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A Cu(II)-based chemosensing ensemble bearing rhodamine B fluorophore for fluorescence turn-on detection of cyanide†

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A Cu(II)-based 2 : 2 chemosensing ensemble bearing rhodamine B fluorophore was developed for fluorescence turn-on detection of CN^- with high selectivity and sensitivity based on the CN^- complexation to the Cu^{2+} centre in the nearly planar central binding moiety.

Anion recognition is an area of growing interest in supramolecular chemistry due to its important role in a wide range of environmental, clinical, chemical, and biological applications.[1] Among various anions, cyanide is one of the most studied anions because of it being widely used in synthetic fibers, resins, herbicides, and the gold-extraction process.[2] However, cyanide anions are extremely detrimental, and could be absorbed through lungs, gastrointestinal track and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death.[3] Thus, there is a need for an efficient sensing system for cyanide to monitor cyanide concentration from contaminant sources. A variety of colorimetric and fluorescent probes for cyanide have been developed over the past ten years by making use of the coordination ability and the nucleophilic reactivity of cyanide,[4] which involve addition with Zn^{2+}–porphyrin,[5a] Ru^{2+}–pyridine,[5b] and Co^{2+}–salen,[5c] as well as bond-forming reaction between the cyanide and either an electrophilic carbon[4,6] or a boron center.[7] Other strategies were also involved, such as hydrogen bonding interactions,[8] quantum dots technology,[9] single-electron transfer reaction,[10] and copper–cyanide affinity.[11,12]

Among the various approaches to sense cyanide, sensors utilizing copper–cyanide affinity draw our special attention. It is known that Cu^{2+} usually acts as a fluorescence quencher *via* a PET (photoinduced electron transfer) or EET (electronic energy transfer) process between the fluorophores and Cu^{2+}.[13] It is also known that cyanide can react with Cu^{2+} to form very stable $Cu(CN)_2$ species.[12] Based on the recovered fluorescence of the signaling unit by detaching Cu^{2+} with CN^- from the corresponding non-fluorescent copper complexes (displacement approach, Fig. 1a), some excellent Cu^{2+}-based ensemble systems for fluorescence "turn-on" detection of cyanide have been reported.[11] On the other hand, it is also possible that if the stability of the Cu^{2+} complex is high enough, alternatively, the added CN^- will likely coordinate to the Cu^{2+} centre rather than snatching Cu^{2+} from the complex. It was envisioned that the negatively charged CN^- complexation to Cu^{2+} would alter the energy levels of the chelated Cu^{2+}, and accordingly interfere with the PET or EET quenching process between the fluorophore and the chelated Cu^{2+}, probably leading to an enhancement in the fluorescence intensity of the fluorophore (complexation approach, Fig. 1b). If so, this would serve as an attractive fluorescence "turn-on" sensing platform for cyanide anions. However, as far as we are aware, the "complexation approach" based on a Cu(II) complex platform has not been previously exploited to design fluorescent "turn-on" probes for the detection of CN^-.

As a proof-of-concept, in this paper we hope to report a new Cu(II)-based chemosensing ensemble (**1**·**Cu**) bearing rhodamine B fluorophore for detection of cyanide based on the proposed "complexation approach" (Fig. 2). An X-ray diffraction study revealed a nearly planar conformation for the central moiety of **1**·**Cu** with two vacant axial coordination positions for each Cu^{2+} ion. Such a planar conformation closely resembles the natural products Cytochrome a_3 and Vitamin B_{12} that are known to have strong interaction with cyanide.[3b,14] The large fluorescence turn-on response as well as the excellent selectivity and high sensitivity toward the detection of CN^- in MeCN/Tris–HCl buffer (pH 7.0) over a wide range of tested anions were demonstrated by the system.

