



Efficient colorimetric fluoride anion chemosensors based-on simple naphthodipyrrolidone dyes



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ABSTRACT

Two novel lactam-containing compounds based on simple naphthodipyrrolidones have been developed as colorimetric sensors for fluoride anion with high selectivity and sensitivity. The two compounds can selectively act with fluoride anion and exhibit the naked-eye visible color change from purple to blue, and the detection limit could reach the concentration as low as 3.0×10^{-6} M. The proton nuclear magnetic resonance titrations reveal the happen of intermolecular proton transfer between the hydrogen atom on the lactam N and the fluoride anion. Quantum chemical calculations indicate that the deprotonation can alleviate the distorted degree between the peripheral phenyl and the naphthodipyrrolidone core, and raise the frontier molecular orbital energy levels and decrease the band gap, rendering the protonated molecules a new more batho-chromic absorption band.

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Introduction

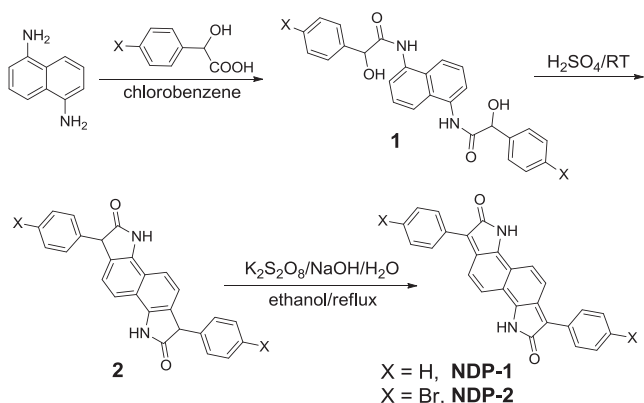
Recently, the design and development of chromogenic and fluo-rogenic chemosensors for cations and anions has gained much attention because sensing systems are needed in many fields of applications, such as chemistry,^{1–3} physics,^{3–5} biology,^{6–9} military industry,^{10,11} etc. It is challenging yet necessary to exploit chemosensors which can detect various ions by optical signal changes such as absorption and emission wavelength and intensity. Following the definition given by IUPAC, a chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The term chemosensor has been defined as a molecule of abiotic origin that signals the presence of matter or energy. Therefore, one of the more attractive approaches in this field involves the construction of new chemosensors. A significant amount of work has been devoted to obtain specific chemosensors that are able to change one or several macroscopic properties upon addition of the target species. The extensively used changes are the fluorescence and/or absorbance output intensity and color signals in developing optical chemosensors. In this context, the linear ratiometric and naked-eye visible colorimetric chemosensors are desirable due to

the simplicity and convenience for continuous monitoring of the presence of chemical species. For example, there have been a number of chemosensors developed for the sensing of various metal ions.^{12–15}

As one of the smallest anions and the most electronegative atom, fluoride with high charge density has special functions in chemistry, physics and biology. However, it is very difficult to detect fluoride in aqueous media through spectroscopic methods because of its strong hydration. Alternatively, a variety of fluoride sensors worked in organic solvents have been developed, but the simple-to-use colorimetric fluoride sensors exhibiting excellent selectivity and sensitivity in the visible region of the spectrum and allowing the naked eye detection are rather rare at present. Therefore, it is still necessary to utilize some simple and high performance pigments to design fluoride sensors. It is known that fluoride can interact with the N–H of urea, 1,4-diketo-pyrrolo[3,4-c]pyrrole, and naphthalimide moieties to form the intermolecular hydrogen bond, which could be used to construct fluoride anion sensors.^{16,17} While we developed new broad absorption and low band gap conjugated polymers, a tetracyclic intermediate with two lactam units (NDP) was obtained (Scheme 1). NDP has a workable solubility in organic solvents, and we expect that NDP derivatives could be used as new colorimetric chemosensors for fluoride anion. We now report that NDP exhibits colorimetric sensors for fluoride anion with high selectivity and sensitivity, and the sensing mechanism is investigated by the proton NMR titration and quantum chemical computation.

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Scheme 1. The structure and synthetic route of tetracyclic lactam derivatives.

Results and discussion

The target compounds tetracyclic lactam derivatives (**NDP-1** and **NDP-2**) could be prepared facily by the condensation of 1,5-diaminonaphthalene and mandelic acid derivatives, followed by cyclodehydration in sulfuric acid and dehydrogenation in alkaline potassium persulfate (**Scheme 1**), and the details for synthesis and characterization were shown in the **Supporting Information**. The interaction between the **NDP** derivatives with fluoride anion was firstly investigated in THF solution through spectrophotometric titration experiments. A standard solution of tetrabutylammonium fluoride (TBAF, 1.0×10^{-3} M) was gradually added to a 5.0×10^{-6} M solution of **NDP-1** or **NDP-2** at room temperature. **Fig. 1** shows that **NDP-2** itself displayed one main absorption band at 560 nm with high extinction coefficient up to 2.60×10^4 M $^{-1}$ cm $^{-1}$. Upon progressive addition of F $^{-}$ added, the absorption intensity at about 560 nm was gradually decreased with slight bathochromic shift, while a new absorption band at 812 nm was formed and gradually developed with a clear isobestic point at 609 nm before 1.8 equiv of ammonium fluoride. In the meantime, the color of **NDP-2** in solution changed from dark purple to light purple (insert of **Fig. 1**). When F $^{-}$ was further added, the absorption band around 560 nm was slightly decreased and broadened, and the long-wavelength absorption band was increased initially and then hardly changed. It is noted that, while the solution color changes from light purple to blue with high visiblens to the

