1,2-Bis[(4-phenylpyridinio)methyl]benzene Dication. Its Unprecedented Selective Complexation with $H_2PO_4^-$

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The anion complexation ability of 1,2-bis[(4-phenylpyridinio)methyl]benzene dichloride in MeCN was examined by UV-titration. The compound produced selectively the sufficiently strong $H_2PO_4^-$ complex in a 1:2 molar ratio. The presence of both of the 4-phenyl moieties was required for the $H_2PO_4^-$-selection. The X-ray crystallography of the complex structure is presented.

Crown ethers and cryptands have been well-recognized as neutral organic host molecules for small cations, which have opened the way to the area of supramolecular chemistry;[1] thus, most of the early subjects in this field have been associated with development of cation-selective hosts.[2] Meanwhile, another important subject has been directed to the selective detection of biologically important phosphate[3] and sulfate ions[4] by simple molecules; thus, designing neutral anion-binding host molecules potentially utilizable as anion-sensing devices[5] has attracted considerable attention. Selective binding in these hosts takes place by a combination of a cation/anion or Lewis acid/base interaction and hydrogen bondings. Particularly, the appropriate number and proper direction of hydrogen-bonds would be one of the important factors to be taken into consideration for attaining the selection of an anion. However, our recent study reveal that symmetrical per-*O*-methylated tripyridinio-α-cyclodextrin exhibiting no explicit hydrogen bonding ability shows high selectivity for weak acid anions such as phosphates, CN^- and $MeCO_2^-$ over strong acid anions, although this cyclodextrin was unable to discriminate sufficiently between those weak acid anions.[6] These observations have led us to an anticipation that a certain kind of polycation systems, even if including no hydrogen-bond forming units, could be a good candidate for a phosphate anion-specific binding site. Thus, we have now found that the title cationic compound (BPPMB; Figure 1a), inspite of its extremely simple structure, exhibits the selectivity for dihydrogen phosphate anion ($H_2PO_4^-$) in an unprecedented way.

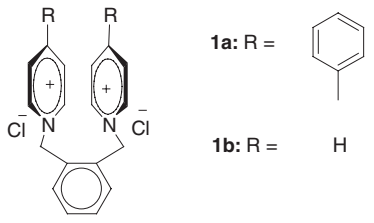

Figure 1. Chemical structures of BPPMB (**1a**) and BPMB (**1b**).

UV spectra of BPPMB in aqueous and MeCN solutions were almost the same, exhibiting a maximum absorption at 300 nm with $\varepsilon = 18000\,M^{-1}\,cm^{-1}/py^+$ assignable to the 4-phenylpyridinium moiety (Figure 2). The observation that both the wavelength and the intensity of the compound were virtually unchanged by the solvent supports the notion that the electronic state of the 4-phenylpyridinio moiety is totally insusceptible to their microenvironments. In Figure 2 is included plots of the decreasing absorbances at 300 nm as a function of concentration of $H_2PO_4^-$ as the tetrabutylammonium salt in MeCN, and addition of Na_2HPO_4 dissolved in a small amount of water to BPPMB in MeCN also provided the same UV spectral change as mentioned above (data not shown); this decrease is indicative of formation of the BPPMB complex solution with either of HPO_4^{2-} or $H_2PO_4^-$. The resulting complex itself was fully stable to long-term storage. Figure 2 shows plots of the decreasing absorption at 300 nm with portionwise addition of MeCN solution of various ammonium salts to the constant concentration of BPPMB in MeCN. Careful inspection of the plot reveals that the titration trace consists of two phases; namely, the absorbance decreases linearly with addition of up to one equiv. of $H_2PO_4^-\cdot NBu_4^+$ and then decreases more rapidly up to two equiv., suggesting that the 1:1 and 1:2 and/or higher order of complexes are formed in the titration process. As expected, addition of 100 equiv. of water to the complex solution regenerated the spectrum originated from the BPPMB absorption.

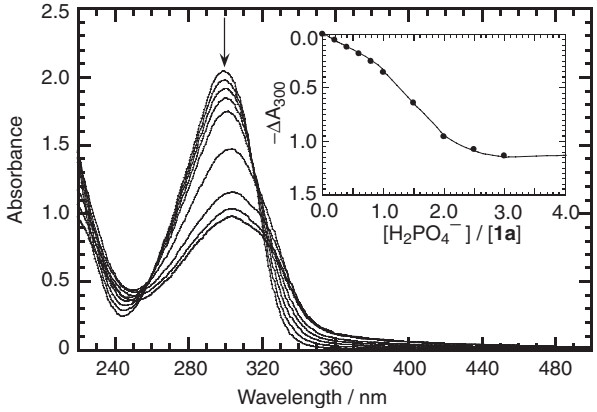

Figure 2. UV titration for **1a** (0.060 mM) with $Bu_4N^+H_2PO_4^-$ at 25 °C in CH_3CN. Inset: Plot of ΔA_{300} *vs* $[H_2PO_4^-]/[\mathbf{1a}]$.

