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Fluorogenic and chromogenic detection of biologically important fluoride anion with schiff-bases containing 4-amino-1,8-naphthalimide unit

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ABSTRACT

Two new kinds of dual-channel naphthalimide-based chemsensors for selective detection of fluoride anion was designed and synthesized. Upon the addition of F^-, they displayed dramatic color changes from orange to blue, together with drastically quenched fluorescence, through hydrogen bonding interactions. The maximum absorption wavelength was red-shifted for over 100 nm to the near-infrared region (NIR region). In addition, **L1** showed high selectivity toward fluoride ion among test anions such as F^-, AcO^-, Cl^-, Br^- and I^-, and the maximum fluorescent region was also at the NIR region.

1. Introduction

The design and preparation of systems capable of recognizing biologically important anions have attracted increasing attention due to their important roles in the field of biology, chemistry, and environment [1–5]. Three kinds of signals such as optical, electrochemical, and mass signals are extensively used to study the anion recognition events. Among them, colorimetric and fluorescent sensors are especially attractive, since they allow the so called "naked-eye" detection, and they are qualified with fast response, high selectivity as well as inexpensive installations [6,7]. Especially, the probes possessing optical signals in NIR region are of great interest owing to its merit of avoiding interference from endogenous chromophores in biological system [8–10].

1,8-naphthalimide structure with ICT process (Intermolecular charge transfer) have extensively employed in the dye industry [11–13]. It is no surprise that the structure had extensively application in the field of biologically relevant ion sensors, laser materials, targeting biomolecules [14–18]. Construction of 4-amino-1,8-naphthalimide derivatives for anion sensing is of considerable interest in recent years. To data, many excellent paradigms of 4-amino-1,8-naphthalimide based anion sensors were reported by co-workers, however, very few of them could discriminate F^- with AcO^- in NIR spectra [19]. Here, two new kinds of Schiff base compounds containing 4-amino-1,8-naphthalimide units were designed and synthesized (Scheme 1). Carbazole and indole as the electron donor were introduced to the π system in order to enhance the planarity of molecule and extend the UV–vis and fluorescent spectrum of **L1** or **L2** in NIR region, so the resulting D-L-D-A structures endowed **L1** and **L2** with typical ICT feature. The hydrogen bonding interaction of NH and anions would prohibit the electron transfer from *N* atom to naphthalimide group, thus resulting in the fluorescent quenching for sensing purpose. The two binding sites of **L1** might supply the proper space to selective sense anions. As expected, both of them can operate as efficient fluorescent and colorimetric sensors for naked eye detection of anions. Amazingly, **L1** could selectively recognize fluoride anions among test anions such as F^-, AcO^-, Cl^-, Br^- and I^-. Several experiments revealed that the two binding sites and rigid molecular structure were the main factors for the high selectivity of **L1**.

2. Experimental

2.1. Materials

All reagents and solutions were obtained from commercial suppliers and were used without further purification. Aromatic

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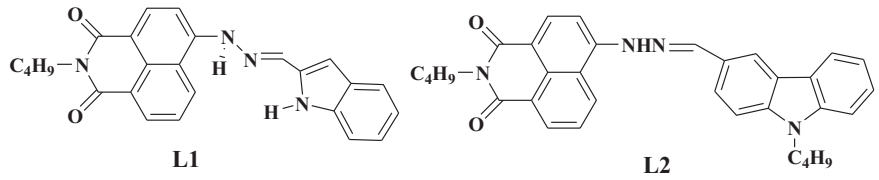

Scheme 1. The chemical structures of **L1** and **L2**.

