



# A selective acetate anion binding receptor: participation via cationic CH<sub>3</sub> donors



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## ABSTRACT

A novel receptor **1**, which has only C–H hydrogen bonds as recognition element has been designed and synthesized. The receptor **1** utilizes cationic CH<sub>3</sub> in 2-methyl benzimidazole and naphthalene benzylic C–H as hydrogen bonding donor. The binding cavity formed in receptor **1** prefers to accommodate small negatively charged atom such as oxygen. Therefore, acetate and nitrite show strong affinity for receptor **1** in acetonitrile due to negatively charged oxygen in them. In addition, the order of binding affinity for halides are Br<sup>−</sup> > Cl<sup>−</sup> > I<sup>−</sup>. These results reflect the size and basicities of halides. Further, <sup>1</sup>H NMR titration of halide clearly indicates the anion– $\pi$  interaction. The experimental data from UV–vis, fluorescence and <sup>1</sup>H NMR titration are consistent with DFT results.

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## 1. Introduction

Carboxylate anion sensor has been thriving area of research getting much attraction from all over the supramolecular groups because of enormous applications in pharmaceutical, biological areas.<sup>1</sup> In addition, carboxylates are the most fundamental importance in nature and in chemical technology.<sup>2</sup> Recent physiological studies evidenced that the anions of weak aliphatic acids such as acetate transiently inhibits myocardial contraction by increasing mitochondrial calcium uptake.<sup>3</sup> For these logical reasons selective detection of acetate is an impressive facet of anion receptor chemistry. Generally, as the recognition unit for anions, N–H hydrogen such as urea, thiourea, and amide has been utilized.<sup>4</sup> However, various polarized C–H groups are proven to be effective hydrogen bond donors. For example, imidazolium,<sup>5</sup> triazolium,<sup>6</sup> perimidium<sup>7</sup> groups are successfully utilized for anion recognition elements. In addition, aliphatic hydrogen bond donor units such as benzylic<sup>8</sup> and pure aliphatic<sup>9</sup> have been shown to be effective hydrogen bonding element in anion recognition. Further, there have been many detailed studies of C–H hydrogen bonding in gas phase<sup>10</sup> and solid state<sup>11</sup> level as well as solution level for the diverse anions.

In addition, Sensors for nitrite anion based on gas phase reactions, electrochemical, colorimetric determination of paper micro fluidic devices and gelators have been developed. However, nitrite sensors generally have developed by using Griess reaction because of its high selectivity. Still, a simple probe for detection of NO<sub>2</sub><sup>−</sup> anion is challenging among the field of supramolecular analytical chemistry. Besides, the primary source of nitrite in our diets is processed (cured) meat or fish, and nitrites are considered a potential reactant precursor for nitrosamines. The serious health risks caused by high nitrite exposure are blue baby syndrome, spontaneous abortion, and birth defects in the central nervous system. Because of these reasons determination of nitrite anion has received great interest.<sup>12</sup>

Anion– $\pi$  interactions are usually restricted to aryl derivatives bearing electron-withdrawing substituents. The aryl rings are electron-deficient  $\pi$  center. This phenomenon is ascribed to Coulombic attraction between a negatively charged anion and electron-deficient aromatic ring. Even though the numerous solid-state examples, theoretical experiments, few solution-phase examples recognize the anion– $\pi$  interaction.<sup>13</sup>

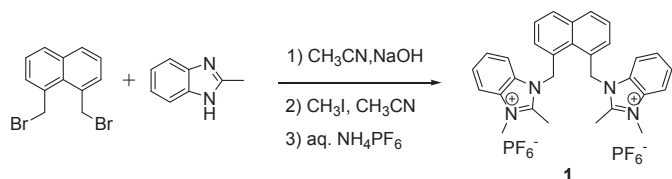
As an effort to develop a new anion receptor, which utilizes only C–H hydrogen bonding, we designed and synthesized a new anion receptor **1**, which has naphthalene spacer and 2-methyl benzimidazole as anionic recognition element. Here we'd like to report the synthesis and binding properties of receptor **1**. The binding phenomena of receptor **1** could be monitored by UV–vis,

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fluorescence and  $^1\text{H}$  NMR spectra and the results are consistent with DFT analysis.

## 2. Results and discussion

### 2.1. Synthesis



Receptor **1** was synthesized by the reaction between two equivalents of 2-methyl benzimidazole and 1,8-bis(bromomethyl) naphthalene. Then, anion exchange with ammonium hexafluorophosphate gave receptor **1** bearing two 2-methyl benzimidazole arms on naphthalene in 49% overall yield. Receptor **1** was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and high-resolution mass spectrometry.

### 2.2. Interactions with acetate

The ability of receptor **1** to recognize acetate was studied in acetonitrile using UV–vis titration spectra. The receptor **1** displayed strong absorption band at 226 nm in acetonitrile. Fig. 1a shows the family of UV–vis spectra obtained over the course of the titration of solution **1** with tetrabutylammonium acetate in acetonitrile. As acetate ions were added to the 20  $\mu\text{M}$  acetonitrile solution of **1**, the absorbance peak at 279 nm was gradually decreased with small bathochromic shift. In addition, there were well-defined isosbestic points at 223 nm, 231 nm, 238 nm, which indicated that new species were formed by the interaction of **1** and acetate. In addition, the receptor **1** displayed strong fluorescence emission in acetonitrile as shown in Fig. 1b. The excitation and emission wavelength were 271 and 347 nm, respectively. The intensity of emission spectrum from 20  $\mu\text{M}$  solution of the receptor **1** gradually decreased as the concentration of tetrabutylammonium acetate was increased (1–26 equiv), which also indicates the association between the receptor **1** and acetate.

