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An investigation of the deprotonation of hydrazone-based receptors on interaction with anion: develop a colorimetric system distinguishing cyanide from anions

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ABSTRACT

Hydrazone-based receptors, containing fluorene-skeleton substituents, in a THF solution, in the presence of fluoride or cyanide, do not only form H-bond complexes, but mainly undergo deprotonation of the N–H fragments, an event, which is signaled by the color change, the ability of the deprotonation is associated with the fluorene skeleton. The deprotonation process is also reversible by the addition of metal ions, while cyanide from fluoride could be distinguished by the addition of copper (II).

1. Introduction

There exists a current interest in the synthesis of colorimetric receptors for anions.[1] Detection of cyanide anion is an emerging field of research due to obvious reasons, even very small amounts of the cyanide anions are thus highly toxic to living creatures. Nonetheless, cyanide salts are widespread used in gold mining, electroplating, and metallurgy.[2] Thus, there is a well demand for cyanide-selective receptors. Indeed, much effort has been devoted to designing such species.[3] Recently, chemosensors for the naked eye detection of cyanide are attracting great attention due to fast and simple colorimetric assays.[4] Many cyanide anion receptors reported to date have relied on either hydrogen-bonding,[5] metal coordination,[6] or bond-forming reactions between the nucleophilic cyanide and either an electrophilic carbon[7] or boron center.[8] However, one of major problem to overcome is that most of the cyanide receptors are often disturbed by other anions during the detection. Especially, fluoride anion tends to mask the response of cyanide.

The chemo-sensors usually contain a chromogenic fragment and a neutral receptor with selective interactions to the envisaged anion.[9] To this extent, the receptor usually interacts with the anion by one or more H-bonds, in most cases using the N–H fragment(s) of ureas,[10] sulfonamides,[11] pyrroles, and amides.[12] However, chemo-sensors for anion with receptor containing N–H fragment of hydrazones are rare.[13]

For the study of the interactions between N–H fragment of hydrazone and anion, we consider system **1a**–**c**, in which a hydrazone subunit has been used to connect one naphthalenimide moiety with a planar fluorene-skeleton ring. We are attracted to this system because (1) naphthalenimide is a yellow-color chromophore due to charge-transfer transition, if the N–H group is adjacent to the chromogenic subunit, the negative charge of the anion may change the dipole associated to the charge-transfer transition, leading to a variation of the UV–vis spectrum and to a color change. (2) fluorene-skeleton hydrazone modifies conjugation of the system and then stabilizes the excited state of the chromophore, causing a drastic color change when interacting with anion. 4,5-Diazafluorene, fluorene, and 1,8-diazafluorene motif are introduced into the system **1a**–**c**, respectively, in our research work. (3) They can be obtained by simple synthetic procedures (Scheme 1).

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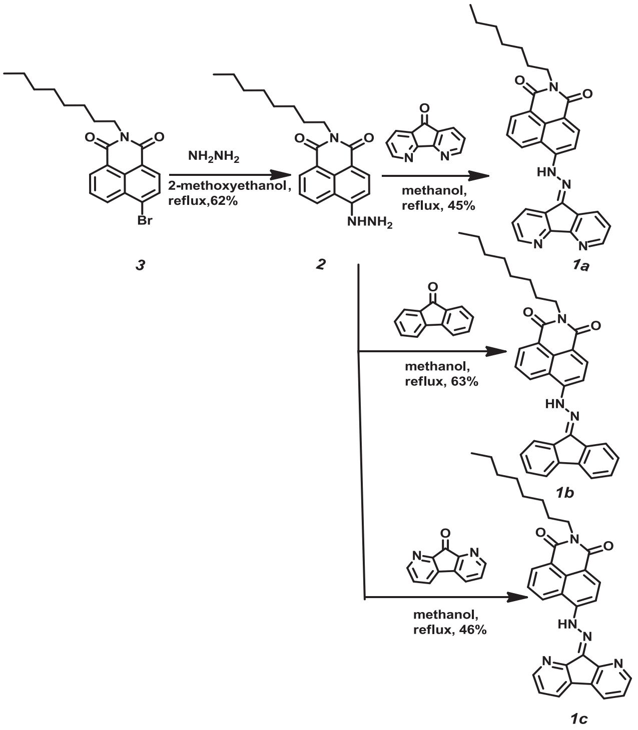


Scheme 1. Synthetic route to **1a**–**c**.

2. Results and discussion

The anions, such as F^-, Cl^-, Br^-, I^-, SO_4^{2-}, CN^-, SCN^-, ClO_4^-, and $H_2PO_4^-$ are used to study the selectivity of **1a** (20 μM) in THF. We found, in the presence of 10 equiv of the CN^- or F^-, the color of the solution immediately changed from yellow to green. While the other control anions (Cl^-, Br^-, I^-, SO_4^{2-}, SCN^-, ClO_4^-, and $H_2PO_4^-$) are added into the solution of **1a**, no obvious color changes of the solution could be detected (except SO_4^{2-} has little change from yellow to yellow-green) (Fig. 1).

