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Anion Receptors with Glycoluril Molecular Scaffold

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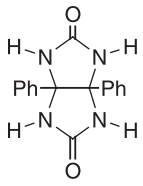
For a synthetic receptor with an amide group, the amide groups are arranged through a space in a rigid and convergent manner. This has been achieved by incorporating amide groups into various molecular scaffolds. The geometry of diphenylglycoluril allows the synthesis of concave molecular structures. In addition, the rigidity of the molecule provides a solid molecular scaffold to arrange suitable binding moieties such as hydrogen bonds. We have developed various anion receptors based on diphenylglycoluril. The association of these receptors with various anions reflects the shape, size and basicity of the anions.

Keywords: Glycoluril; Anion receptor; Synthetic receptor; Molecular scaffold

Artificial receptors for selective anion recognition are an area of intensive investigation due to their importance in a wide range of chemical and biological processes [1–4]. Many successful positively charged receptors [5–9] and neutral receptors incorporating Lewis acids [10–12] have been reported. However, their selectivity is generally modest and limited as their interactions with anions are non-directional. Many anions have diverse geometries, which require shape selective recognition. Therefore many researchers have used hydrogen bonds as a recognition element as they are directional. Correct orientation of hydrogen bonds can differentiate between anionic guests with different geometries. In nature, proteins utilize neutral amide N—H groups to achieve anion binding [13]. For synthetic receptors with amide group, the amide groups are arranged through a space in a rigid and convergent manner. This has been achieved by incorporating amide groups inside a macrocycle [14–24] or utilizing molecular scaffolds to arrange amide groups. Benzene rings [25–27], pyrrole [28–30], azulene [31] cyclohexane [32], cholic acid [33,34], tris(aminoethylamine) [35] and calixarenes [36–38] have been utilized as molecular scaffolds to arrange amide bonds.

One of the goals of our research has been the design and synthesis of new types of anion receptor. Towards this goal, we have designed and studied anion receptor systems based on diphenylglycoluril. The geometry of diphenylglycoluril (**1**) allows the synthesis of concave molecular structures. In addition, the rigidity of the molecule provides a solid molecular scaffold to arrange suitable binding moieties such as hydrogen bonds. Furthermore, the four amide NH groups at the corners of the glycoluril can be easily alkylated in basic conditions. Therefore, over the past years glycoluril has been utilized as an element of molecular receptors such as polyrotaxanes [39–43], molecular clips [44–49] and the formation of molecular capsules [50–52]. In this mini review, we discuss the diphenylglycoluril based anion receptor system.



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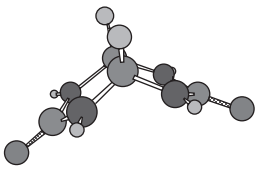

The first anion receptor based on diphenylglycoluril was the receptor **2** which has four amide groups arranged at the corner of the diphenylglycoluril [53]. The four amide N—H hydrogens attached at the

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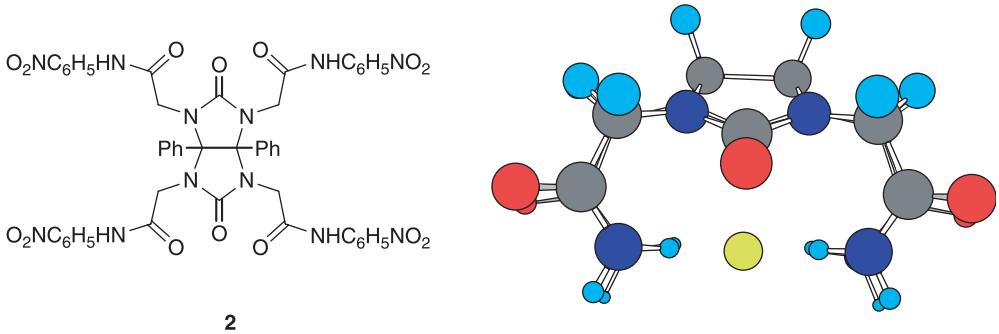

