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Iodide selective fluorescent anion receptor with two methylene bridged bis-imidazolium rings on naphthalene

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Abstract—We have designed and synthesized fluorescent anion receptor **2**, bearing two methylene bridged bis-imidazolium ring on 1,8-positions of naphthalene. Anion binding studies carried out using fluorescence spectroscopy and ^{1}H NMR revealed that this compound displays selective affinities for iodide ion.

Artificial receptors for selective anion recognition is an area of intensive investigation as anions play a fundamental role in a wide range of chemical and biological process.[1] Receptors based on guest anion induced changes of color or fluorescence seem to be attractive due to their high sensitivity and low detection limit.[2] In many cases, hydrogen bonds are utilized as anion recognition element as host–guest complementarity could be achieved from the directionality of hydrogen bonds. The orientation of hydrogen bonds can differentiate anionic guests with different geometries. While most of the hydrogen bond anion receptors utilize N–H–X$^-$ or O–H–X$^-$ hydrogen bonds,[3] 1,3-disubstituted imidazolium groups are recently introduced as a new anion binding hydrogen bond moiety by forming (C–H)$^+$–X$^-$ hydrogen bonds between C(2)–H in imidazolium rings and the guest anion. Depending on the spatial arrangement of 1,3-disubstituted imidazolium groups, halide,[4] dihydrogen phosphate,[5] dicarboxylate,[6] and sulfate[7] selective receptors have been reported. In addition, we have shown that the methylene bridged bis-imidazolium receptor **1** binds acetate strongly over other anions[8] (Fig. 1).

To extend possible utility of methylene bridged bis-imidazolium receptor **1**, we have designed and synthesized the receptor **2**, bearing two methylene bridged bis-imidazolium rings on 1,8-positions of naphthalene. For the synthesis of naphthalene receptor **2**, methylene bridged bis-imidazole **3** was synthesized in 64% yield from the reaction of imidazole and bromochloromethane. Then the bis-imidazole **3** was reacted with 0.3 equiv of ethyl bromide to give imidazolium ion **4** in 37% yield. This intermediate was refluxed in acetonitrile for 4 h with 1,8-bis(bromomethyl)naphthalene. Anion exchange with ammonium hexafluorophosphate gave receptor **2** bearing two methylene bridged bis-imidazolium ring on 1,8-positions of naphthalene. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, and high resolution mass spectrum (Scheme 1).

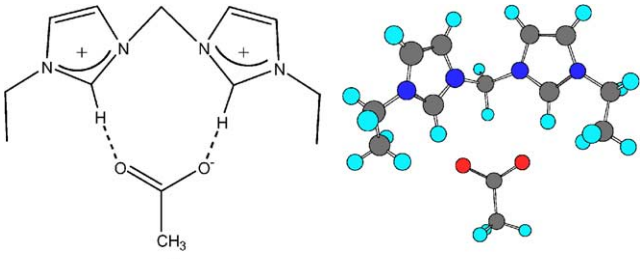

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Figure 1. The energy minimized structure of 1:1 complex between methylene bridged bis-imidazolium receptor **1** and acetate (Cache 3.2 MOPAC calculation).

Molecular modeling showed that the anion receptor **2** has a concave structure. The four C(2)–H in imidazolium rings form a concave cavity and point to the anion located at the center of cavity. The shape of the cavity seemed to be suitable size for spherical halide ions. The energy minimized structure of receptor **2** and iodide

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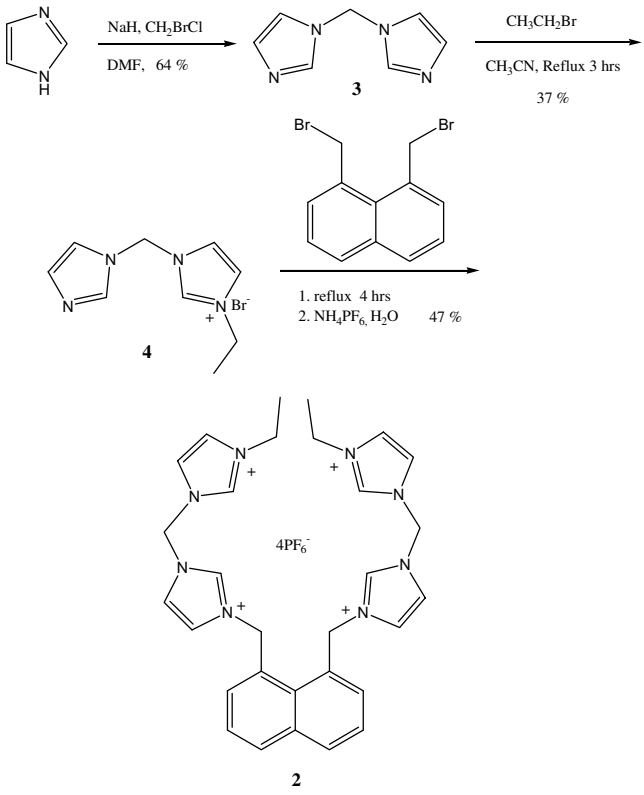

Scheme 1. The synthetic procedure for the anion receptors **2**.