The complexation abilities of receptor **1** to acetate was also measured by standard  $^1\text{H}$  NMR titration experiments in  $\text{CD}_3\text{CN}$  using a constant host concentration (2 mM) and increasing concentrations of acetate anions. The addition of tetrabutylammonium acetate salts to the solution of receptor **1** in  $\text{CD}_3\text{CN}$  resulted in large downfield shifts of benzimidazole  $\text{C}_2\text{--CH}_3$  and benzylic  $\text{C--H}$

(Fig. 2). For example, addition of tetrabutylammonium acetate moved benzimidazole  $\text{C}_2\text{--CH}_3$  from 2.84 to 2.89 ppm and benzylic  $\text{C--H}$  from 6.41 to 6.70 ppm. The downfield shifts of these protons indicate the presence of a hydrogen bond interaction between these  $\text{C--H}$  hydrogens and acetate ion.

The stoichiometry between receptor **1** and acetate was determined to be 1:1 using a UV Job plot in acetonitrile (Fig. 3).

A Benesi–Hildebrand plot<sup>14</sup> by use of change at 279 nm in UV–vis spectrum and 347 nm in fluorescence spectrum gave the association constants. The association constants calculated were  $1.0 \times 10^4 \text{ M}^{-1}$  from UV–vis titration and  $1.0 \times 10^4 \text{ M}^{-1}$  from fluorescence titration, respectively. In addition, analysis of chemical shift utilizing EQNMR<sup>15</sup> gave the association constant of

$1.1 \times 10^4 \text{ M}^{-1}$ , which is similar to the values obtained from UV–vis and fluorescence titrations.

### 2.3. Interactions with nitrite

The abilities of receptor **1** to recognize with nitrite were also studied in acetonitrile using UV–vis titration spectra. The receptor **1** in acetonitrile exhibits absorption band at 226 nm, 271 nm and 279 nm. When the amount of nitrite was increased, small bathochromic shift of  $\lambda_{\text{max}}$  observed with an isosbestic point at 254 nm (Fig. 4a). The existence of isosbestic point for UV–vis titrations of receptor **1** with nitrite suggests a 1:1 complexation, and this binding stoichiometry was confirmed by UV–vis Job's plot analysis (Fig. 3).

In addition, the intensity of emission spectrum from the receptor **1** gradually decreased as the concentration of tetrabutylammonium nitrite salts was increased (1–30 equiv), which also indicates the association between the receptor **1** and nitrite (Fig. 4b). From these experiments, association constants for nitrite were calculated as  $8.8 \times 10^3 \text{ M}^{-1}$  and  $8.7 \times 10^3 \text{ M}^{-1}$  from the UV–vis and fluorescence titrations, respectively.

Hydrogen bond formation was confirmed by  $^1\text{H}$  NMR titration. When nitrite was added, benzimidazole  $\text{C}_2\text{--CH}_3$  and benzylic  $\text{C--H}$  moved to downfield (Fig. 5). For example, benzimidazole  $\text{C}_2\text{--CH}_3$  moved from 2.84 to 2.87 ppm and benzylic  $\text{C--H}$  from 6.41 ppm to 6.66 ppm, respectively. The association constants calculated for nitrite were calculated as  $9.2 \times 10^3$  for  $^1\text{H}$  NMR titration. Surprisingly, the resulting association constant for nitrite anion is much comparable with acetate anion complex with receptor **1**.

### 2.4. Interactions with halides

The receptor **1** showed similar titration behaviors for halides. For example, when the amount of bromide was increased, small

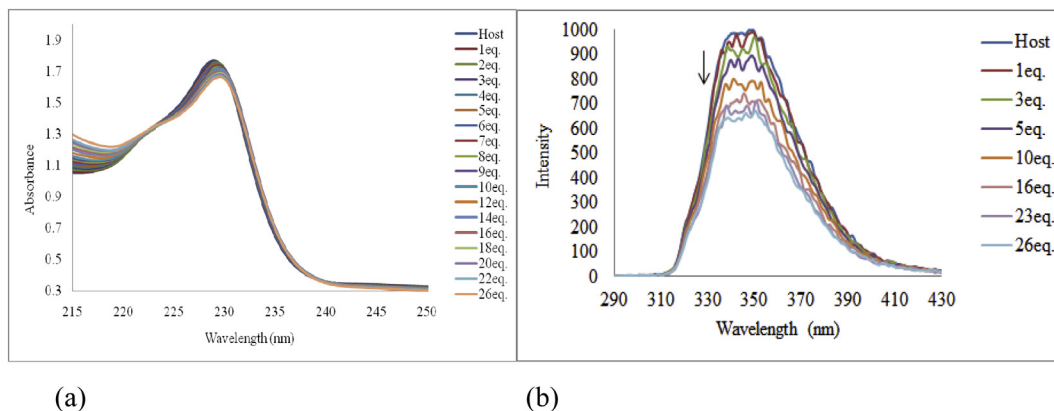


Fig. 1. Family of UV–vis spectra (a) and fluorescence spectra (b) recorded over the course of titration of 20  $\mu\text{M}$  acetonitrile solutions of the receptor **1** with the standard solution tetrabutylammonium acetate.

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