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# A Molecular Lock and Key: "Unlocked–Locked" Conformational Switching of a Receptor by Anions

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The design of molecular devices with molecular recognition functionality and signal transduction ability has gained considerable attention in the fields of chemistry,<sup>[1]</sup> biology,<sup>[2]</sup> and sensors.<sup>[3]</sup> The importance and significance in this regard are the receptors that detect anions,<sup>[4]</sup> in particular, phosphate ions that play a crucial role in many physiological processes. In recent years, several synthetic receptors containing amine, amide,<sup>[5]</sup> urea,<sup>[6]</sup> thiourea,<sup>[7]</sup> pyrrole,<sup>[8]</sup> and pyridine moieties as well as metal-assisted organic frameworks<sup>[9]</sup> bearing multiple binding sites have been reported for sensing of phosphate ions in solution. In such cases, detection was observed through changes in UV/Vis spectra, <sup>1</sup>H NMR chemical shifts, luminescence spectroscopy patterns, and the binding modes which were determined through experimental result supported by optimization calculations at different levels of theory.<sup>[10]</sup> However, single-crystal X-ray analysis of phosphate-ion-bound receptors are very rare owing to the tetrahedral structure of the dihydrogenphosphate ion which creates problems for effective binding with tailored hydrogen-bonded, donor-acceptor receptors.<sup>[11]</sup>

Herein, we demonstrate a conceptually new molecular device ("molecular lock") that acts as a selective  $H_2PO_4^-$  receptor. The dihydrogenphosphate ion ("key") can lock the molecular free rotation of the fluorophoric unit of receptor **1** ("molecular lock"), as evidenced by single-crystal X-ray analysis. The restriction of free rotation results in the enhancement of fluorescent intensity of **1** in CH<sub>3</sub>CN solution. On the other hand,  $HSO_4^-$  ("key") forms a hydrogen-bonded complex ("unlocked" conformation of the "molecular lock") as evidenced by single-crystal X-ray analysis and the fluorescent intensity of **1** which did not change remarkably.

Receptor 1 was synthesized by reduction of the Schiff base 2, which was prepared from imidazo[1,2-*a*]pyridine-2-carboxaldehyde 4 and 1,2-diamino-4-nitrobenzene 3 (Scheme 1). Compound 1 was characterized by <sup>1</sup>H NMR spectroscopy, IR analysis, and mass spectrometry (see Figure S1–S4 in the Supporting

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Scheme 1. Top: "Unlocked–locked" conformational switching; bottom: synthetic approach to give receptor 1.

Information). The structure of receptor 1 and its complex with  $H_2PO_4^-$  and  $HSO_4^-$  were determined by X-ray crystal structure analysis. The anion recognition capability and binding affinity of 1 were studied by absorption and emission spectroscopic changes in the presence of various anions such as  $F^-$ ,  $H_2PO_4^-$ ,  $AcO^-$ ,  $NO_3^-$ ,  $CIO_4^-$ ,  $CI^-$ ,  $Br^-$ ,  $I^-$ , and  $HSO_4^-$  in  $CH_3CN$  medium.

Receptor **1** crystallized in the  $P\bar{1}$  space group and comprised two molecular units and one water molecule (see Figure 1, and Figure S5 and Table S1 in the Supporting Information).<sup>[12]</sup> The



Figure 1. Crystal structure of 1 "molecular lock" with a water molecule. Green C, white H, blue N, red O.

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structure of "molecular lock" 1 is really interesting because the o-phenylenediamine and imidazo[1,2-a]pyridine moieties are twisted by an angle of approximately 76.38 ° from one another and it forms a stable conformer where, the nitrogen atom of the amino group and nitrogen atom of the imidazo group are orthogonal to each other and form intermolecular hydrogen bonds. As shown in Figure 1, two different orientations of each molecular unit are connected by two different types of intermolecular hydrogen bonds, namely; 1) through direct intermolecular hydrogen bonding where N6 and N7 of one molecular unit act as hydrogen donors and N1 of the other molecular unit acts as a hydrogen acceptor (bond lengths are: N7---N1 3.043 Å and N6--N1 3.202 Å),<sup>[13]</sup> and 2) through water-assisted intermolecular hydrogen bonding where the water molecule (O1) is located in between N2 and N3 of the o-phenylenediamine moiety and N5 of the imidazo[1,2-a]pyridine moiety and thus forms strong hydrogen-bonding interactions (bond lengths are: N3--O1 2.918 Å, N2--O1 3.022 Å, and N5--O1 2.738 Å; Table S2). These intermolecular hydrogen bonds bring two imidazo[1,2-a]pyridine moieties and two o-phenylenediamine rings in close proximity and form a  $\pi$ - $\pi$  stacking interaction within distances of 3.69(2) Å and 4.07(3) Å, respectively.