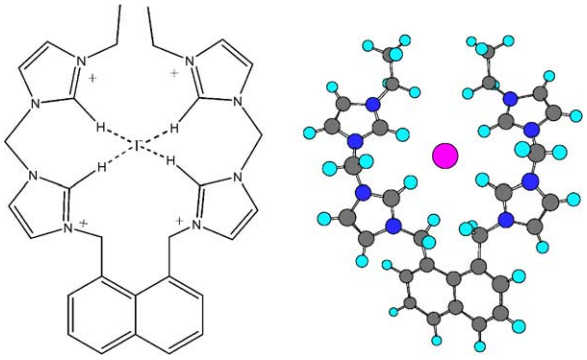

Figure 2. The possible binding mode of receptor **2** and iodide and energy minimized structure of 1:1 complex between receptor **2** and iodide (Cache 3.2 MOPAC calculation).

is shown in Figure 2 (Cache 3.2 MOPAC calculation). From modeling, the distance between the hydrogen in the C(2)–H and iodide fell in the range of 2.06–2.23 Å.

The complexation ability of receptor **2** to the halides was measured by standard ^{1}H NMR titration experiments in 10% DMSO-d_6 in CD_3CN using a constant host concentration (4 mM) and increasing concentrations of anions (1–10 equiv). The chemical shift data were analyzed by EQNMR.[9] The addition of tetrabutylammonium halide salts to the solution of **2** in 10% DMSO-d_6 in CD_3CN resulted in downfield shifts in two C(2) proton peaks of imidazolium ring. In case of iodide ion, two C(2) protons originally resonating at $\delta = 9.10$ and 8.94 were shifted to $\delta = 9.56$ and 9.50 upon addition of 3 equiv of iodide ion, which indicates that all C(2) protons are involved in binding events. Assuming 1:1 binding stoichiometry, the association constant calculated from the chemical shift change of C(2)–H of imidazolium ring was 1600±220. The shifts of two C(2)–H proton peaks were also observed for bromide. The two C(2) protons peaks moved to 10.00 ppm and 9.90 ppm with 5 equiv of bromide ion. The association constant was calculated as 140±7.0. We were not able to obtain consistent and reliable association constant for fluoride and chloride from ^{1}H NMR titration due to broadening of ^{1}H NMR spectrum.

The naphthalene receptor **2** displayed strong fluorescence emission in 10% DMSO in acetonitrile solution as shown in Figure 3. The excitation and emission wavelengths were 292 nm and 330 nm, respectively. The associations between the naphthalene receptor **2** and spherically shaped halides were investigated by fluorescence titration. The fluorescence change of the receptor **2** was monitored in 10% DMSO in acetonitrile. The intensity of emission spectrum from 10 μM solution of the naphthalene receptor **2** decreased as the concentration of tetrabutylammonium halides salts was increased, which indicates the association between the receptor **2** and halides. The stoichiometry between host and guest was determined by fluorescence Job plot, which showed evident 1:1 stoichiometry[10] (Fig. 4). A Benesi–Hildebrand plot[11] by use of change in the 330 nm fluorescence intensity gave association constants. From the experiments, the association constants for iodide, bromide, and chloride are found to be 5000±470, 243±15, and 185±13, respectively. We could not obtain reliable asso-

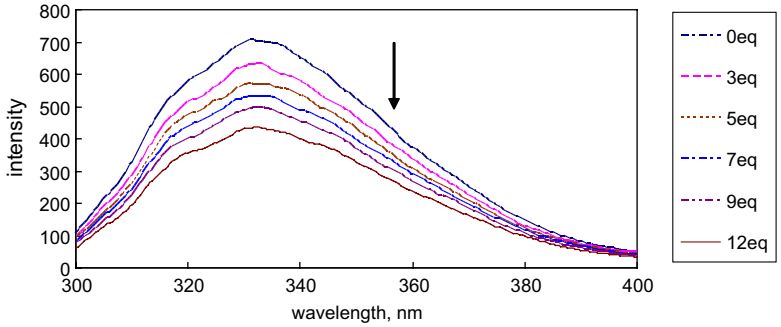

Figure 3. The change of fluorescence spectra in the receptor **2** when tetrabutylammonium iodide was added.

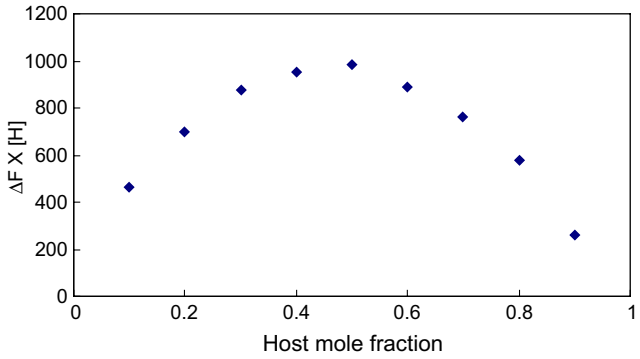

Figure 4. Job plot between the receptor **2** and iodide.

ciation constant for fluoride from fluorescent titration experiment since the emission intensity did not consistently decrease upon the addition of fluoride ion. However, we note that the order of association constants is $I^- > Br^- > Cl^-$ from the ^1H NMR titration and fluorescence titration. Complementarity of receptor to the anion is critical factor in achieving selectivity due to diverse geometry of anions.[12] The complementarity for halides is generally achieved by the size of receptor binding site as halides are spherically shaped. The preference for iodide with receptor **2** suggests that the cavity formed by four C(2)–H is more complementary to the size of the iodide ion than to the size of other halide ions.

We also investigated the binding of other anions with receptor **2** with fluorescence titration. In case of hydrogen sulfate, cyanide, and benzoate, the Job plots were not symmetric and showed maxima when the mole fraction of host is between 0.4 and 0.5, which indicates a mixed stoichiometry. Therefore, it was not possible to obtain accurate association constants for these anions.

In summary, we have designed and synthesized fluorescent imidazolium receptor **2**, which displays selectivity for iodide over other halides.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.06.068.

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