A Strategy of Visible Anion Recognition by Simple Polycyclic Aromatic Acid

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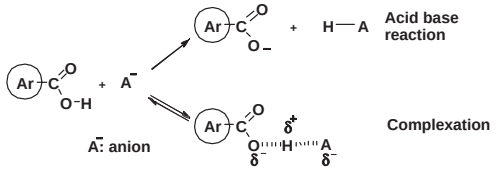
Polycyclic aromatic 1-pyrenecarboxylic acid (**2**) was investigated as an anion selective probe by means of UV–vis and fluorescence titrations in CH_3CN. Acid **2** showed stronger affinity and higher selectivity to HPO_4^{2-} and SO_4^{2-} over monovalent anions, such as F^-, Cl^-, Br^-, $H_2PO_4^-$, ClO_4^-, HSO_4^-, NO_3^-, BF_4^-, and PF_6^-. Complete fluorescence quenching upon complexation of acid **2** with HPO_4^{2-} and SO_4^{2-} was successfully observed by the eye.

Anions are important chemical species in the wide fields ranging from chemistry, pharmacy, biology, and environmental science. Much effort has been done in the design and syntheses of artificial anion receptors,[1a,1b] especially for visible anion recognition in this regard.[1c–1e] Recently, we have proposed a quite simple methodology for anion recognition using an aromatic acid.[2] Our strategy for the anion recognition is as follows: if the aromatic acid interacts with the guest anion whose basicity is stronger than that of the conjugate base of the acid, the proton of the acid should be transferred from the acid to the anion to yield the corresponding complete anion species of the acid (Scheme 1). On the contrary, if the basicity of the guest anion is weaker than that of the conjugate base of the acid, the proton transfer between the acid and the anion would be quite difficult. However, complexation between the acid and the anion could occur through hydrogen bonding to give a partially anionic species of the acid followed by spectral changes. As a preliminary experiment, we have selected commercially available and simple aromatic acid, 4-(*N*,*N*-dimethylamino)benzoic acid (**1**) (Figure 1), as a probe to prove the strategy.[2] In this paper, we wish to report on anion recognition properties of 1-pyrenecarboxylic acid (**2**), and its visible spectral changes by representative anions.

Acid **2** showed mainly three strong absorptions at 243, 281, and 348 nm in CH_3CN (Figure 2a). In order to estimate the association properties of acid **2** towards a variety of anions, UV–vis titrations were carried out according to the method similar to that described before.[2–4] Gradual additions of HPO_4^{2-}, whose basicity ($pK_b = 6.79$)[5] is much stronger than that of the conjugate base of **2** ($pK_b = 10.3$),[6] led to remarkable spectral changes of acid **2** (Figure 2a).[7] The absorbance changes of acid **2** monitored at 349 nm were plotted against anion/acid **2** ratios (Figure 3a). The absorbance increased rapidly until the addition of ca. 0.5 equivalent amounts of HPO_4^{2-}, and the titration curve saturated



Scheme 1.

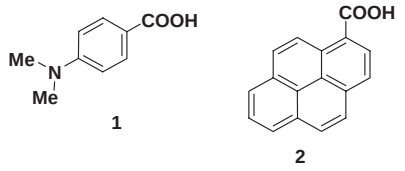


Figure 1. Structures of 4-(*N*,*N*-dimethylamino)benzoic acid (**1**) and 1-pyrenecarboxylic acid (**2**).

thereafter (Figure 3a), indicating that the stoichiometry of the association is 1:2 (anion:acid **2**), clearly.[8] Interestingly, the addition of SO_4^{2-} also caused the increase of absorbance, even though the basicity of SO_4^{2-} ($pK_b = 12$)[9] is weaker than that of the conjugate base of **2**. The inflection point, however, appeared at SO_4^{2-}/acid **2** = 1.0, suggesting that 1:1 interaction occurred in the case of SO_4^{2-}. On the other hand, titrations of acid **2** by F^- ($pK_b = 10.8$)[9] and $H_2PO_4^-$ ($pK_b = 11.8$)[6] resulted in monotonic increase in both cases. No change was observed during the titrations by other monovalent anions (Cl^-, Br^-, ClO_4^-, HSO_4^-, NO_3^-, BF_4^-, and PF_6^-), indicating that the interactions between acid **2** and the monovalent anions are so weak. Association constants, K_1 and K_2, were roughly estimated to be $\log K_2 > 10$ for HPO_4^{2-}, $\log K_1 = 5.9$ for SO_4^{2-}, $\log K_1 = 5.2$ for F^-,[10] and $\log K_1 = 3.5$ for $H_2PO_4^-$ by curve fitting of the titration profiles monitored at 349 nm, where K_1 and K_2 denote 1:1 (anion:acid **2**) and 1:2 association constants, respectively. As a result, host **2** exhibited strong affinity and high selectivity to divalent anions, HPO_4^{2-} and SO_4^{2-}.

