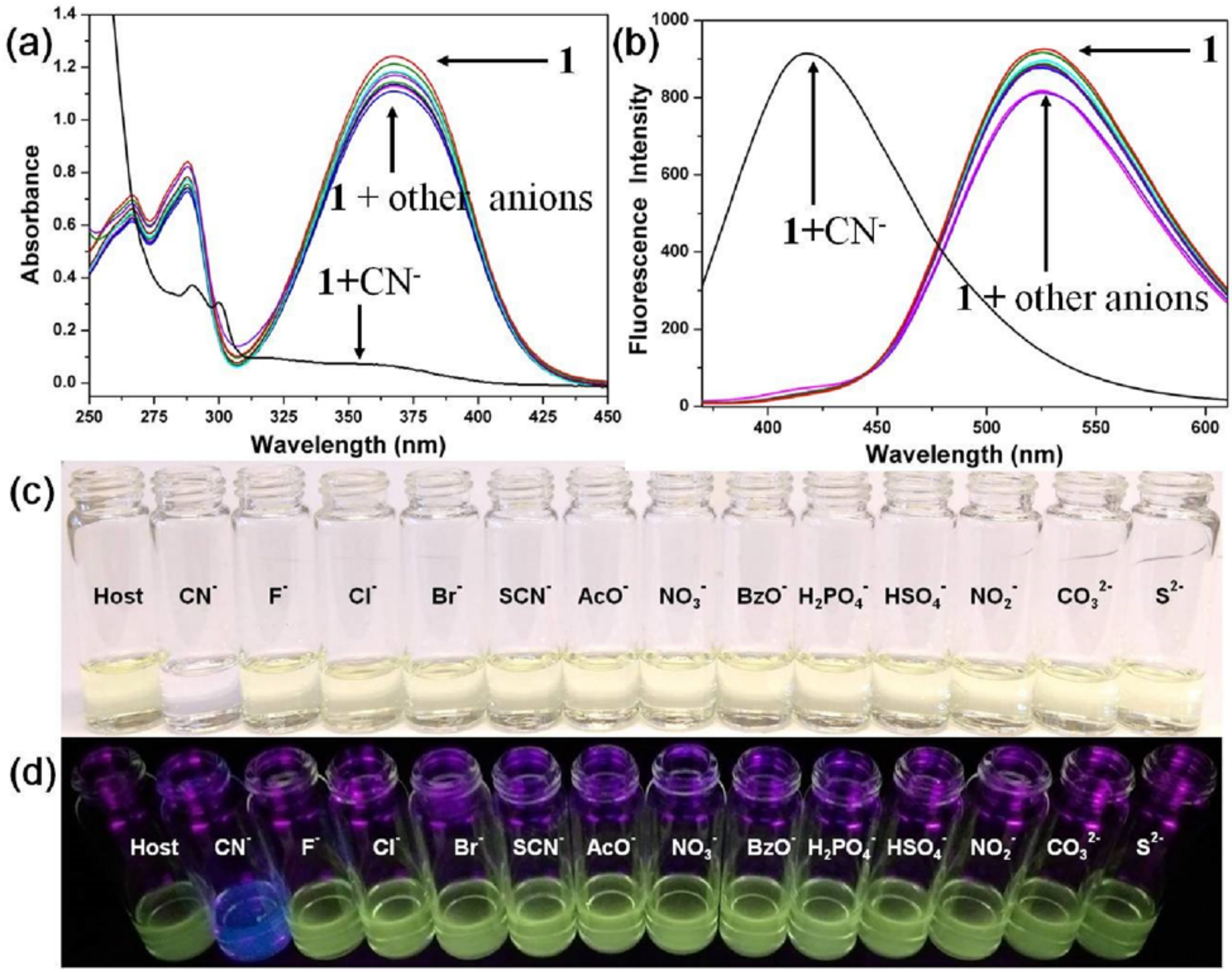

Fig.2. (a) Absorption and (b) emission spectra and (c) colorimetric and (d) fluorimetric responses of 1 (1.0 × 10-5 M) in a THF/H2O (9:1, v/v, containing 0.01 M HEPES, pH = 7.3) solution upon the addition of 25 equiv. of various anions.

Motivated by the obvious color (fluorescence) change of the system in solution, test strips were prepared by immersing filter papers (2 × 1 cm^2) in the THF/H_2O solution of **1** and then drying them in air. When the **1**-based test strips were immersed in the aqueous media of $CN^?$ with different concentrations, an obvious color change was observed under ambient and UV light (Fig. 1); competitive ions might not have exerted a significant influence on the detection of $CN^?$ with test strips. Consequently, sensor **1** has excellent fluorescence sensing performance in the solid state, and the **1**-based test strips can conveniently detect $CN^?$ without requiring any additional equipment. Moreover, the optical sensor **1** can also be used for the ultrasensitive determination of $CN^?$in real samples, including drinking water, distilled water, domestic sewage, river water, and industrial wastewater.

Publication

A ratiometric chemodosimeter for highly selective naked-eye and fluorogenic detection of cyanide.
Lin WC, Hu JW, Chen KY
Anal Chim Acta. 2015 Sep 17