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Crown ether-appended calix[2]triazolium[2]arene as a macrocyclic receptor for the recognition of H_2PO_4^- anion†

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A crown ether-appended calix[2]triazolium[2]arene, which exhibits excellent selectivity for H_2PO_4^- compared to other anions, has been designed and synthesized. The selectivity of the prepared receptor for H_2PO_4^- is caused by the stabilization of H_2PO_4^- by the neighboring triazolium hydrogen bond donors and crown ether hydrogen bond acceptors.

The development of novel types of receptors for the selective recognition of anionic substrates has received considerable attention in recent years.¹ Anions are omnipresent in the natural world and important in a broad range of chemical and biological processes. Among various anions, phosphate is essential to all lifeforms, because it serves as a building block of bones and genetic materials and plays a pivotal role in metabolic and signal transduction pathways.² Therefore, the recognition of phosphates is particularly important and several receptors for phosphates have recently been reported.³ Inorganic phosphate consists predominantly of a mixture of H_2PO_4^- and HPO_4^{2-} at physiological pH. Unlike most other important biological anions, phosphate is capable of being both a hydrogen bond donor and acceptor. In nature, phosphate-binding proteins utilize this characteristic for recognition of phosphate.⁴ However, there are only a few artificial receptors which take advantage of dual hydrogen-bonding properties to selectively recognize phosphate in the form of dihydrogen phosphate (H_2PO_4^-).⁵

Macrocyclic structures have been widely used as a basic molecular scaffold for the anion receptors due to their intrinsic rigidity and preorganization.⁶ We have recently developed the macrocyclic calix[2]triazole[2]arene (**1**, Scheme 1), and showed

that the incorporated 1,2,3-triazole moiety was involved in the interaction with specific ions.⁷

The 1,2,3-triazole can act both as a hydrogen-bond donor as well as an acceptor. The triazole nitrogen atoms have hydrogen-bond-accepting properties, whereas the C5-H is sufficiently polarized to interact with the anion through hydrogen bonding.⁸ Furthermore, the hydrogen bond donor ability of the 1,2,3-triazole can be improved by converting it to a triazolium ring. A number of types of triazolium-based anion receptors have been developed recently.⁹ However, most triazolium-based phosphate receptors are limited to acyclic systems.¹⁰ To the best of our knowledge, the only macrocyclic triazolium-based receptor for phosphate recognition is the pyrrole-based triazolium-phane¹¹ developed by the Sessler group, which exhibits a high selectivity for tetrahedral oxyanions such as pyrophosphate and sulfate, relative to monoanions and trigonal planar anion in a mixed polar organic-aqueous media.

Due to the presence of Lewis basic oxygen atoms, crown ether molecules can form supramolecular complexes with various protonated guests by acting as a hydrogen-bond acceptor, in addition to binding metal cations by forming ion-dipole bonds. The rich properties of crown ethers have been used to design sensors and receptors for cationic substances.¹² However, they have yet to be extensively used in anion recognition chemistry.¹³

We envisioned that the conjunction of a crown ether with the calix[2]triazole[2]arene **1** scaffold would yield the selective recognition of phosphate ions. Thus, we designed and synthesized crown ether incorporated calix[2]triazole[2]arenes **2–4** and the corresponding calix[2]triazolium[2]arenes **5–7** (Scheme 1). A notable feature of these macrocyclic structures is that they contain both the hydrogen bond donor and acceptor functions. The size of the cavity was modulated by changing the number of repeating ethyleneoxy units. Herein, we report that crown ether incorporated calix[2]triazolium[2]arene **7** exhibits excellent selectivity for H_2PO_4^- over other anions. Based on theoretical calculations and NMR studies conducted in this investigation, we proposed that the H_2PO_4^- recognition is

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acquired *via* a combination of hydrogen bond donor ability of the 1,2,3-triazolium motif and the hydrogen bond acceptor ability of the crown ether unit. To the best of our knowledge, this is the first report on a macrocyclic triazolium-based receptor showing selective recognition for H_2PO_4^- with the aid of a crown ether unit. The results presented here would serve to underscore the benefits of conjunction of hydrogen bond donor and acceptor subunits to efficiently recognize anions.

Scheme 1 Synthesis of crown ether containing calix[2]triazole[2]arenes **2–4**, calix[2]triazolium[2]arenes **5–7** and alkyl chain containing calix[2]triazolium[2]arene **9**.