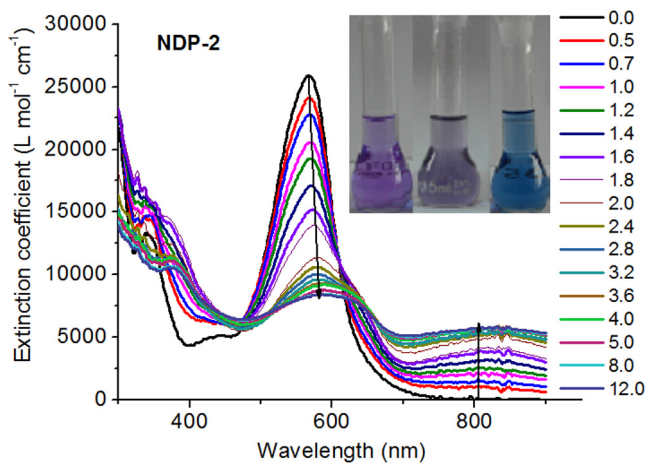


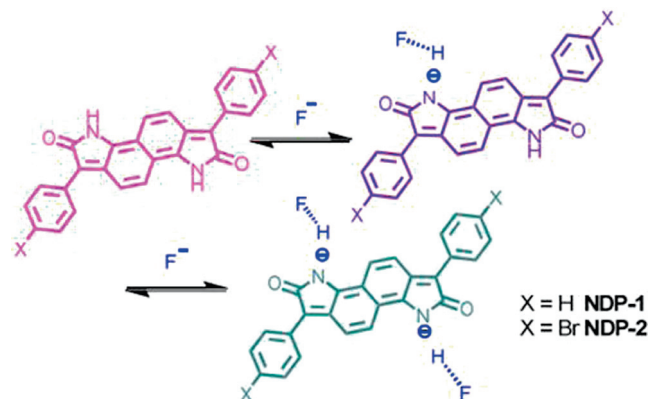
Fig. 1. The UV/vis absorption spectra of **NDP-2** (5.0×10^{-6} M) in the presence of F $^{-}$ anions (0–12 equiv.) in THF. Inset is the color change of **NDP-2** (5.0×10^{-6} M) upon adding F $^{-}$ anion (from left to right: free ligand, 1.8 equiv., and 3.0 equiv.).

naked eye in ambient light, a new isobestic point at 653 nm was formed when ammonium fluoride is beyond 2 equiv. The appearance of two isobestic points implies that the qualitatively stepwise formation of fluoride-bonding species in which the dual fluoride-bonding species could afford significant color change. Similar results were also obtained by the **NDP-1** (**Fig. S1**).

Since the changes in color and the absorption spectra of **NDP-1** and **NDP-2** have indicated that the formation of bonding species is stepwise and the second has stronger push–pull electron effect, we propose that the color changes are due to the deprotonation of the lactam NH moiety (Ph–NH–naphthyl–NH–Ph) by F $^{-}$ (inter-molecular proton transfer, IPT, **Scheme 2**). Ph–NH–naphthyl–NH–Ph is electronically neutral in the absence of fluoride anion, and the negatively charged species with one negative charge (Ph–NH $^{-}$ –naphthyl–NH–Ph) was first formed in the presence of fluoride, or (Ph–NH $^{-}$ –naphthyl–NH $^{-}$ –Ph). The negatively charged Ph–NH $^{-}$ –naphthyl–NH–Ph could weaken the further IPT process, and dual negative charge species (Ph–NH $^{-}$ –naphthyl–NH $^{-}$ –Ph) could be formed in the presence of a large amount of fluoride anion. Electron-withdrawing bromine favored the IPT process, and **NDP-2** was more sensitive to fluoride anion than **NDP-1**. IPT is a reversible process because of the still existence of pristine absorption band at 560 nm, regardless of fluoride anion concentration, which could explain the non-quantitative and lagging response to the fluoride anion. The negatively charged species could enhance the intramolecular charge transfer (ICT) and afford the bathochromic shift and decreased intensity of the absorption band.

To confirm our assumption, the proton nuclear magnetic resonance titrations and quantum chemical calculations were conducted. **Fig. 2** showed the ^1H NMR spectra of **NDP-1** and **NDP-2** in DMSO- d_6 with different equiv of TBAF. Apart from other protons, the specific signal for the lactam–NH protons at about 11.5 ppm decreased and finally disappeared with the increase of fluoride anion, indicating the happen of IPT event. It was noted that the NH proton signals of **NDP-1** and **NDP-2** disappeared finally at 8 and 5 equiv of fluoride anion, respectively (**Fig. S2**). This indicated that the **NDP-2** with end bromine is much easy and sensitive interaction with fluoride anion compared with **NDP-1**, which was consistent with the UV/vis absorption spectrophotometric titration (**Figs. 1** and **S2**), and demonstrated that the subtle manipulation of end groups could further improve the optical and responsive properties.

Density functional theory calculations were employed to understand the molecular geometry and frontier molecular orbital (FMO) changes before and after IPT event (**Fig. 3**). It can be seen that the torsion angles between the phenyl ring and the NDP core are 28.45 $^{\circ}$ and 15.57 $^{\circ}$ for the pristine **NDP-2** without deprotonation



Scheme 2. The proposed mechanism for sensing fluoride anion of tetracyclic lactams.

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