



Approach to modulate the sensing range of molecular transducers



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ABSTRACT

Transduction occurs upon binding of an analyte with a transducer. Specific binding involves the design and synthesis of receptors that is non trivial. Indeed, the task of designing a receptor for the smallest anion fluoride is very challenging. Herein, we take advantage of the basicity of fluoride ions that has affinity toward acidic proton. A commercially available 6-bromoisatin can sense fluoride ion in the concentration range of 0.5–3.9 ppm. Although the sensor is reaction based, the response is rapid. To further increase the linear range, dibromoisindigo was synthesized. The linear range of this transducer was found to be between 0.5 ppm and 10.4 ppm. The transducer can be regenerated by adding proton source such as trifluoroacetic acid. Thus, transducers with variable sensing range have been designed and synthesized using acid base interaction.

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1. Introduction

The interaction between an analyte and transducer is a key event in sensing. The interaction/binding can be classified into two major categories, specific [1–5] and non specific [6–12]. Non specific binding based sensors take advantage of differential binding interactions of a set of non specific receptors to impart desired specificity. This approach is attractive due to the simplicity of the sensing protocol [6,7,12,13]. On the other hand, selective binding based sensors involve the use of receptors that bind to a specific analyte [5,14,15]. While designing a receptor, multiple factors such as cavity size, non covalent attractive forces and the type of linker to the transducer are taken into account to impart high selectivity [5,15,16]. Despite the demanding task, variety of approaches has been developed to synthesize receptors for ions, neutral molecules and biomolecules [17–22]. Amongst the ions, design of receptors for anions is a challenge due to the low charge to radii ratios, variations in geometries, charge distribution and high solvation energies [16,23,24]. The challenge is even more daunting for the smallest anion fluoride, albeit receptors have been developed for this anion too [25]. The receptors contain porphyrin [26], quaternary ammonium [27], pyridinium [28], pyrroles [29], sulfonamides [30], imides [31,32], urea [33,34], thiourea [35,36], and organoboron compounds [37–44]. These receptors are usually synthesized by multi step organic reactions to achieve the desired selectivity. Another approach is the use of molecules that comprise silicon,

which has strong affinity for fluoride ion [45–47]. It must be noted that the synthesis of silicon comprising molecules is non trivial. The strong basic nature of fluoride ions has also been exploited for fluoride ion sensing [48,49]. Strong hydrogen bond formation with –NH and –OH moieties due to the high electronegativity of fluoride ion was also used for sensing applications [50].

It is desirable to identify a simple transducer that is commercially available [51]. We have identified commercially available 6-bromoisatin (BI) (Chart 1), which has been recently explored for the synthesis of organic semiconductors, as the transducer [52–54]. It must be noted that the BI is extracted from plants, mollusc and fungi and used as anticancer drug as well [55]. The BI has a five membered lactam ring connected with bromo benzene. Thus, modifications in the lactam ring are expected to impact the electronic properties of bromo benzene, which will be of interest for the sensing of fluoride ion. The imide in the lactam is connected with a carbonyl that makes the imide proton more acidic. The reason for choosing BI over 6-bromooxindole (BOI) (Chart 1), which has one carbonyl moiety in the lactam ring is related to the acidity variation as function of number of carbonyl moieties. Indeed, the importance of this carbonyl moiety will be demonstrated by comparing the sensing properties of BI and BOI. The fluoride anion interacts with the imide proton and changes the absorption properties of BI. Considering this sensor mechanism, we hypothesized that the increase in the number of imide proton would increase the linear region of the sensor. To test this hypothesis, dibromoisindigo (D-iInd) (Chart 1) was synthesized. The synthesis involves the condensation of BI and BOI in presence of acid [53]. The product, D-iInd, is purified by washing without use of column chromatography. Thus, the synthesis is extremely simple. While carrying out sensor

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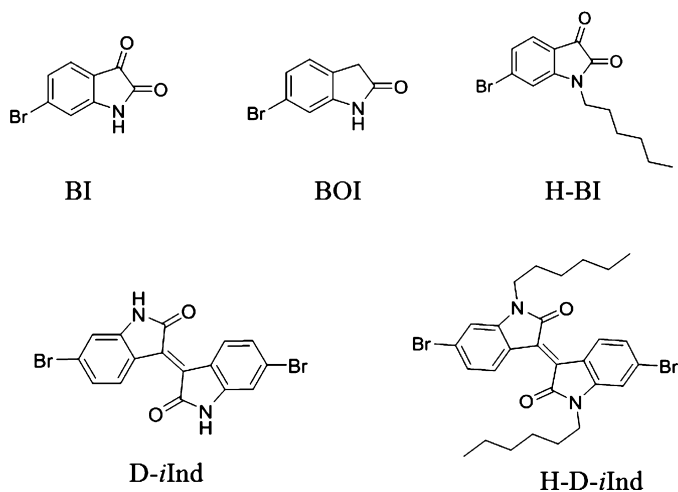


Chart 1. Molecular structures of transducers containing acidic proton and molecules with alkyl substituents.

experiments with D-iInd the linear region of the sensor was found to be between 0.5 ppm till 10.4 ppm. This linear region is more than two times longer than that observed for BI.