The crystal packing diagram shows that the O1 atom of the water molecule (Figure 1) is already involved in hydrogenbonding interactions with N2, N3, and N5 of dimeric 1 and has formed a one-dimensional supramolecular polymer network through hydrogen-bonding interactions with the O4 atom (belonging to NO<sub>2</sub>) of the next dimeric unit (2.971 Å; Figure S6).

This suitable arrangement of "molecular lock" **1** has been exploited by  $H_2PO_4^-$  ("key") as a result it can easily lock the molecular device through hydrogen-bonding interactions. The X-ray crystal structure of the  $1 \cdot H_2PO_4^-$  complex (Figure 2 and Figure S7) shows that the dihydrogenphosphate ion reinforces the N3 atom of the imidazo[1,2-*a*]pyridine moiety pointing unidirectionally with respect to the N1 and N2 atoms of the amine group. As a result, the O3 and O5 atoms of  $H_2PO_4^-$  form hydrogen-bonding interactions with the N3, N1, and N2 atoms of **1** (bond lengths are: N3···O5 2.691 Å, N1···O3 2.784 Å, and N2···O3 2.858 Å; Table S3). Thus, hydrogen-bonding interactions restrict the free rotation of receptor **1**; namely,  $H_2PO_4^-$  ("key") locks the bending conformation of receptor **1** due to simulta-



Figure 2. Crystal structure of  $1 \cdot H_2 P O_4^-$  in a "locked" conformation. Tetrabuty-lammonium cations are omitted for clarity. Green C, white H, blue N, red O, orange P.

neous hydrogen-bonding between  $H_2PO_4^-$  and two amine nitrogen atoms (N1, N2) as well as one imidazo[1,2-*a*]pyridine nitrogen atom (N3).

The lattice diagram shows that receptor **1** undergoes dimer formation with the help of a water molecule and  $H_2PO_4^-$  (Figure 3). Interestingly, the O1 atom of the water molecule is already involved in hydrogen-bonding interactions with



Figure 3. Dimeric crystal structure of  $1\mbox{-}H_2PO_4^-$  complex. Tetrabutylammonium cations are omitted for clarity. Green C, white H, blue N, red O, orange P, yellow S.

 $H_2PO_4^{-}$ , which is also involved in dimer formation through a hydrogen-bonding interaction with the O5 atom of the nearest  $H_2PO_4^-$  (bond length is: 2.873 Å). Meanwhile, the O2 atom of the  $H_2PO_4^-$  ion interacts with the O4 atom of another  $H_2PO_4^$ ion through a hydrogen-bonding interaction (bond length is: 2.613 Å) and forms the  $\{(H_2O)_2, (H_2PO_4^{-})_2\}$  cluster. Furthermore, one dimeric unit containing a water molecule (O1) is hydrogen-bonded with the N1 atom of another dimeric unit containing o-phenylenediamine and vice versa to generate a one-dimensional hydrogen-bonded channel consisting of water-dihydrogenphosphate (see Figure S8 in the Supporting Information). The one-dimensional supramolecular structure is further stabilized through  $\pi$ - $\pi$  interactions of the imidazo[1,2-*a*]pyridine ring (distance is: 3.365 Å; Figure S9) and hydrogen-bonding interactions with another one-dimensional channel to build up a two-dimensional supramolecular water-dihydrogenphosphate architecture (Figure S10).

On the other hand, the crystal structure of 1-HSO<sub>4</sub><sup>-</sup> shows that the O1 atom of HSO<sub>4</sub><sup>-</sup> is hydrogen bonded with only two amine nitrogen atoms (N1, N2) of **1** (bond lengths are: N1···O1 2.945 Å and N2···O1 2.954 Å; Figure 4, Figure S11) and interestingly, the N3 atom of the imidazo[1,2-*a*]pyridine moiety is hydrogen bonded with the O2 atom of the next hydrogensulfate ion. This structure is completely different from the structure of the **1**·H<sub>2</sub>PO<sub>4</sub><sup>-</sup> complex (bond length is: N3···O2 2.700 Å; Figure 5). Furthermore, the lattice diagram shows that the N1 atom of one molecular unit is hydrogen bonded with the O4 atom of another HSO<sub>4</sub><sup>-</sup> and forms a one-dimensional, hydrogen-bonded bisulfate channel (Figure S12). Thus, hydrogen-bonding interactions between HSO<sub>4</sub><sup>-</sup> and receptor **1** lead an "unlocked" conformation even though the geometries of the H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> ions are quite similar.