In fact, based on the unique photophysical properties and the change in structure between the spirocyclic and open-cycle forms, a large number of rhodamine-based chemosensing systems for transition- or heavy-metal ions have been developed in recent years.[15] However, only a few examples have been made available for anion detection so far.[12d,16] Especially, only one rhodamine-based Cu^{2+} ensemble was reported as a colorimetric chemosensor for selective

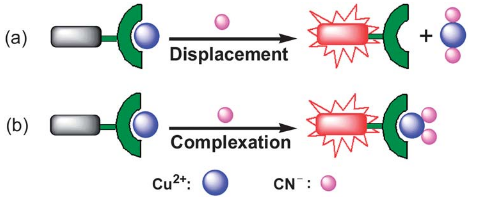

Fig. 1 Two approaches (a and b) for the turn-on fluorescence probes for CN^- on the basis of the Cu^{2+} complex.

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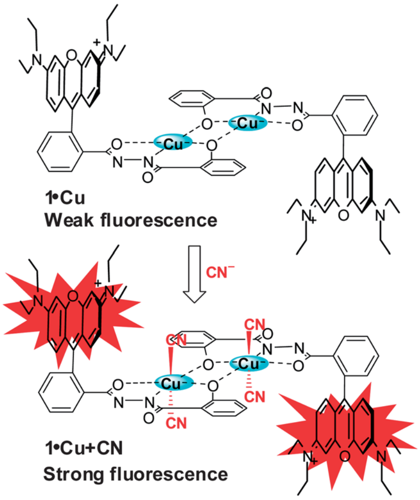

Fig. 2 The proposed sensing mechanisms of **1**·**Cu** for CN⁻.

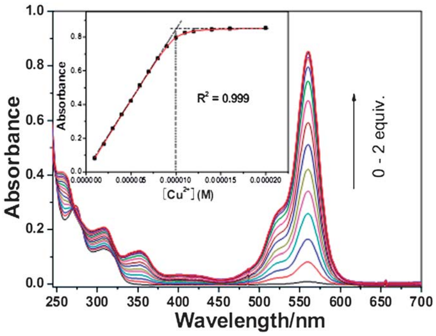

Fig. 4 Changes in absorption spectra of **1** (10 μM) in 9 : 1 (v/v) MeCN/water solution (10 mM Tris–HCl, pH 7.0) with various amounts of Cu^{2+} ions. Inset: absorption titration profile of **1** *vs.* concentration of Cu^{2+}.

detection of CN⁻ by applying the displacement approach.[12d] Strategically, it is very difficult to design a fluorescence "turn-on" probe for CN⁻ based on the rhodamine–Cu(II) ensemble by the displacement approach, because the snatching of Cu^{2+} from the complex with CN⁻ will result in the formation of a spirocyclic form of rhodamine that is colorless and nonfluorescent. However, we envisioned that the problem could be solved by incorporating a ligand with strong coordination ability for Cu^{2+} into the rhodamine skeleton to produce a ring-opened rhodamine–Cu(II) complex with high stability, so that the added CN⁻ will complex to the chelated Cu^{2+} rather than snatching it, by which the desired fluorescence "turn-on" response could be obtained based on the aforementioned "complexation approach". With this consideration in mind, a *N*-salicyloyl rhodamine B-hydrazide-based ligand **1** (Fig. 3) was designed, synthesized (ESI†), and applied to the present investigation.

To get insight into the binding of Cu^{2+} with **1**, the absorption spectra of **1** upon titration with Cu^{2+} were recorded. As shown in Fig. 4, the absorption spectrum of **1** (10 μM) in 9 : 1 (v/v) MeCN/water solution (10 mM Tris–HCl, pH 7.0) showed almost no absorbance above 500 nm, which is ascribed to its spirolactam form in solution. Upon addition of Cu^{2+} to the solution of **1**, the absorbance was significantly enhanced with a new peak appearing at 562 nm until saturation after 1 equiv., suggesting the formation of the ring-opened amide form of **1** as a result of Cu^{2+} binding. In fact, only 1 equiv. of Cu^{2+} used in this assay to achieve a maximal spectra signal is indicative of the strong **1**–Cu^{2+} interaction. In addition, the high selectivity of **1** to Cu^{2+} over other cations was also confirmed (Fig. S1, ESI†).

Surprisingly, the ESI-MS spectra of the complex of **1** with Cu^{2+} revealed a 2 : 2 binding mode, in which the peaks at *m*/*z* 1278.3 corresponding to [2**1** + 2Cu^{2+}] were clearly observed (Fig. S2, ESI†). Moreover, this 2 : 2 binding mode was also supported by a Job plot analysis (Fig. S3, ESI†).