Furthermore, neither phenylphosphate ($PhOP(OH)O^{2-}$) nor β-D-glucose-6-phosphate is capable of undergoing complexation under the identical conditions, implying that the presence of two protons being left on the anion is required for the complexation, concluding that $H_2PO_4^-$ alone is capable of participating in the 1:2 complexation event.

Incidentally, addition of various ions commonly possessing less than two available protons such as AcO^-, I^-, ClO_4^-, Br^-,

SCN^-, and even HSO_4^- except CN^- and SSO_3^{2-} exerted no influence on the BPPBM absorption, indicating that BPPMB fails to bind anions which have not two protons available for formation of two hydrogen-bonds in the complex. This anion-selectivity differs remarkably from that of a series of the reported polypyridinio-substituted α-cyclodextrins, where lipophilic, nonbasic anions such as I^-, ClO_4^-, and SCN^- are preferentially accommodated inside the host molecule.[7] Of course, no change in the UV spectral pattern was also observed in the titration with 1-benzyl-4-phenylpyridinium bromide. Unlike BPPMB, 1,2-bis(pyridiniomethyl)benzene dichloride (Figure 1b; BPMB), which lacks 4-phenyl groups, is also unable to respond to even $H_2PO_4^-$ as well as the common anions. Thus, the 4-phenyl groups in BPPMB play a crucial, unique role in discriminating $H_2PO_4^-$ from other anions. Solids crystallized out from a solution of a 10-fold higher complex concentration than that used for the UV titration provided elemental analysis that supports 1:2 stoichiometry. In order to delineate the origin of the high selectivity, the X-ray crystallographic determination of the complex structure was made, which is presented in Figure 3, and the conceptual drawing is displayed in Figure 4. Generally, X-ray crystallography will allow exact positioning of the guest molecules in the host molecule. In fact, the crystallography shows that there are included four $H_2PO_4^-$ molecules per two BPPMB molecules. Differing from the original anticipation, however, the two phenyl groups in the BPPMB molecule assume an open structure rather than a closed structure, and each two of the four $H_2PO_4^-$ molecules are bound together through two hydrogen-bonds to form a tetramer in the open space of the crystal lattice.[8] The role of the phenyl groups is substantial for creating enough open space in the crystal lattice to accommodate an $H_2PO_4^-$ tetramer.

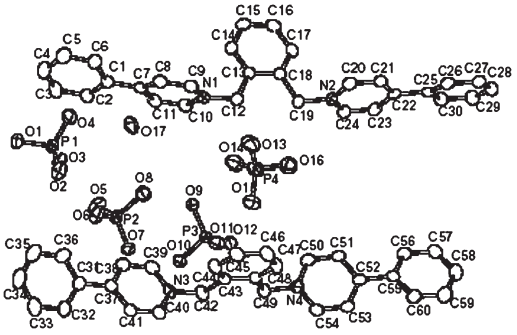

Figure 3. ORTEP drawing of BPPMB with thermal ellipsoid plot. Crystallographic date for $C_{30}H_{30}N_2O_8P_2{\cdot}0.5H_2O$, orthorhombic, space group $Pna2_1$ (#33), $a = 23.0795(8)$, $b = 16.4337(6)$, $c = 14.4851(5)$ Å, $V = 5493.9(6)$ Å^3, $Z = 8$.

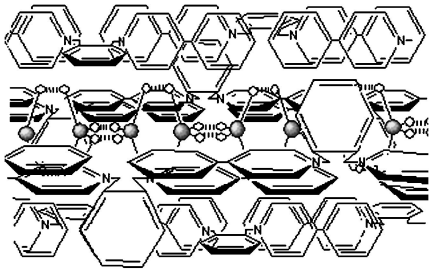

Figure 4. Conceptual stereoview of phenylpyridinium moieties around an $H_2PO_4^-$ chain.

In conclusion, it was quite noticeable that the selectivity of BPPMB for $H_2PO_4^-$ anion differed entirely from that of the 4-phenyl-lacking counterpart BPPM; namely, in spite of the loss of its explicit hydrogen-bond donation ability the BPPMB molecule was capable of trapping only $H_2PO_4^-$ anion selectively. The X-ray crystallography of the complex suggests that the origin of the selectivity is attributed to formation of a hydrogen-bonded $H_2PO_4^-$ tetramer trapped inside the crystal lattice composed of BPPMB molecules.

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