The binding nature of 1 with anions was investigated with the help of UV/Vis titrations in  $CH_3CN$  solvent. Receptor 1 has



**Figure 4.** Crystal structure of  $1 \cdot \text{HSO}_4^-$  in an "unlocked" conformation. Tetrabutylammonium cations are omitted for clarity. Green C, white H, blue N, red O, yellow S, orange P.



**Figure 5.** Dimeric crystal structure of  $1 \cdot HSO_4^-$  hydrogen-bonded complex. Tetrabutylammonium cations are omitted for clarity. Green C, white H, blue N, red O, yellow S, orange P.

absorption bands at 312 nm and 405 nm (Figure 6). Upon addition of an increasing amount of  $H_2PO_4^-$ , the band at 405 nm was gradually red-shifted to 415 nm. The Benesi–Hildebrand (BH) plot<sup>[14]</sup> of  $1/[A-A_0]$  versus  $1/[H_2PO_4^-]$  for the titration of 1 and  $H_2PO_4^-$  exhibits a straight line (inset of Figure 6), thus indicating that a 1:1 complex was formed with an association constant of  $K=2.8\times10^2$  m<sup>-1</sup>. A similar kind of spectral change for 1 was observed in the presence of HSO<sub>4</sub><sup>-</sup> and AcO<sup>-</sup>. Furthermore, in the presence of other competitive anions (such as NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and l<sup>-</sup>) receptor 1 remains almost unchanged, thus indicating an absence of interaction or complexation between these anions with the receptor (see Figure S13).



**Figure 6.** UV/Vis spectroscopic changes of 1 (1 mM) upon addition of  $H_2PO_4^-$  ion (0–2 equiv) in CH<sub>3</sub>CN solution. Inset: the BH plot for the titration of 1 with  $H_2PO_4^-$  anion.

However, upon addition of the highly basic  $F^-$ , a new absorption peak at 450 nm was observed (Figure S13), and this peak might correspond to deprotonation of NH<sub>2</sub> rather than hydrogen-bonding interaction.<sup>[15]</sup> Deprotonation of the amino group increases the electron density on the nitrogen atom (donor), which undergoes an internal charge transfer (ICT) to an electron-withdrawing nitro group (acceptor) and therefore is the cause of the spectral bathochromic shift. Similar types of spectral change were observed when [Bu<sub>4</sub>N]OH was added, and this supports our assumption of deprotonation and ICT phenomena in the case of  $F^-$ .

To investigate the selectivity and excited-state phenomena of receptor **1** towards the anions, we performed steady-state fluorescence experiments in CH<sub>3</sub>CN solvent. Upon excitation at 312 nm, receptor **1** exhibits an emission maximum at 375 nm. A remarkable fluorescence enhancement of receptor **1** at 375 nm was observed with the addition of an increasing concentration of  $H_2PO_4^-$  (Figure 7). This enhancement of fluorescence intensity may be attributed to the conformational freez-



Figure 7. Emission spectroscopic changes of 1 (0.5 mm) upon addition of  $H_2PO_4^-$  ion (0–2 equiv) in CH<sub>3</sub>CN solution.

ing ("locked") and hindering of free rotation ("unlocked") of the fluorophoric unit (imidazo[1,2-*a*]pyridine moiety) upon complexation with  $H_2PO_4^-$ . The conformation restriction ("locked") that occurs through hydrogen-bonding interactions was confirmed by single-crystal X-ray analysis. The fluorescence titration of receptor 1 with  $H_2PO_4^-$  also indicates a 1:1 complexation (Figure S14) with an association constant  $K=0.7 \times$  $10^2 M^{-1.[14]}$  The association constants determined from absorption and emission spectra are of similar order, and the small difference in association constant may be attributed to the weakening of hydrogen-bonding interactions upon excitation.

Under similar experimental conditions, the fluorescence intensity of receptor 1 in the presence of  $HSO_4^-$  is considerably lower than that of  $H_2PO_4^-$ , but higher than that of the other anions. This outcome might be due to the intermolecular hydrogen-bonding interaction between the fluorophoric unit (N3 atom) of 1 and the bisulfate ion (O2 atom; Figure 5) causing a partial restriction in free rotation as evidenced by single-crystal X-ray analysis. On the other hand, fluoride and acetate anions exhibit only a tiny increase in fluorescence intensity—most probably owing to an absence of such intermolecular hydrogen-bonding capability (compared to that of bisulfate and di-

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hydrogenphosphate ions)—and as a result the fluorophoric unit of **1** remains completely "unlocked". Other anions tested did not show any significant change in fluorescence intensity (see Figure 8 as well as Figure S15 in the Supporting Information). This result indicates that the fluorophoric unit (imidazo-[1,2-*a*]pyridine moiety) can rotate freely ("unlocked" conforma-



Figure 8. Relative change in fluorescence of 1 (0.5 mm) upon addition of different anions in  $CH_3CN$  solution.

tion, as evidenced by the X-ray crystal structure) about the C– C bond and that the energy in the excited state can be dissipated by nonradiative decay channels. As shown in Figure 8, receptor 1 can selectively detect  $H_2PO_4^-$  over the other anions tested (F<sup>-</sup>, AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and HSO<sub>4</sub><sup>-</sup>). It is obvious that the hydrogen-bonding interaction of receptor 1 with the anion imparts rigidity ("locked") to the entire molecular framework, thereby decreasing the rotation/vibrational degrees of freedom and hence contributing to fluorescence enhancement.