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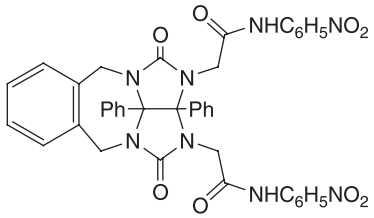
FIGURE 1 The energy minimized structure of receptor **2** and fluoride (Cache 3.2 MOPAC calculation) aromatic rings are omitted for clarity.

corner of diphenylglycoluril would form a cavity and point to the anion located at the center of concave structure of diphenylglycoluril. The shape of the cavity seemed to be suitable for spherical halide ions and the size of the cavity seemed to be appropriate for the fluoride ion. The energy minimized structure of receptor **2** and fluoride is shown in Fig. 1 (cache 3.2 MOPAC calculation). From modeling, the distance between amide N—H hydrogen and fluoride appeared in the range of 1.75–1.77 Å. The four amides in the receptor **2** are arranged symmetrically to bind to the fluoride ion. From a structural point of view, an anion is inserted within the closed cavity composed of four amides attached to the glycoluril. ^{1}H NMR titration experiments were performed in CD_3CN and the chemical shift data were analyzed by EQNMR [54]. The addition of tetrabutylammonium anion salts to the solution of **2** in CD_3CN resulted in downfield shifts in both the amide N—H hydrogen and CH_2 hydrogen next to amides. For example, CH_2 signals moved downfield about 0.1 ppm for one equivalent fluoride ion and no more shift was observed, which indicates 1:1 binding. The association constant was calculated as $3.6 \times 10^4\,M^{-1}$. Control experiments were performed to elucidate that the binding of **2** with fluoride is the cooperative action of four amide hydrogen bonds. The compounds **3** and **4** were synthesized and their bindings to the fluoride ion under the same condition were investigated. As the compound **4** was completely insoluble in CD_3CN, the binding constants were investigated in DMSO-d_6. The binding constants of fluoride in DMSO-d_6 were calculated as $1028\,M^{-1}$ for **2**, $159\,M^{-1}$ for compound **3** and $336\,M^{-1}$ for compound **4**. This control experiment indicates that at least three hydrogens or more plausibly all four amide hydrogens are involved in the binding event with the fluoride ion. The association constants between other halides and receptor **2** were also investigated in CD_3CN. The results are summarized in Table I.



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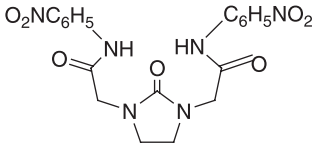

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Table I shows that the association constants of receptor **2** for halides follow the diameter and basicity of the halide ions. The smallest size and the largest basicity of the fluoride ion allowed a much better fit into the cavity and the formation of shorter and stronger hydrogen bonds. For **2**, about 550 fold selectivity for fluoride over iodide was observed.

TABLE I Association constants of **2** and **5** for the tetrabutylammonium anions in CD_3CN

Anion	**2**	**5**
F^-	$3.6 \times 10^{4\dagger}$	$2.7 \times 10^{3\dagger}$
Cl^-	$1.5 \times 10^{3\dagger}$	$2.3 \times 10^{3\ddagger}$
Br^-	$7.8 \times 10^{2\dagger}$	$2.2 \times 10^{2\dagger}$
I^-	$6.6 \times 10^{\ddagger}$	$1.3 \times 10^{\ddagger}$
NO_3^-	$2.6 \times 10^{3\dagger}$	$3.2 \times 10^{\ddagger}$
$CH_3CO_2^-$	$2.7 \times 10^{6\dagger}$ ($\beta_2 = K_1K_2$)	$9.1 \times 10^{4\P}$
$C_6H_5CO_2^-$	–	$2.4 \times 10^{4\P}$
NC^-	–	$5.3 \times 10^{2\dagger}$
$H_2PO_4^-$	–	$1.6 \times 10^{2\ddagger}$
HSO_4^-	–	$1.1 \times 10^{2\dagger}$

† Errors in K_a are estimated to be less than 10%. ‡ Errors in K_a are estimated to be less than 20%. ¶ Association constants were calculated from UV–VIS titration.