Subsequently, an X-ray diffraction study was performed to get further insight into the **1**–Cu^{2+} interaction. The single crystal of **1**–Cu^{2+} complex was obtained by slow evaporation of the MeCN solution of **1** and $CuCl_2$. As expected, the rhodamine groups are present in the form of a ring-opened amide conformation (Fig. 5), which is responsible for the long wavelength absorption as observed in UV-vis titration investigation. Noteworthy is that two central Cu^{2+} ions [Cu(1) and Cu(1A)] are tightly coordinated to *N*-salicyloyl hydrazide-based binding units from two ligands, with average Cu–O and Cu–N separations being *ca.* 1.948 Å and 1.894 Å, respectively. The total coordination numbers for each central Cu^{2+} ion are equal to four, and a slightly distorted square coordination geometry could be observed. Moreover, such a **1**–Cu^{2+} coordination mode also leads to a nearly planar conformation for the central moiety of the complex (Fig. S4, ESI†).

In addition, two peripheric Cu^{2+} atoms [Cu(2) and Cu(2A)] were found to coordinate to the remaining sites [N(3), O(4) and N(3A),

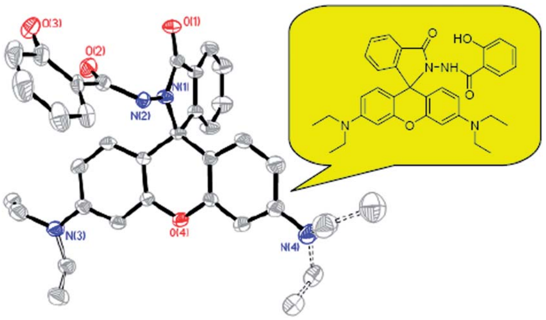

Fig. 3 The crystal structure and chemical structures of ligand **1**.

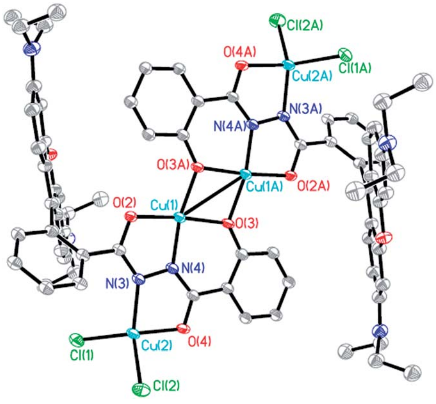

Fig. 5 Crystal structure of the **1**–Cu^{2+} complex, face-on view, with displacement atomic ellipsoids drawn at the 30% probability level.

O(4A)] of the binding group in the crystal structure. However, in solution such coordination interaction appears to be unstable, as is suggested by the aforementioned UV-vis titration investigation, Job plot analysis as well as ESI-MS investigation, where only a 2 : 2 **1**–Cu^{2+} binding mode was observed. Presumably, this is due to the poor coordination capability of the bidentate unit in the ligand as well as the absence of the additional stabilizing factors for such coordination in solution. On the basis of these results, in solution, the structure of the **1·Cu** ensemble, involving two ring-opened *N*-salicyloyl rhodamine B-hydrazide-based ligands **1** and two central Cu^{2+} ions arranged in a 2 : 2 binding mode, can be corroborated (see Fig. 2).

In general, Cu^{2+} can form stable 4-, 5-, 6-coordinated complexes. However, the coordination numbers for each central Cu^{2+} ion in **1·Cu** are equal to four. That is to say, there are still two vacant axial coordination positions for each Cu^{2+} ion in **1·Cu**. Obviously, the structural feature will provide an opportunity for CN^- complexation to the two central Cu^{2+} ions due to the strong coordination ability of CN^- to Cu^{2+}.

