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Anion receptors based on 4-nitrophenylhydrazone

Jaeyoung Jo [a], Raghunath Putikam [b], M. C. Lin [b,*], Jongmin Kang [a,*]

[a] Department of Chemistry, Sejong University, Seoul 143-747, Republic of Korea
[b] Center for Interdisciplinary Molecular Science, Department of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan

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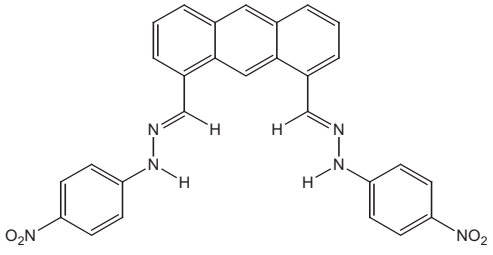
ABSTRACT

We have designed and synthesized new chromogenic anion receptors **1** and **2**, which utilized 4-nitrophenylhydrazone as anion recognition moiety. UV–vis and ^{1}H NMR titration showed that receptors **1** and **2** bound anions utilizing two hydrazone N–H hydrogen bond and two C–H hydrogen bond. Despite the weak hydrogen bonding abilities of binding motifs, receptor **1** showed affinities for dihydrogen phosphate and acetate and receptor **2** showed relatively strong affinities for dihydrogen phosphate in polar solvent such as 5% DMSO in CH_3CN.

Phosphate and carboxylate-binding receptors have become highly favorable targets in molecular recognition chemistry due to the importance of biological and environmental roles of these anions. For example, phosphate is an essential component of chemotherapeutic and antiviral drugs.[1] Moreover, phosphate is becoming the main water pollutant in many countries, and is causing serious environmental problems.[2] Therefore, several systems designed to selectively coordinate phosphate have been reported.[3] In addition, carboxylates are the most fundamental importance in nature and in chemical technology.[4] Recent physiological studies evidenced that the anions of weak aliphatic acids such as acetate transiently inhibits myocardial contraction by increasing mitochondrial calcium uptake.[5] Many chemical sensors follow the approach of the covalent attachment of signaling subunits and binding sites.[6] Chromogenic or fluorogenic groups that are covalently linked to the receptor moiety as signaling subunits and multiple hydrogen-bonding interactions as binding sites have been utilized in this regard. For binding sites, molecules containing highly polarized N–H fragments such as ureas,[7] thioureas,[8] pyrroles,[9] and amides[10] have been widely used as receptors for recognition and sensing purposes in aprotic solvents such as $CHCl_3$, CH_3CN, and DMSO. Artificial receptors utilizing amines[11] and C–H hydrogen bonds[12] are still scarce as their polarization and binding abilities are usually weak. However, they play important roles in nature.[13] As an attempt to anion receptors using only these weak hydrogen bonds, we designed receptors **1** and **2**, which utilized 4-nitrophenylhydrazone as anion recognition moiety. The receptor **1** would bind anion utilizing two hydrazone N–H hydrogen bond and two C–H hydrogen bond while the receptor **2** has one additional amine N–H binding moiety. Here we would like to report the synthesis and binding properties of receptors **1** and **2** with various anions.



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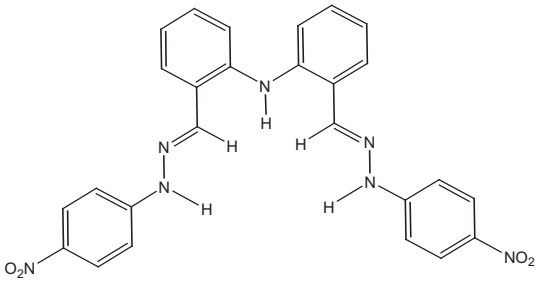

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* Corresponding authors.
E-mail addresses: chemmcl@emory.edu (M.C. Lin), kangjm@sejong.ac.kr (J. Kang).

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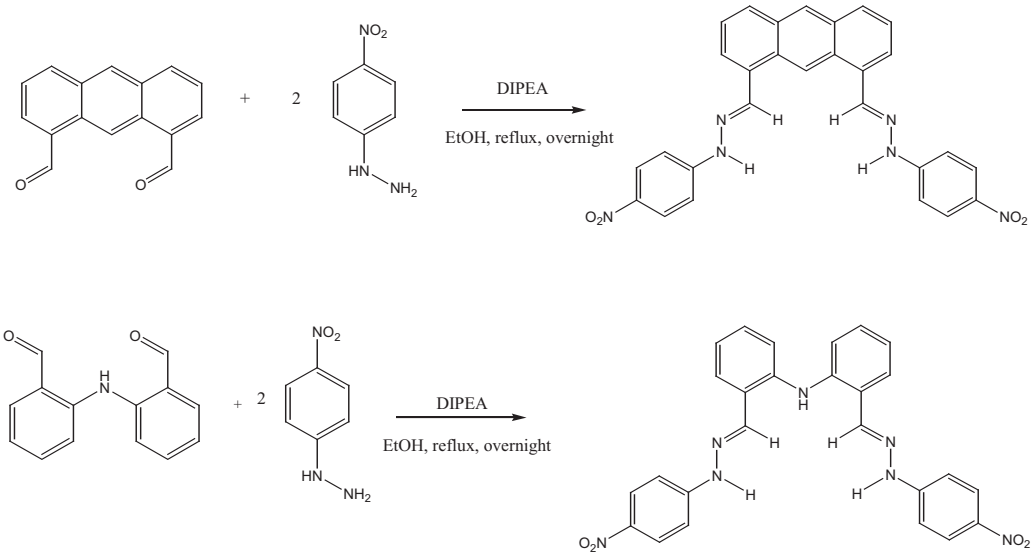
Synthesis