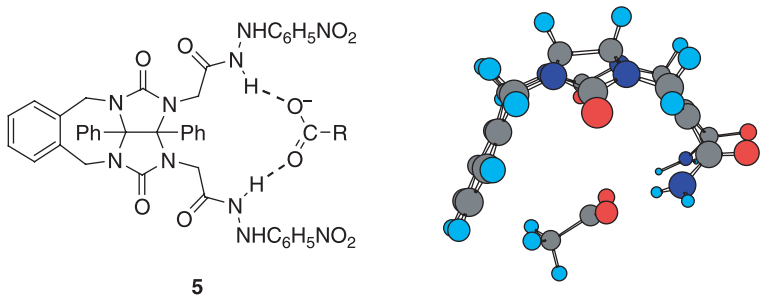

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FIGURE 2 The energy minimized structure of 1:1 complex between receptor **5** and acetate (Cache 3.2 MOPAC calculation); aromatic rings are omitted for clarity.

While the receptor **2** binds halides with a 1:1 stoichiometry, Job plot showed that the receptor **2** binds to acetate in a 1:2 fashion. The calculated association constants for acetate were $2.7 \times 10^6\,M^{-2}$ ($\beta_2 = K_1K_2$).

As the receptor **2** binds two acetate with high affinity, we began to investigate the association of acetate and glycoluril based tweezer-type receptor **5**, which has only two amide hydrogen bonds [55]. Anion binding studies carried out using ^{1}H NMR and UV–Vis revealed that this compound displays good affinities for Y-shaped anions such as acetate and benzoate, while binding spherical shaped anions and tetrahedral shaped anions only weakly. In CD_3CN, The plot of induced ^{1}H NMR chemical shifts versus acetate or benzoate concentration gave typical titration curves corresponding to the formation of a 1:1 complex. However, The association constants calculated from ^{1}H NMR titration was too large to accept from ^{1}H NMR titration experiments [56]. Therefore, the binding properties of **5** with acetate or benzoate were further assessed by UV–Vis spectroscopy. Increasing the concentration of acetate produced a bathochromic shift in the λ_{max} from 317 nm to 329 nm and clear isosbestic point appears at 321 nm. Similar spectrum was observed for the titration of **5** with benzoate. Association constants calculated using a computer program ENZFITTER [57] gave $9.1 \times 10^4\,M^{-1}$ for acetate $2.4 \times 10^4\,M^{-1}$ for benzoate. The possible binding mode and energy minimized structure of receptor **5** and acetate were shown in Fig. 2. We also investigated the associations of receptor **5** and spherical anions such as halides, tetrahedral anions such as dihydrogen phosphate and hydrogen sulfate or linear anion such as cyanide. Job plot experiments showed 1:1 binding stoichiometry for all kinds of anions irrespective of anion shapes. For receptor **5**, the association constants of other anions are much smaller values than acetate or benzoate irrespective of anion shapes. The results are also summarized in Table I. The association constant for acetate is about 30–50 times higher than those of fluoride or dihydrogen phosphate. Probably the binding site of receptor **5** does not fit to the spherical halide ions, tetrahedral anions or linear cyanide anion. However, for these anions the association constants still reflect basicity of these anions [58]. Fluoride and dihydrogen phosphate are stronger hydrogen acceptor than other halide or hydrogen sulfate respectively.