The synthesis of crown ether appended calix[2]triazole[2]arenes **2–4** and calix[2]triazolium[2]arenes **5–7** is depicted in Scheme 1. Calixtriazole crown ethers **2–4** were synthesized by reacting **1** with tetra-, penta- or hexaethylene glycol ditosylate, respectively, in the presence of Cs_2CO_3 in DMF. The conformation of **2–4** was confirmed by X-ray crystal structures to have a 1,3-alternate conformation,^{7a} where the phenolic oxygen atoms and triazole protons are on the same side of the annulus (Fig. S1–S3 and Table S1–S3, ESI[†]). Calixtriazolium crown ethers **5–7** were obtained *via* methylation of **2–4** with $(\text{Me}_3\text{O})^+\text{BF}_4^-$. The conformation of triazolium crown ethers **5–7** were elucidated by NOESY spectral analysis. NOESY correlations indicated that receptors **5–7** also have a 1,3-alternate conformation (Fig. S6–S8, ESI[†]). The single crystal structure of receptor **7**, which was grown slowly in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at room temperature, also revealed a 1,3-alternate conformation (Fig. S4 and Table S4, ESI[†]). However, one triazolium ring is more flattened, somewhat different from the 1,3-alternate conformation predicted in the solution. This conformation might result from intermolecular hydrogen bonding and crystal packing forces (Fig. S5, ESI[†]). In addition, to determine the role of the ethyleneoxy unit in the receptor for anion binding, the corresponding alkyl chain appended calixtriazole **8** and calixtriazolium **9** were also prepared as controls. The 1,3-alternate conformation of **8** and **9** was confirmed by NOESY analysis (Fig. S9 and S10, ESI[†]).

In the ^1H NMR spectra (CD_3CN), all triazolium crown ethers **5–7** displayed one singlet peak for both triazolium hydrogen atoms (H_d), methyl and *tert*-butyl signals, respectively, which indicates the symmetry of the molecules (Fig. S11, ESI[†]). And the eight methylene protons (H_c , $\text{H}_{c'}$, H_e and $\text{H}_{e'}$) appear as two pairs of AB doublets, which typically occurs when two opposing phenyl rings of calix[2]triazole[2]arene adopt a *syn* orientation.^{7a}

Initially, the anion recognition abilities of triazole crown ether **4** with various anions (F^- , Cl^- , Br^- , I^- , H_2PO_4^- , NO_3^- , HSO_4^- and OAc^- (10 equiv)) as their tetrabutylammonium salts were investigated by ^1H NMR in CD_3CN (Fig. S12, ESI[†]). No changes were observed after the addition of these anions, indicating no hydrogen bonding between anions and triazole CH. Likewise, triazolium crown ethers **5–7** also showed no such chemical shift changes in the ^1H NMR spectra in the presence of most tested anions. However, the changes of ^1H NMR spectra induced by F^- and H_2PO_4^- were significant (Fig. 1 and S13, ESI[†]). The chemical shift patterns for F^- and H_2PO_4^- were very different.

Fig. 1 ^1H NMR spectra of triazolium crown ether **7** (1 mM) in CD_3CN in the presence of various tested anions (F^- , Cl^- , Br^- , I^- , H_2PO_4^- , NO_3^- , HSO_4^- and OAc^- (10 equiv)). The positions of the labeled protons are marked in Scheme 1.

Upon gradual addition of F^- to triazolium crown ethers **5–7**, the triazolium protons (H_d) shifted downfield slightly, with decreasing peak intensity, and finally disappeared (Fig. S14, ESI[†]). Due to the high charge density and basicity, F^- initially forms hydrogen bonds with C5-H of the triazolium and then causes deprotonation of triazolium protons when an excess of F^- was added.¹⁴ In addition, the color of **5–7** changed from clear to yellow-orange during the addition of F^- . With the change of the triazolium signal, two pairs of AB doublets of the eight methylene protons (H_c , $\text{H}_{c'}$, H_e and $\text{H}_{e'}$) gradually merged which implies a conformational change of the receptor framework.^{7a,15} This conformational change is presumably caused by a change in the intramolecular hydrogen bonding environment of the receptor due to the deprotonation of the triazolium protons.¹⁶