Receptor **1** was obtained from the reaction between anthracene-1,8-dicarbaldehyde and 4-nitrophenylhydrazine in dry ethanol in 81% yield. Receptor **2** was obtained from the reaction between *o*-$(C_6H_4–CHO)_2NH$[14] and 4-nitrophenylhydrazine in 30% yield.



Results and discussion

The receptor **1** displayed strong absorption bands at 436 nm in 5% DMSO in CH_3CN. Figure 1 shows the family of UV–vis spectra obtained over the course of the titration of solution **1** with tetrabutylammonium dihydrogen phosphate and tetrabutylammonium acetate in 5% DMSO in CH_3CN. The titrations were performed at 40 μM solution for the receptor **1**. When tetrabutylammonium dihydrogen phosphate or tetrabutylammonium acetate was added to the solution of **1**, λ_{max} of **1** was moved to the longer wavelength up to 450 nm and intensity of absorption band at this wavelength increased with isosbestic point at 414 nm in both spectra. (Fig. 1) These results suggested that a typical hydrogen bonding complex formed between receptor **1** and these anions.

Receptor **1** showed a fluorescence emission spectrum in 5% DMSO in CH_3CN. The excitation wavelength was 436 nm and emission wavelength was 533 nm. The intensity of the emission spectrum from the solution of receptor **1** gradually decreased as the concentration of tetrabutylammonium dihydrogen phosphate or tetrabutylammonium acetate increased, which also indicated the association between receptor **1** and these anions (Fig. 2).

The association constants of these anions for the receptor **1** could be calculated from the Benesi–Hildebrand plot.[15] For example, the association constants calculated for dihydrogen phosphate were 3.3×10^3 from UV–vis titration and 3.2×10^3 from fluorescence titration, respectively. In addition, the association constants calculated for acetate were 2.5×10^3 from UV–vis titration and 2.8×10^3 from fluorescence titration, respectively.

However, only tetrabutylammonium acetate showed the formation of hydrogen bonding in ^1H NMR titration. In 5% DMSO-d_6 in CD_3CN, both hydrazone N–H peak and vinylic C–H peak moved

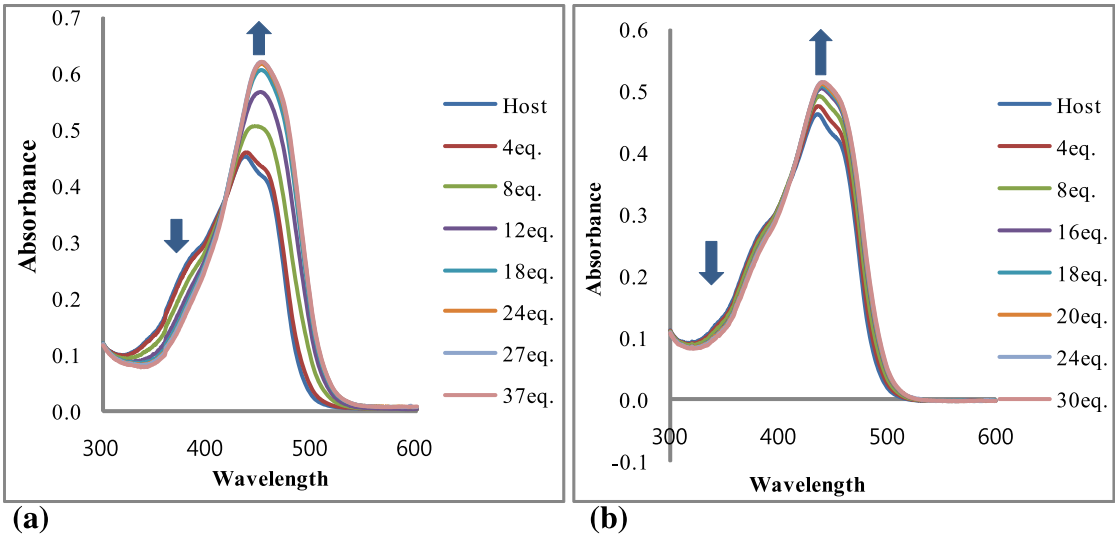


Figure 1. Family of UV–vis spectra recorded over the course of titration of 5% DMSO in CH_3CN solution of the receptor **1** with the standard solution tetrabutylammonium dihydrogen phosphate (a) and acetate (b).

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