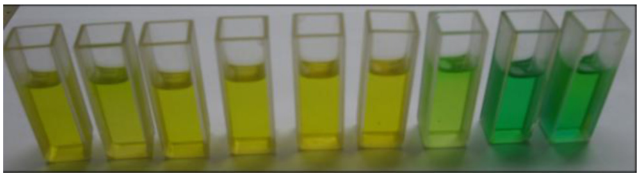


Fig. 1. Color change of **1a** ([1]=20 μM, [other anions]=200 μM). Left to right: Cl^-, Br^-, I^-, SCN^-, ClO_4^-, $H_2PO_4^-$, SO_4^{2-}, F^-, and CN^-.

The changes are also recorded by absorption spectra. Compared to other anions examined, F^- or CN^- generates great change, the original absorption of **1a** at 440 nm (ascribed to the absorption of naphthalenimide moiety) almost disappears and a new absorption band around 660 nm forms with strong intensity (Fig. 2). It is suggested that the new band at 660 nm pertains to the interactions between **1a** with anions.

These results also indicate that **1a** could be used as a potential candidate of colorimetric receptor for CN^- and F^-. We, however, are more interested in the understanding of the behavior of hydrazone-based receptors on interaction with cyanide or fluoride. Considering the nature of cyanide and fluoride and the feature of the N–H fragment, we proposed three possible modes of interactions between **1a** and anion (Scheme 2). The first is H-bond interaction mechanism based on the facts that fluorine, as the electronegative atom, rightfully establishes the H-bond interactions. The second possible mechanism is a deprotonation of the N–H fragment: anion takes a proton from receptor. The third plausible process is bond-forming reaction relied on strong nucleophilicity of cyanide, the cyanides attack C=N or C=O to give the addition product.

We observed that, upon addition of a few equivalents of metal ions, such as Pb^{2+} or Zn^{2+}, into the green mixture of **1a** and cyanide, the color of solution return to original bright yellow (Fig. S1), which indicates the process of interaction between **1a** and the anion is reversible. The results of experiments also demonstrate that the interaction mechanism is not bond-forming reaction since the

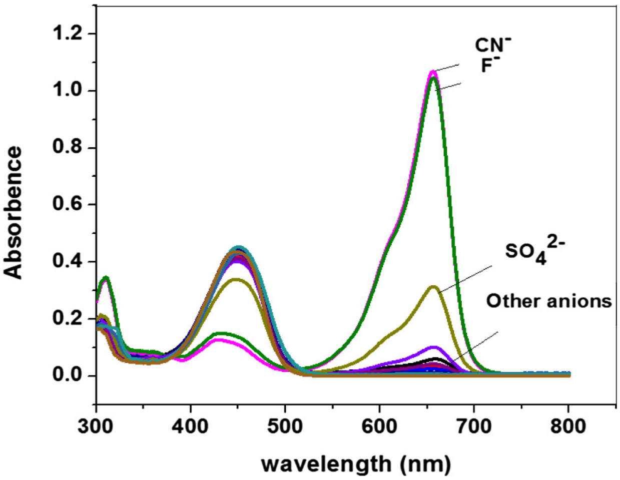
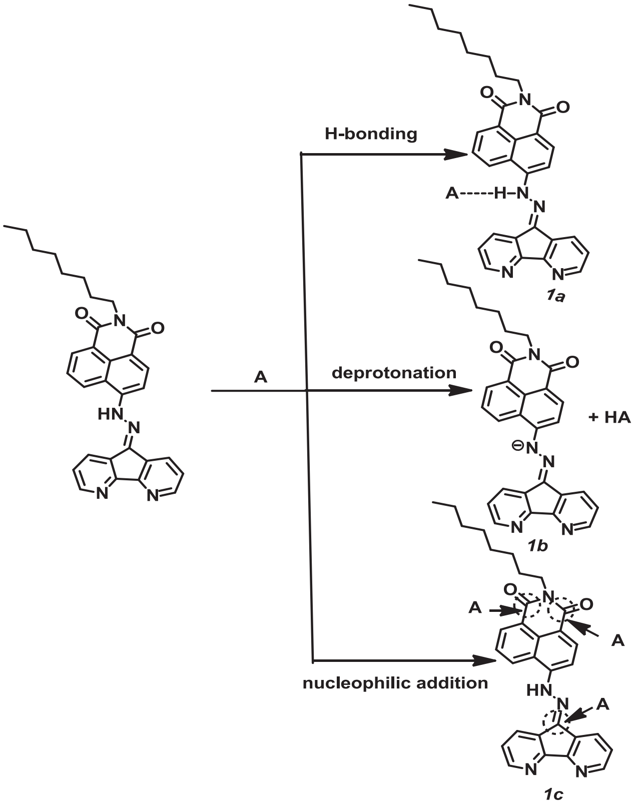


Fig. 2. UV–vis spectra of **1a** (12.5 μM) with various anions (10 equiv) in THF.



Scheme 2. Proposed possible mechanisms for **1a** on the interaction of anion.