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Bromide selective fluorescent anion receptor with glycoluril molecular scaffold

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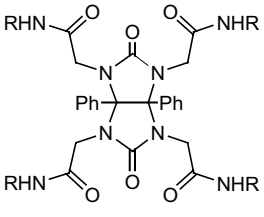
Abstract—Glycoluril based fluorescent anion receptor has been designed and synthesized. Anion binding studies carried out using fluorescence spectroscopy and ^{1}H NMR revealed that this compound displays good affinities for bromide ion.

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] However, fluorogenic or chromogenic sensors for selective detection of anions are much less explored despite the fact that many examples of anion receptors or cation sensors have been reported.[2] For sensing approach, anion recognition site is usually coupled to the reporting groups, which binding process is transduced into a signaling event. Anion complexation induces changes in the spectroscopic properties of host molecules, leading to guest anion specific color change or fluorescent emission spectrum.

Recently, we introduced a diphenyl glycoluril moiety into the framework of hosts and produced host molecule **1** capable of binding anions by the cooperative action of multiple amide hydrogen bonds.[3] The anion receptor **1** binds with spherically shaped halide ion in 1:1 stoichiometry and has a high affinity for fluoride ion. Four amide N–H hydrogens attached at the corner of glycoluril form a cavity and point to the anion located at the center of the concave structure of glycoluril. In these studies, mainly guest-induced ^{1}H NMR shifts were used to determine the association constants. However, ^{1}H NMR titration method is limited when the host and guest associate strongly.[4] This limitation can be overcome by the incorporation of fluorescent chromophores into the host due to their high sensitivity and low detection limit.[5] Therefore, to enlarge the scope of the receptor **1** as a fluorescent sensor, we designed fluorescent receptor **2**, which has fluorescent naphthalene moieties instead of the phenyl groups. Here we would like to report the binding properties of receptor **2** with various anions (Fig. 1).

The new naphthalene receptor **2** was synthesized in 70% yield from the reaction of tetraacylchloride **3**[3b] and 2-naphthaleneamine. The compound **2** was characterized by ^{1}H NMR, ^{13}C NMR, and high resolution mass spectrum.[6]

The naphthalene receptor **2** displayed strong fluorescence emission in acetonitrile as shown in Figure 2. The excitation and emission wavelength were 242 and 350 nm, respectively. The relative quantum yield of receptor **2** was investigated by comparing the ratio of the fluorescence emission intensity maximum to



1 R= 4-nitrophenyl

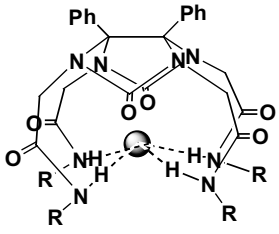


Figure 1. The structure of receptor **1** and the proposed binding mode with halide ion.

Keywords: Anion receptor; Glycoluril.
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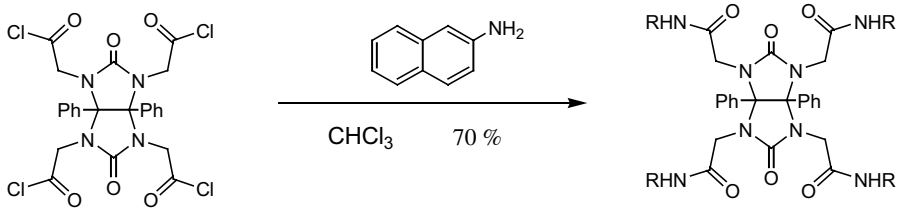

3 **2** R= 2-naphthalene

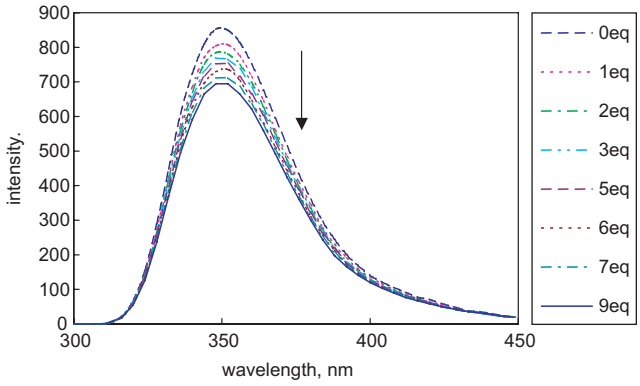

Figure 2. The change of fluorescence spectra in the receptor **2** when tetrabutylammonium bromide was added.