As the receptor **5** has high affinity for the acetate, we designed the receptor **6** which incorporates chiral building blocks near binding sites [59]. These chiral building blocks may discriminate between enantiomeric guests due to side chain interactions as shown in Fig. 3. Binding studies carried out using ^{1}H NMR revealed that the receptor **6** showed moderate enantioselectivity with a general preference for D-amino acids. For example, The association constants calculated from ^{1}H-NMR titration in CD_3CN gave $8.9 \times 10^2 \pm 35\,M^{-1}$ for N-Boc-D-leucine and $2.5 \times 10^2 \pm 12\,M^{-1}$ for N-Boc-L-leucine, $7.2 \times 10^2 \pm 2\,M^{-1}$ for N-Boc-D-glutamine and $4.2 \times 10^2 \pm 3\,M^{-1}$ for N-Boc-L-glutamine respectively.

Binding studies with chiral receptor **6** and a range of N-protected amino acid derivatives such as tetrabutylammonium carboxylate salts in CD_3CN were carried out and the results are summarized in Table II. Although the difference of association constant between D- and L-amino acid was small,

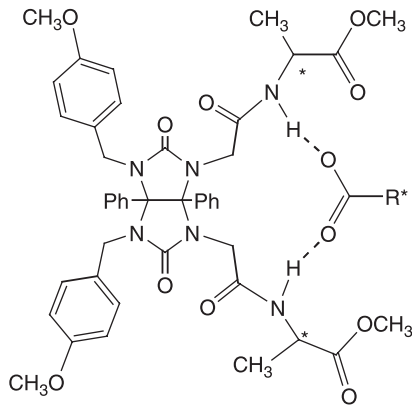

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FIGURE 3 The proposed binding of carboxylates in various amino acids by the receptor **6**. R* represents a chiral group.

TABLE II Binding constants (K_{ass}) for the 1:1 complexes formed between the receptor **6** and tetrabutylammomium carboxylate salts of various N-protected amino acids in CD_3CN

Entry	Substrate	K_{ass} (M^{-1})
1	N-Boc-D-Leu-CO_2^- NBu_4^+	$8.9 \times 10^2 \pm 35$
2	N-Boc-L- Leu-CO_2^- NBu_4^+	$2.5 \times 10^2 \pm 12$
3	N-Boc-D-Gln-CO_2^- NBu_4^+	$7.2 \times 10^2 \pm 2$
4	N-Boc-L-Gln-CO_2^- NBu_4^+	$4.2 \times 10^2 \pm 3$
5	N-Boc-D-Phe-CO_2^- NBu_4^+	$8.0 \times 10^2 \pm 98$
6	N-Boc-L-Phe-CO_2^- NBu_4^+	$6.0 \times 10^2 \pm 30$
7	N-Boc-D-Val-CO_2^- NBu_4^+	$6.0 \times 10^2 \pm 36$
8	N-Boc-L-Val-CO_2^- NBu_4^+	$2.5 \times 10^2 \pm 12$
9	N-Boc-D-Ala-CO_2^- NBu_4^+	$5.7 \times 10^2 \pm 23$
10	N-Boc-L-Ala-CO_2^- NBu_4^+	$4.3 \times 10^2 \pm 21$
11	N-Boc-D-Trp-CO_2^- NBu_4^+	$2.7 \times 10^2 \pm 19$
12	N-Boc-L-Trp-CO_2^- NBu_4^+	$2.4 \times 10^2 \pm 12$

D-amino acid showed better affinity to the receptor **6** consistently for all the amino acids we investigated. As it was hard to get a crystal of receptor and amino acid in binding, we used semi-empirical calculation to explain this phenomena. The molecular modeling from *ab initio* calculation shows the details of complexation between the host **6** and the guest amino acids. We tried several complexation modes for both D- and L-amino acids. All the complexation modes we tried have been reduced to the same structure during the course of structure optimization process. Therefore just one complexation mode exists for both D- and L- forms. The final energy for D-form is −2764.39028558 Hartree while for L form, −2764.38826472 Hartree. This means D-form is energetically preferred to L-form by 1.27 kcal/mol in agreement with experimental results. The main difference between D and L complexes are the number of H—bonds as depicted in Fig. 4. Two H—bonds connected to negatively charged carboxylate group exist for both complexes. However, for D-form, additional H—bonding is available, i.e., the distance of H···O is 2.34 Å, and angle of N—H···O is 151°. This H—bond is broken in L-form, i.e., the distance of H···O is 4.954 Å which is out of normal H—bonding distance. Because the difference is only chirality of alanine, the difference should come from the methyl group attached to chiral carbon of alanine. The C···C distance (depicted in yellow) is 6.74 Å for D-form, becomes 4.95 Å for L-form and this is close to steric contact. In other words, it appears to be that this steric repulsion between two methyl groups is responsible for breaking the H—bond.