Subsequently, the fluorescence spectra of **1·Cu** (2.5 μM) upon titration with CN^- were recorded. As expected, **1·Cu** shows very weak fluorescence ($\Phi_F = 0.041$) at 580 nm (a featured emission of rhodamine B) in solution due to the quenching effect *via* the well-known PET or EET process (Fig. 6).[13,17] However, the fluorescence of **1·Cu** at 580 nm was dramatically enhanced with the virtually unchanged emission shift upon the subsequent addition of CN^-. The changes of the emission intensities became constant ($\Phi_F = 0.406$) when the amount of CN^- added reached 40 equiv., and a large fluorescence enhancement could be clearly observed. Moreover, the recognizing event could complete in less than 5 min (Fig. S5, ESI†), suggesting the relatively rapid detecting ability of **1·Cu** for CN^-. Further, we evaluated the analytical performance of **1·Cu** for the determination of CN^-. Under the present conditions, when **1·Cu** was employed at 0.5 μM and the slit was adjusted to 20 nm/20 nm, an excellent linear working range of 0–1.2 × 10^{-5} M was observed (Fig. S6, ESI†). The detection limit was measured to be 1.4 × 10^{-7} M at *S*/*N* = 3. According to the World Health Organization (WHO), CN^- concentrations lower than 1.9 μM are acceptable in drinking water.[18] This means that our system is sensitive enough to monitor cyanide concentrations in drinking water.

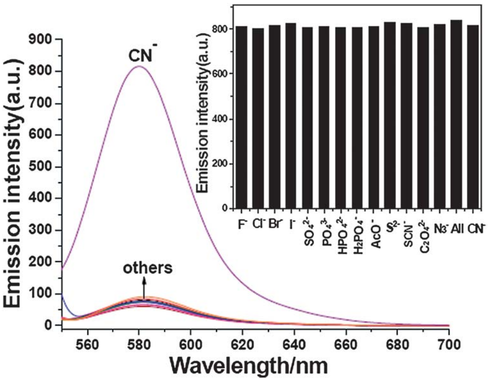

Fig. 7 The fluorescence spectra of **1·Cu** (2.5 μM) upon addition of CN^- (40 equiv.) and various other anions (100 equiv.). Inset: fluorescence responses of **1·Cu** to CN^- containing various anions. $\lambda_{ex}/\lambda_{em}$ = 535 nm/580 nm. Slit: 10 nm/20 nm.

An important feature of **1·Cu** is its high selectivity toward the CN^- over the other competitive anions. Changes of fluorescence spectra of **1·Cu** (2.5 μM) caused by CN^- (40 equiv.) and miscellaneous anions (100 equiv.) including F^-, Cl^-, Br^-, I^-, SO_4^{2-}, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, AcO^-, S^{2-}, SCN^-, $C_2O_4^{2-}$, and N_3^- in 9 : 1 (v/v) MeCN/water solution (10 mM Tris–HCl, pH 7.0) were recorded in Fig. 7. As can be seen, these competitive anions, including S^{2-} and $C_2O_4^{2-}$ which are known to have high affinity to Cu^{2+},[19] did not lead to any significant fluorescence changes at 580 nm, and the fluorescence emission spectrum of **1·Cu** remained almost undisturbed. Moreover, in the presence of a miscellaneous competitive anion, the CN^- still resulted in the similar fluorescence changes (Fig. 7, inset).

Although the fluorescence of **1·Cu** is modulated upon addition of CN^-, under the same conditions, the absorbance of **1·Cu** remains constant (Fig. 8), indicating that CN^- coordinates to the Cu^{2+} centre rather than snatching the Cu^{2+} ions from **1·Cu**; if not, the colorless spirocyclic form of **1** will recover.[12d] In fact, among various anions tested, only EDTA can capture Cu^{2+} from the **1·Cu** complex to release **1**, as the absorbance of **1·Cu** at 562 nm instantly disappeared upon the addition of EDTA (Fig. 8), suggesting the strong coordination interaction of **1** with Cu^{2+}.

Noteworthy is that the ESI-MS spectra of **1·Cu** upon addition of CN^- revealed a 1 : 4 binding mode, in which the peaks at *m*/*z* 1504.6 corresponding to [**1·Cu** + $4CN^-$ + $2NO_3^-$ − $2H^+$] were clearly observed (Fig. S7, ESI†). Thus, it was concluded that each central Cu^{2+} ion in **1·Cu** binds two cyanide anions at its two vacant axial coordination positions.