UV–vis absorbance at excitation wavelength used for the sample with that of standard.[7] 9,10-Diphenylanthracene ($\Phi = 0.96$) was used as fluorescence standard.[8] The quantum yield of receptor **2** was determined to be 0.12. 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 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 plot of F^0/F versus the concentration of halides gave a straight line as shown in Figure 3. The linearity of Stern–Volmer plot further confirms the formation of one type complex between receptor **2** and halide. The stoichiometry between host and guest was determined by fluorescence Job plot, which showed evident 1:1 stoichiometry (Fig. 4).[9] A Benesi–Hildebrand plot[10]

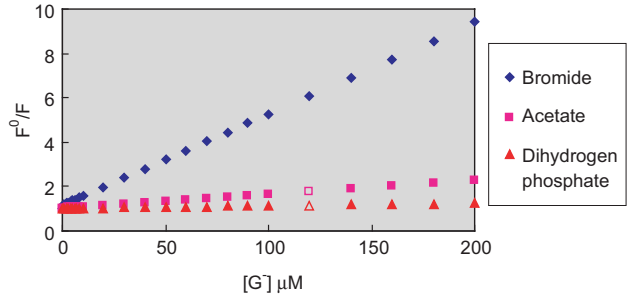

Figure 3. The Stern–Volmer plot for the association of receptor **2** and various anions.

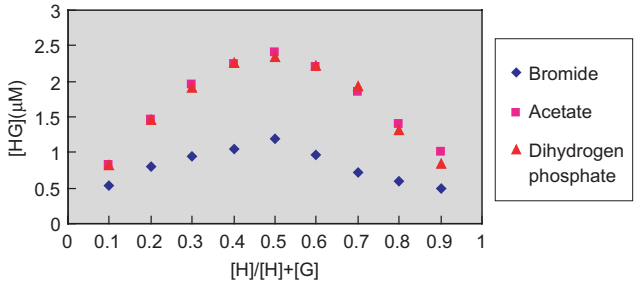

Figure 4. Job plot between receptor **2** and various anions. The complex concentration, [HG] was calculated by the equation[9] $[HG] = \Delta F/F^0 \times [H]$.

by use of change in the 350 nm fluorescence intensity gave association constants. The results are summarized in Table 1. From the experiments, the receptor **2** showed the highest association constant $1.2 \times 10^5 \pm 1.4 \times 10^4$ for bromide. The order of association constants was $Br^- > Cl^- > F^- > I^-$.

The complexation abilities of receptor **2** to the halides were also measured by standard ^1H NMR titration experiments in DMSO-d_6 using a constant host concentration (2 mM) and increasing concentrations of anions (1–10 equiv). The chemical shift data were analyzed by EQNMR.[11] The addition of tetrabutylammonium halide salts to the solution of **2** in DMSO-d_6 resulted in downfield shifts in both the amide N–H hydrogen and CH_2 hydrogens next to amides. Therefore, the signals of amide N–H or the signals of CH_2 protons located next to amide groups were used to determine the association constants for receptor **2** and halides. Whichever

Table 1. Association constants (M^{-1}) of receptor **2** with tetrabutylammonium anions in acetonitrile from fluorescence titration

Anion	Association constants (K_a)
F^-	$1.4 \times 10^4 \pm 8.0 \times 10^2$ (14[b])
Cl^-	$2.4 \times 10^4 \pm 2.8 \times 10^3$ (34[a])
Br^-	$1.2 \times 10^5 \pm 1.4 \times 10^4$ (2.8×10^2[a])
I^-	$1.3 \times 10^4 \pm 5.3 \times 10^2$ (7.6[a])
$CH_3CO_2^-$	$1.2 \times 10^4 \pm 1.8 \times 10^2$
$C_6H_5CO_2^-$	$9.6 \times 10^3 \pm 10$
$H_2PO_4^-$	$7.5 \times 10^4 \pm 9.5 \times 10^2$

The numbers in parentheses are association constants in DMSO-d_6 from ^1H NMR titration.

[a] Errors in K_a are estimated to be less than 10%.

[b] Errors in K_a are estimated to be less than 20%.