^{1}H NMR titration method is limited when the host and guest associate strongly [56]. This limitation can be overcome by the incorporation of fluorescent chromophores into the host due to their high sensitivity and low detection limit [60–64]. Therefore, to enlarge the scope of the receptor **2** as a fluorescent sensor, we designed fluorescent receptor **7**, which has fluorescent naphthalene moieties instead of the phenyl groups [65]. The naphthalene receptor **7** displayed strong fluorescence emission in acetonitrile. The excitation and emission wavelength were 242 nm and 350 nm respectively. The intensity of emission spectrum from 10 μM solution of the naphthalene receptor **7** decreased as the concentration of tetrabutylammonium halides salts was increased, which indicates the association between the receptor **7** and halides. The linearity of Stern-Volmer plot further confirms the formation of one type complex between receptor **7** and halide. The stoichiometry between host and guest was determined by fluorescence Job plot, which showed evident 1:1 stoichiometry. A Benesi-Hildebrand plot [66] by use of change in the 350 nm fluorescence intensity gave association constants. The receptor **7** showed the highest association constant $1.2 \times 10^5 \pm 1.4 \times 10^4\,M^{-1}$ for bromide. The order of association constants was $Br^- > Cl^- > F^- > I^-$ From the ^{1}H NMR experiments in DMSO-d_6, the receptor **7** showed the highest affinity for bromide again. The results are summarized in Table III. The preference for bromide suggests that the cavity formed by four amide bonds is more complementary to the size of the bromide ion than to the size of other halide ion. We proposed that four naphthalenes in receptor **7** would form larger cavity than the cavity formed from four benzenes in receptor **2** as naphthalene is larger than benzene. Therefore, the cavity in receptor **7** fits well to

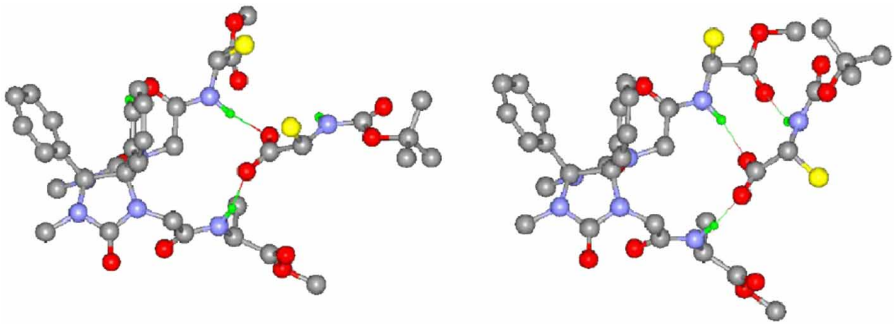


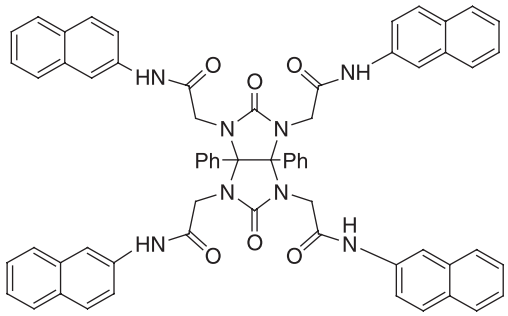
FIGURE 4 Comparison of both L- and D- complexes with N-Boc-Ala-COO^- Hydrogen atoms attached to carbons are omitted for clarity. The yellow spheres are methyl groups seemingly responsible for chiral recognition.