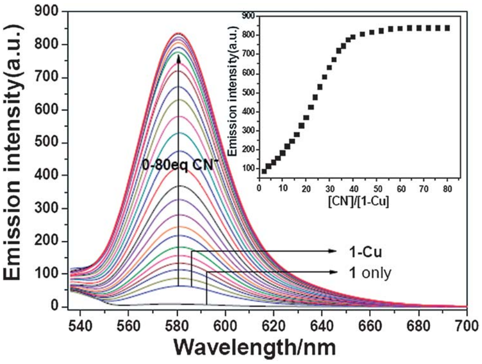

Fig. 6 Fluorescence response of **1·Cu** (2.5 μM) to CN^- in 9 : 1 (v/v) MeCN/water solution (10 mM Tris–HCl, pH 7.0). $\lambda_{ex}/\lambda_{em}$ = 535/580 nm. Slits: 10 nm/20 nm. Inset: titration curve of $I_{580\ nm}$ *vs.* CN^- concentration.

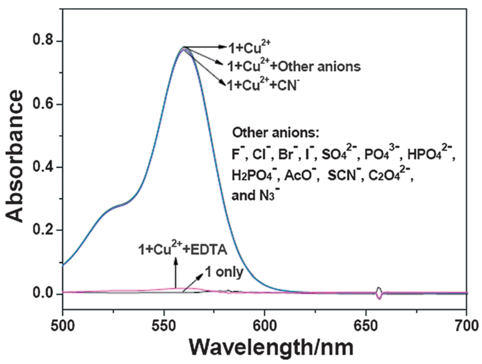

Fig. 8 The UV-vis spectra of **1·Cu** (5 μM) in the presence of various anions (40 equiv.) as well as EDTA (20 equiv.).

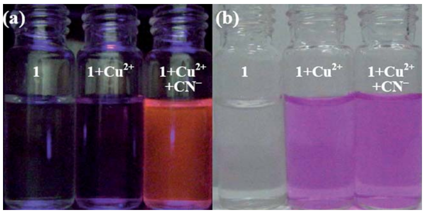

Fig. 9 The fluorescence (a) and color (b) changes of **1** to Cu^{2+} as well as **1·Cu** to CN$^-$ in 9 : 1 (v/v) MeCN/water solution (10 mM Tris–HCl, pH 7.0). [**1**] = 20 μM, [Cu^{2+}] = 20 μM and [CN$^-$] = 400 μM.

In view of these results, as shown in Fig. 2, a possible sensing mechanism for the fluorescence turn-on response of **1·Cu** toward CN$^-$ was proposed as follows: when CN$^-$ ions are absent, **1·Cu** complex shows a weak fluorescence emission due to a PET or EET quenching process between the rhodamine B unit and the chelated Cu^{2+}; the strong coordination of CN$^-$ toward Cu^{2+} at its two vacant axial coordination positions would alter the energy levels of the chelated Cu^{2+}, accordingly interfere the PET or EET quenching, thereby leading to a remarkable fluorescence enhancement. In fact, the unchanged emission shift (Fig. 6) as well as the unchanged absorption spectrum of **1·Cu** upon addition of CN$^-$ (Fig. 8) are indicative of the PET or EET-modulated fluorescence turn-on mechanism.[20] Furthermore, the addition of CN$^-$ immediately turned the fluorescence of **1·Cu** from dark to red (Fig. 9a), whereas its color remained unchanged (Fig. 9b), which provides further evidence for the proposed mechanism.

In conclusion, we have developed a rhodamine–Cu(II) complex (**1·Cu**) in a 2 : 2 binding stoichiometry as a fluorescence "turn-on" chemosensing system for CN$^-$. X-Ray diffraction studies of **1·Cu** revealed a nearly planar central structural moiety with two vacant axial coordination positions for each Cu^{2+} ion. **1·Cu** could detect CN$^-$ in 9 : 1 (v/v) MeCN/water solution (10 mM Tris–HCl, pH 7.0) with high sensitivity and selectivity. Although the detailed fluorescence turn-on mechanism needs to be further demonstrated, the results presented here may contribute to the development of a novel type of sensing system for CN$^-$ based on the proposed "complexation approach".

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