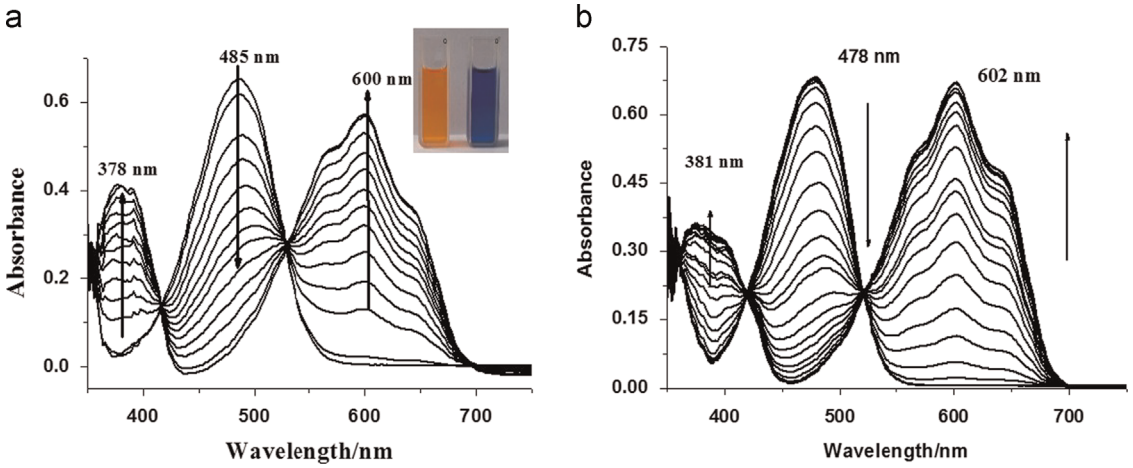

Fig. 1. (a) UV–vis titrations of **L1** with flouride anions and (b) UV–vis titrations of **L2** with fluoride anions.

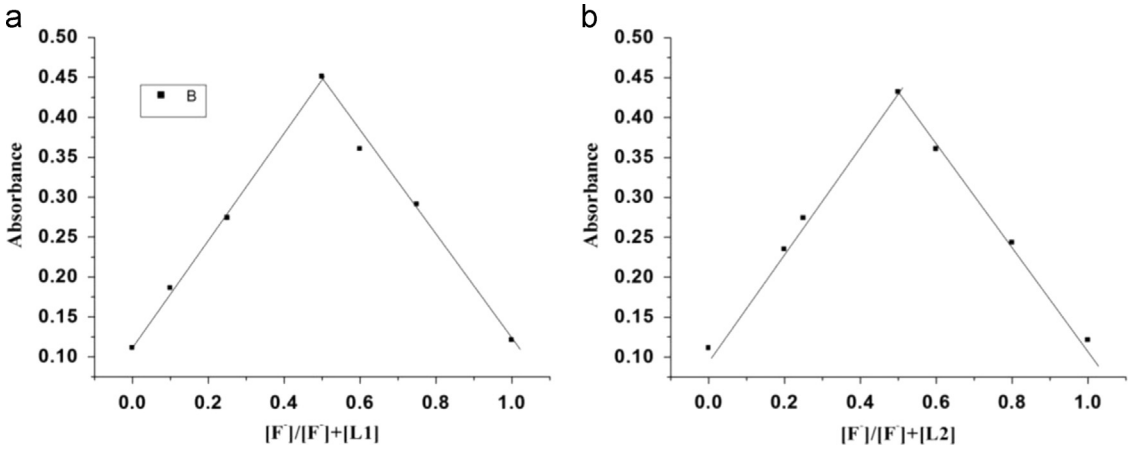

Fig. 2. (a) Job plot of **L1**-F^- complexes in DMSO solution, the monitored wavelength was at 600 nm, the total concentration was 1×10^{-4} M and (b) job plot of **L2**-F^- complexes in DMSO solution, the monitored wavelength was at 602 nm, the total concentration was 1×10^{-4} M.

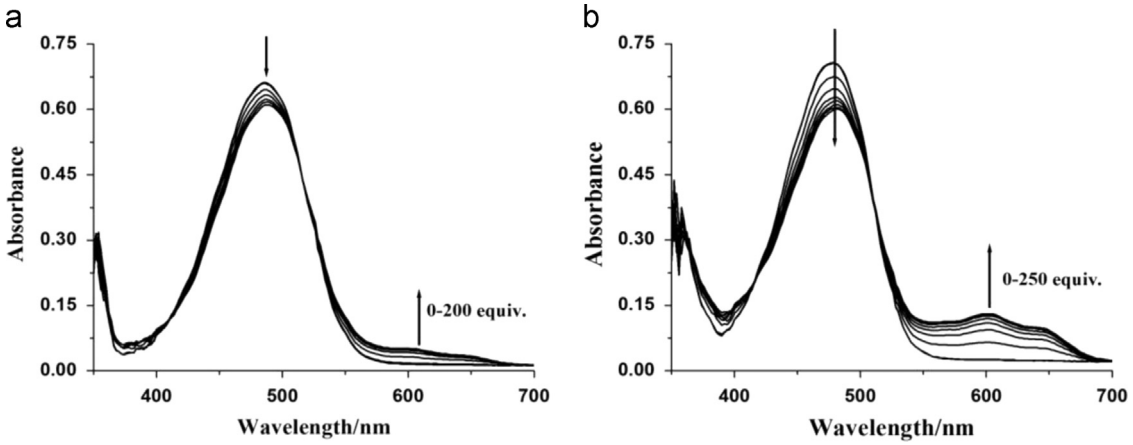

Fig. 3. (a) UV–vis titrations of **L1** with AcO^- and (b) UV–vis titrations of **L2** with AcO^-.