2. Experimental

2.1. Reagents and instruments

Solvents were procured from Sigma–Aldrich and dried using standard procedures. 6-bromoisatin and 6-bromo-2-oxindole were purchased from TCI chemicals. All the anions Cl^- , Br^- , I^- , NO_2^- , ClO_4^- and PF_6^- were in the form of tetrabutylammonium salts which were purchased from Sigma–Aldrich. Trifluoroacetic acid and DMSO- d_6 were also purchased from Sigma–Aldrich. ^1H NMR spectra were recorded on Bruker arx 400 MHz spectrometer. UV–vis spectra were recorded in 1 cm quartz cuvette on Varian Cary 500 spectrophotometer. IR spectra were recorded in Bruker Tensor 27 spectrometer using KBr pellets. Single crystal X-ray diffraction data were collected using Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics.

2.2. Synthetic procedures

2.2.1. 6,6'-Dibromoisindigo

One milliliters of concentrated HCl was added to the suspension of 6-bromoisatin (1.89 g, 8.4 mmol) and 6-bromooxindole (1.8 g, 8.4 mmol) in 54 ml of acetic acid. The mixture was heated at 100°C for 24 h. It was allowed to cool and filtered. The solid was washed using ethyl acetate (100 ml), ethanol (100 ml) and water (100 ml). The dried product was red in color.

2.2.2. 6,6'-(*N,N'*-hexyl)-dibromoisindigo

To the suspension 6,6'-dibromoisindigo (1 g, 2.3 mmol), K_2CO_3 (0.85 g, 5.7 mmol) and 1-bromohexane (0.86 g, 5.2 mmol) in 25 ml of dry *N,N'*-dimethylformamide were added. The mixture was stirred at 100°C for 24 h. Then it was allowed to cool at room temperature and poured into water (200 ml). The organic phase was extracted in dichloromethane, washed with water and dried over Na_2SO_4 . Solvent was removed under reduced pressure and product was purified by silica column chromatography eluting with DCM: pet ether (50:50).

2.2.3. *N*-hexyl-6-bromoisatin

To the suspension of 6-bromoisatin (0.5 g, 2.3 mmol) and K_2CO_3 (0.68 g, 4.9 mmol) in dry *N,N'*-dimethylformamide solution (20 ml), 1-bromohexane was added (0.54 g, 3.5 mmol). The mixture was stirred at 100°C for overnight then poured into the water (50 ml). The organic phase was extracted in ethyl acetate and washed with water and dried over Na_2SO_4 . Solvent was removed under reduced pressure and the product was purified using silica column chromatography eluting with pet ether: ethyl acetate (80:20).

3. Results and discussion

D-iInd was synthesized by carrying out a condensation reaction between 6-bromooxindole and 6-bromoisatin with 96% yield [53]. The structure of the D-iInd was confirmed by ^1H NMR, IR spectroscopy and single crystal X-ray diffraction experiments. The D-iInd belongs to triclinic crystal system and P-1 space group. The distance between the nitrogen atoms of D-iInd in the adjacent plans is 3.42 \AA (Fig. 1a). The absorption spectra of BI, BOI and D-iInd were carried out using DMF as solvent. In case of BI, a global maxima was observed at 408 nm that is due to $\pi-\pi^*$ transition (Fig. 1b). For fluoride ion sensing experiment, various concentrations of fluoride ion (0.52 ppm to 9.1 ppm) were added with 500 μM solution of BI. The addition of fluoride ions did not change the absorption profile of BI. Therefore, for the next set of experiments, the concentration of BI was decreased to 100 μM . To this solution, various concentrations of fluoride ion were added. Upon addition of 0.52 ppm fluoride ion, the $\pi-\pi^*$ transition at 408 nm decreased and a new peak evolved at higher wavelength (Fig. 1b). The higher wavelength peak was broad compared to the $\pi-\pi^*$ transition. Upon increase in the concentration of fluoride ion, the intensity of the peak at 408 nm decreased with concurrent increase in the intensity of lower energy peak. After 6.5 ppm, the intensities of the peaks did not vary as a function of increase in fluoride ion concentration. The λ_{max} of lower energy peak is found to be 551 nm (Fig. 1b). In order to identify the linear range of the sensor, the concentration of fluoride ion was plotted as a function of change in absorption intensity at 408 nm. The plot shows linear range between 0.52 ppm and 3.9 ppm (Fig. 1b, inset). Please note that the fluoride ion concentration of interest is below 2 ppm. A clear linear regime is observed in that concentration range.

To a large extent color is a subjective phenomenon and precise description of color is difficult [56,57]. Thus, quantification of color is achieved by CIE coordinates. We have plotted chromaticity diagram for the fluoride ion sensing using BI (Fig. 1c). The *xy* coordinates change as a function of variation in fluoride ion concentration indicating the change in color. The pale yellow solution changed into bluish green upon increase in fluoride ion concentration. The curling at higher concentration is usually attributed to a second trend, which is likely due to decrease in higher energy absorption and increase in lower energy absorption close to near IR region (Fig. 1c) [57]. However, we did not observe any low energy absorption in the near IR portion of the spectrum. The *xy* coordinates were integrated in the horseshoe shaped chromaticity diagram. The **W** (white point) is usually used to draw a straight line toward the periphery of the horseshoe via the point of interest to identify the wavelength associated with the color [58] (Fig. 1d). By this method, the wavelength of the color of BI after fluoride ion addition is determined to be 505 nm.

We hypothesized that the basic fluoride ion abstracts the acidic proton attached with the nitrogen of the lactam ring. Since the proposed mechanism involves $-\text{NH}$ moiety, IR spectroscopy was used to study the variation in the stretching vibrations upon addition of fluoride ion to the BI. The BI exhibits a broad $-\text{NH}$ stretching peak at 3430 cm^{-1} . Upon addition of fluoride ion, this peak

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