In order to understand the binding features **5–7** with H_2PO_4^- ion, ^1H NMR based titration experiments were carried out (Fig. 2 and S15, ESI[†]). In all three triazolium crown ethers (**5–7**), the addition of H_2PO_4^- resulted in downfield shifts of the triazolium protons (H_d), methylene protons ($\text{H}_{c'}$, $\text{H}_{e'}$ and H_e) and crown ether protons (H_f and H_g). In contrast, the aromatic protons of the phenyl rings (H_a and H_b) and the methylene protons (H_c) showed only slight chemical shift changes. As a representative example, the ^1H NMR spectra of **7** in the presence of increasing amounts of H_2PO_4^- is shown in Fig. 2. Upon gradual addition of H_2PO_4^- , the triazolium protons (H_d) and methylene protons in the lower-rim direction ($\text{H}_{c'}$ and $\text{H}_{e'}$) exhibited a significant downfield shift, with $\Delta\delta = 0.55$, 0.39 and 0.30 ppm, respectively. The methylene proton signal in the upper-rim (H_e) also moved downfield ($\Delta\delta = 0.08$ ppm). These downfield shifts suggest a

close proximity to H_2PO_4^- and the participation of these groups in H_2PO_4^- binding. The protons of crown ether (H_f and H_g) also exhibited a downfield shift ($\Delta\delta = 0.29$ and 0.15 ppm), which is caused by the deshielding of these methylene protons due to hydrogen bonding interactions between the crown ether and H_2PO_4^- .¹⁷ In contrast, the aromatic protons of the phenyl rings (H_a and H_b) and the methylene protons in the upper-rim (H_c) displayed only negligible changes in chemical shift. Thus triazolium crown ether **7** is directly involved in the recognition of H_2PO_4^- and H_2PO_4^- is well located in the binding pocket of **7**. In addition, unlike triazolium crown ether **7**, the ^1H NMR titration of triazole crown ether **4** with H_2PO_4^- showed no change in ^1H NMR peaks including triazole protons (Fig. S16, ESI[†]). This indirectly demonstrates that hydrogen bonding by triazolium plays a key role in the recognition of H_2PO_4^- .

Fig. 2 ^1H NMR spectra of **7** (1 mM) in CD_3CN recorded in the presence of increasing concentrations of H_2PO_4^- anion. The positions of the labelled protons are marked in Scheme 1.

^{31}P NMR was used to further confirm the interaction between **7** and H_2PO_4^- (Fig. S17, ESI[†]). The phosphate signal at -1.02 ppm was shifted downfield by 0.23 ppm in the presence of **7**, confirming the binding of the H_2PO_4^- ion with **7**.

The binding stoichiometry of the triazolium crown ether **7**- H_2PO_4^- complex was determined by a ^1H NMR Job's plot at 1 mM. The plot showed a maximum value at the 0.4 mole fraction of **7**, indicating that $1 : 1$ and $1 : 2$ complexes of **7** and H_2PO_4^- coexisted in solution (Fig. S20 and S21). The coexistence of these two complexes may be explained by the dimerization of H_2PO_4^- ¹⁸ or may be resulting from an inherent limitation of the Job's plot method for host-guest complexes.¹⁹ We thus directly assessed three different binding models corresponding to different ratios of host : guest ($1 : 1$, $1 : 2$ or $2 : 1$) using BindFit.²⁰ The $1 : 2$ and $2 : 1$ binding models provided poor fitting results (Fig. S22–24, ESI[†]). In contrast, when a $1 : 1$ binding model was assumed, a good fit was obtained (Fig. S25, ESI[†]), with an association constant of $2971.88 \pm 887 \text{ M}^{-1}$ (Table S5). Additionally, the binding stoichiometry was analysed by a Job's plot using a UV-vis titration at a lower concentration ($10 \mu\text{M}$). Unlike the Job's plot from the ^1H NMR titration, the maximum appeared at the 0.5 mole fraction (Fig. S26 and S27, ESI[†]). An association constant of **7** for H_2PO_4^- was calculated to be $2051.50 \pm 145 \text{ M}^{-1}$ (Fig. S28 and S29, ESI[†]), which correlates well with the ^1H NMR titration data. In addition, the UV-vis limit of

detection (LOD) of **7** for H_2PO_4^- was calculated to be $4.35 \mu\text{M}$ (Fig. S30, ESI[†]).

In order to demonstrate the hydrogen bonding between H_2PO_4^- and the oxygen atom of the crown ether ($\text{P-OH} \cdots \text{O-CH}_2$), the binding capacity of control **9** with H_2PO_4^- was investigated through a ^1H NMR experiment (Fig. S18, ESI[†]). Upon gradual addition of H_2PO_4^- to **9**, unlike triazolium crown ethers **5–7**, the triazolium protons (H_d) migrated upfield and two pairs of AB doublets of eight methylene protons (H_c , H_c' , H_e and H_e') merged gradually. The upfield shift of triazolium protons represents an anion- π interaction,²¹ not triazolium $\text{CH} \cdots$ anion hydrogen bonding, between H_2PO_4^- and electron-deficient triazolium rings and the merging of methylene protons represents a conformational change of **9**. This results demonstrate that crown ether oxygens have a significant effect on the formation of hydrogen bonding between triazolium CH and H_2PO_4^- in the binding pocket of the receptor.