TABLE III Association constants (M^{-1}) of receptor **7** with tetrabutylammonium anions in acetonitrile from fluorescence titration. The numbers in parenthesis are association constants in DMSO-d_6 from ^{1}H NMR titration

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

[†] Errors in K_a are estimated to be less than 20%. [‡] Errors in K_a are estimated to be less than 10%.

the size of bromide while the size of cavity in receptor **2** fits to the size of fluoride.



7

Hydrogen bond between C(2)-H in imidazolium rings and guest anion is currently accepted as an important anion binding interaction [67]. To develop a new imidazolium group based anion receptor, we have designed the receptor **8**, which utilizes glycoluril as a molecular scaffold for four imidazolium groups [68]. In this receptor, four imidazolium groups are arranged at the corner of the glycoluril. The complexation ability of the receptor **8** was measured by standard ^{1}H NMR titration experiments in 10% DMSO-d_6 in CD_3CN. We expected that the four C(2)-H in imidazolium rings attached at the corner of glycoluril would form a cavity and point to the anion located at the center of concave structure of glycoluril. The shape and size of cavity seemed to be suitable for spherical halide ions. Therefore, we expected 1:1 binding with halides. However, the Job plot experiments showed 1:2 binding stoichiometry for chloride. The association constant calculated from the chemical shift change of C(2)-H of imidazolium ring was $1.5 \times 10^6 \pm 1.2 \times 10^3\,M^{-2}$ ($\beta_2 = K_1K_2$). Job plot for other halides also showed 1:2 stoichiometry irrespective of size of halides. The association constants ($\beta_2 = K_1K_2$) were summarized in Table IV.

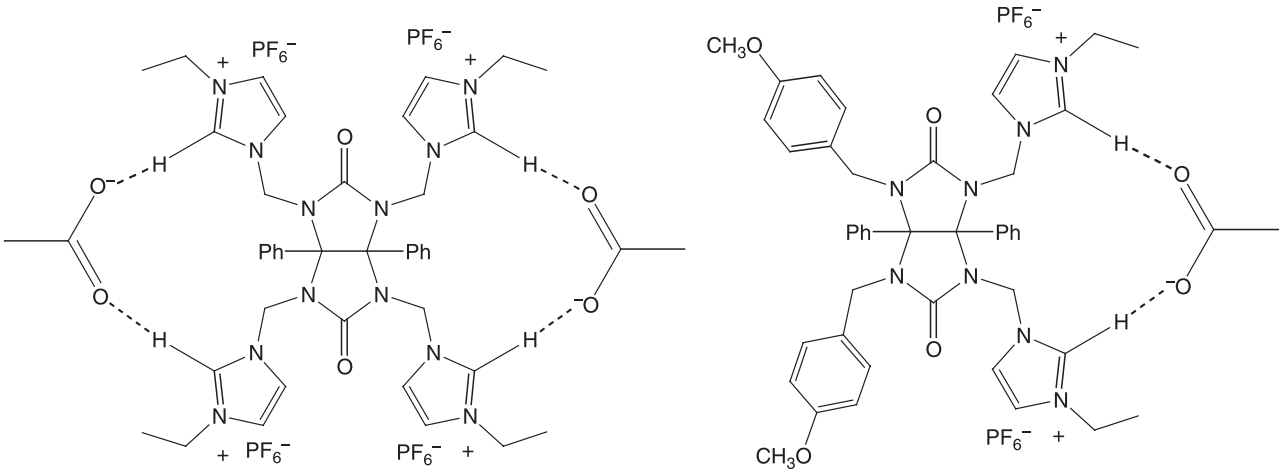
Even though the receptor **8** has enough space to capture halide inside the cavity which is made of four imidazolium rings, the receptor **8** binds halides only 1:2 fashion. The receptor **8** does not seem to like to locate four imidazolium rings closely. Each imidazolium ring has +1 positive charge. When they are located closely to bind with one halide ion, +3 positive charges exist in small area. Therefore, we propose that the receptor **8** chooses to bind halides in 1:2 stoichiometry due to the repulsion of these positive charges. This phenomenon extends to acetate. The binding of acetate was strong enough that the binding curve and Job plot clearly demonstrated the 1:2 stoichiometry of the complex. The association constant was $2.9 \times 10^6 \pm 8.7 \times 10^4\,M^{-2}$ ($\beta_2 = K_1K_2$). As the receptor **8** formed 1:2 complex with acetate, we investigated the binding of dicarboxylate with the receptor **8**. Succinate and glutarate showed 1:1 stoichiometry. The association constants in 10% DMSO-d_6 in CD_3CN were calculated $1.8 \times 10^3 \pm 72\,M^{-1}$ for succinate and $2.7 \times 10^3 \pm 112\,M^{-1}$ for glutarate.