In summary, we have designed a simple molecular device (receptor 1) having complementary hydrogen-bonding, donoracceptor groups for efficient and selective binding of tetrahedral  $H_2PO_4^-$ . The dihydrogenphosphate anion ("key") efficiently freezes ("locked") the conformational free rotation of receptor 1 ("molecular lock") by hydrogen-bonding interactions as evidenced by single-crystal X-ray analysis. The structural changes of 1 in the presence of  $H_2PO_4^-$  effectively enhanced the fluorescence intensity in acetonitrile; however, structurally similar HSO<sub>4</sub><sup>-</sup> did not act in a similar way. In the presence of other competitive anions (F<sup>-</sup>, AcO<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and l<sup>-</sup>) receptor 1 remained unchanged.

### **Experimental Section**

#### Synthesis of Receptor 1

A solution of  $\mathbf{4}^{[16]}$  (1.00 g, 6.8 mmol) in MeOH (10 mL) was added dropwise to a solution of **3** (1.05 g, 6.8 mmol) in MeOH (10 mL). The reaction mixture was heated at reflux for 6 h and then cooled to RT. A yellow residue precipitated from the reaction mixture and was collected by filtration, washed with cold MeOH, and then dried under vacuum. The yellow solid **2** was obtained in 61% yield (1.20 g, 4.2 mmol). Compound **2** was directly used for the next synthetic step. Solid NaBH<sub>4</sub> (0.20 g, 0.005 mmol) was added portionwise to a suspension of **2** (1.00 g, 3.5 mmol) in MeOH (15 mL) at

0 °C with constant stirring for 1 h. The solvent was evaporated under reduce pressure and the resulting solid was dissolved in cold distilled water. A clear red color solution was obtained and then neutralized (pH ≈ 7) with dilute HCl. Compound 1 was precipitated as a light red solid, which was filtered and washed with distilled water. The solid was dried in air and obtained in 85% yield (0.84 g, 3.0 mmol). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  = 4.53 (s, CH<sub>2</sub>), 4.85 (s, NH<sub>2</sub>), 6.68 (d, *J* = 9 Hz, 1H, H<sub>6</sub>), 6.84 (t, *J* = 9 Hz, 1H, H<sub>3</sub>), 7.28 (t, *J* = 9 Hz, 1H, H<sub>4</sub>), 7.5 (m, 2H, H<sub>1</sub>, H<sub>5</sub>), 7.57 (d, *J* = 9 Hz, 1H, H<sub>7</sub>), 7.7 (s, 1H, H<sub>8</sub>), 8.28 ppm (d, *J* = 9 Hz, 1H, H<sub>2</sub>); <sup>13</sup>C NMR (75.5 MHz, [D<sub>6</sub>]DMSO, 20 °C):  $\delta$  = 41.89, 104.21, 110.40, 111.14, 111.93, 116.45, 117.79, 124.60, 126.92, 134.09, 137.11, 144.37, 144.44 ppm; IR (KBr):  $\tilde{\nu}$  = 3388, 3331, 3131, 1608, 1579, 1524, 1493, 1331, 1317, 1297, 1245, 1142, 1112, 857, 746, 669 cm<sup>-1</sup>; ESI-MS: *m/z* calcd for C<sub>14</sub>H<sub>13</sub>N<sub>5</sub>O<sub>2</sub> [*M*<sup>+</sup>]: 283.11; found for [*M* + H<sup>+</sup>]: 283.94.

#### Preparation of crystals suitable for X-ray diffraction

Single crystals of **1** were grown from a solution in water by slow diffusion of methanol to give deep red crystals. Single crystals of  $1 \cdot H_2 PO_4^-$  were grown from a solution of 1/tetrabutylammonium dihydrogenphosphate (1:1) in CH<sub>3</sub>CN by slow diffusion of diethyl ether. Single crystals of  $1 \cdot HSO_4^-$  were grown from a solution of 1/tetrabutylammonium hydrogensulfate (1:1) in CH<sub>3</sub>CN by slow diffusion of diethyl ether.

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