It was observed that the sensitivity of **5–7** towards H_2PO_4^- was increased as the crown ether chain length was increased. When 1 equiv of H_2PO_4^- was added to **7**, the protons of the triazolium-, methylene- and crown ether-moieties in **7** shifted downfield (Fig. 2 and S19, ESI[†]). However, **5** and **6**, with a shorter crown ether chain, did not exhibit any ^1H NMR spectrum changes. This indicates that the strength of H_2PO_4^- stabilization increases with increasing crown ether length. The increased size of the crown ether enabled the recognition of H_2PO_4^- having a larger size and complex tetrahedral shape compared to other anions through an induced-fit recognition mechanism.²²

We also conducted DFT calculations to gain insight into the binding interactions between the calix[2]triazolium[2]arenes and H_2PO_4^- . The geometries of **7** (Fig. S31, ESI[†]) and the **7**- H_2PO_4^- complex were optimized and revealed a tight fit for H_2PO_4^- , showing electrostatic interactions between the triazolium protons (H_d) and the phosphate oxygens with a distance of 1.99 and $2.15 \text{ \AA}$, while the binding is further stabilized by two hydrogen bonds with crown ether oxygens, with intermolecular O-H bond distances of 1.78 and $1.79 \text{ \AA}$ (Fig. 3 and S32, ESI[†]). As is apparent from this structure, the absence of hydrogen bonding in **9** or triazolium based charge interactions in **4** would severely weaken the interactions, to the extent of precluding such an interaction, as is apparent from the ^1H NMR titration experiments. Furthermore, the shorter crown ethers of **5** and **6** would also lead to a non-ideal binding geometry, thus rationalizing the smaller ^1H NMR response for these receptors in Fig. S15 and S19, ESI[†].

The DFT optimized structures were used to simulate the NMR spectra to validate the proposed binding mode of **7**- H_2PO_4^- (Fig. S33, ESI[†]). The general tendencies in the simulated ^1H NMR spectra of **7** and **7**- H_2PO_4^- complex are in good agreement with experimentally obtained spectra except that the methylene protons (H_e and H_e') in **7**- H_2PO_4^- are shifted upfield compared to **7**. The simulated triazolium protons (H_d), methylene protons (H_c) and the crown ether protons (H_f and H_g) of **7** in the presence of H_2PO_4^- , as in the experimentally obtained spectra, were downfield shifted from 8.97 to 10.99 ppm ($\Delta\delta = 2.02$ ppm), 5.75 to 5.86 ppm ($\Delta\delta = 0.11$ ppm), 4.34 to 4.66 ppm ($\Delta\delta = 0.32$ ppm) and 4.01 to 4.52 ppm ($\Delta\delta = 0.51$ ppm), respectively. This

tendency of the simulated NMR chemical shifts and their agreement with the experimental values further supports the calculated binding mode as shown in Fig. 3.

Fig. 3 Ball and stick model of DFT-optimized structure of $7\text{-H}_2\text{PO}_4^-$ at the CAM-B3LYP/6-31+G(d,p) level of theory in acetonitrile. Intermolecular interactions shown in green dotted lines and the numerical values in the structure are the hydrogen bond distances in Å.

In summary, we have successfully synthesized a calix[2]triazolium[2]arene bearing crown ether moiety that selectively recognizes the H_2PO_4^- anion. A 1,3-alternate conformation of the receptor was confirmed by NOESY spectral analysis and X-ray crystal structures. The selectivity of the receptor for H_2PO_4^- results from the perfect harmony of the triazolium hydrogen bond donors and the crown ether hydrogen bond acceptors within the receptor's framework. In addition, the sensitivity of the receptor to H_2PO_4^- can be controlled by the size of the appended crown ether and **7**, bearing the longest crown ether chain, has the highest sensitivity to H_2PO_4^- . The selective and sensitive recognition ability of **5–7** for H_2PO_4^- was confirmed by the downfield shift of triazolium protons, methylene protons in the lower-rim direction and crown ether signals on ^1H NMR. Density Functional Theory (DFT) based theoretical calculations also confirmed that the receptor provides both hydrogen bond donors and acceptors to bind the H_2PO_4^- in its cavity. These findings will provide important information for designing more sophisticated receptors for the effective recognition of phosphates and their derivatives in the future.

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Conflicts of interest

There are no conflicts to declare.

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