Although the receptor **8** showed relatively high affinities for chloride and acetate among the anions we investigated, the association constants for the 1:1 binding could not be calculated. Therefore, we synthesized the receptor **9**. In this receptor, two 1,3-disubstituted imidazolium groups are arranged only at the one side of glycoluril and the receptor **9** would bind various anions in 1:1 stoichiometry. The complexation ability of the receptor **9** was measured by standard ^{1}H NMR titration experiments in 10% DMSO-d_6 in CD_3CN. In case of chloride ion, C(2) protons originally resonating at 8.80 was shifted to 10.00 upon addition of about one equivalent of chloride ion, which indicates 1:1 binding. The association constant was calculated as

TABLE IV Association constants of **8** and **9** for the tetrabutylammonium anions in 10% DMSO-d_6 in CD_3CN

Anions	**8**	**9**
F^-	$1.8 \times 10^6 \pm 4.6 \times 10^4$ [†]	–
Cl^-	$1.5 \times 10^6 \pm 1.2 \times 10^3$ [†]	$3.7 \times 10^4 \pm 6.6 \times 10^3$
Br^-	$4.8 \times 10^5 \pm 1.1 \times 10^4$ [†]	$1.6 \times 10^3 \pm 1.5 \times 10^2$
I^-	$3.1 \times 10^5 \pm 4.6 \times 10^4$ [†]	$1.8 \times 10^2 \pm 9.6$
$CH_3CO_2^-$	$2.9 \times 10^6 \pm 8.7 \times 10^4$ [†]	$>10^5$
$^-O_2C(CH_2)_2CO_2^-$	$1.8 \times 10^3 \pm 72$	–
$^-O_2C(CH_2)_3CO_2^-$	$2.7 \times 10^3 \pm 112$	–

[†] $\beta_2 = K_1K_2(M^{-2})$ * M^{-1}.



8 **9**

FIGURE 5 The possible binding mode of the receptor **8** and **9** with acetate.

$3.7 \times 10^4 \pm 6.6 \times 10^3\,M^{-1}$ The association constants between other halides and receptor **9** were also summarized in Table IV. For the receptor **9**, about 200 fold selectivity for chloride over iodide was observed. In addition, the receptor **9** showed high affinity for Y-shaped anions such as acetate and benzoate. The association constants calculated for both acetate and benzoate exceeded 10^5, which is too large to accept as reliable association constant from ^1H NMR titration experiments. The association constants of acetate and benzoate could be only assessed that they are bigger than 10^5. The possible binding mode of the receptor **9** and acetate is shown in Fig. 5. The binding of receptor **9** to the Y-shaped carboxylate reminds us of the binding of the receptor **2** to the Y-shaped carboxylates (Fig. 2). Hydrogen bonding moieties arranged at the one side of glycoluril are preorganized for the Y-shaped carboxylate anions.

In conclusion, we have synthesized various anion receptors with glycoluril molecular scaffold. The association of the glycoluril molecular scaffold based receptors with various anions reflects the shape, size and basicity of anions. More structural variation of the glycoluril molecular scaffold receptors would open up more possibilities to design a new anion receptor and ditopic receptors. We are currently investigating this possibility.

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