Meanwhile, the existence of two strong fluorescence emissions at 390 and 410 nm by irradiation at 350 nm in CH_3CN makes acid **2** possible to show visible changes by addition of anions (Figure 2b).[11] Addition of divalent anion HPO_4^{2-} caused remarkable quenching of fluorescence intensity of host **2** (Figure 2b). The fluorescence intensity change monitored at 410 nm was plotted against anion/acid **2** ratio (Figure 3b). Complete quenching was accomplished by the addition of 0.5 and 1.0 equimolar amount of HPO_4^{2-} and SO_4^{2-}, respectively (Figure 3b). In the cases of F^- and $H_2PO_4^-$, however, fluorescence intensity of **2** decreased monotonously till large amounts of the anions were added. In addition, no quenching was observed in the case of monovalent anions, such as Cl^-, Br^-, ClO_4^-, HSO_4^-, NO_3^-, BF_4^-, and PF_6^-. Thus, all observations were quite similar to those observed for UV–vis titrations, as anticipated.

Furthermore, fluorescence quenching was also observed by the naked eye (Figure 4). The acetonitrile solution of acid **2** itself, namely, showed quite strong blue emission when it was irradiated at 365 nm. Complete quenching and almost complete quenching were observed by additions of an equimolar amount of HPO_4^{2-} and SO_4^-, respectively, while no or almost no change was observed by the eye upon additions of an equimolar amount of $H_2PO_4^-$, F^-, and ClO_4^- as expected by the fluores-

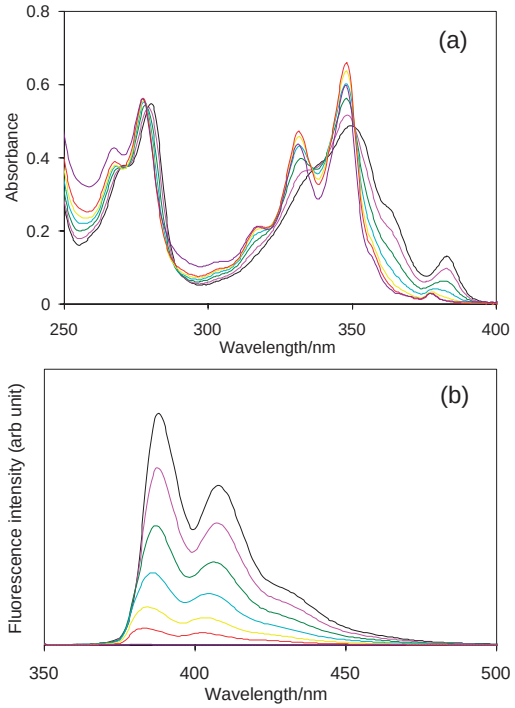


Figure 2. Absorption (a) and fluorescence (b) spectra of acid **2** in CH_3CN (2.0×10^{-5} mol/L) in the absence (—) of and in the presence of 0.1 (—), 0.2 (—), 0.3 (—), 0.4 (—), 0.5 (—), and 10.0 (—) equivalent of $(TBA)_2HPO_4$, respectively. Excitation wavelength for fluorescence measurements: 350 nm.

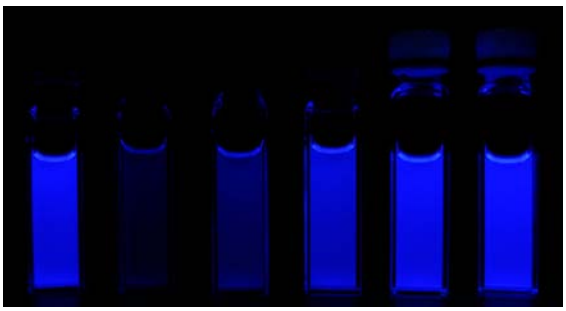


Figure 4. Visible fluorescence quenching of acid **2** (2.0×10^{-5} mol/L) upon additions of an equimolar amount of $(TBA)_2HPO_4$, $(TBA)_2SO_4$, $(TBA)H_2PO_4$, (TBA)F, and $(TBA)ClO_4$. Excitation wavelength: 365 nm.

cence titration profiles.[11]

In conclusion, we have succeeded in recognizing HPO_4^{2-} and SO_4^{2-} by fluorescence in visible region. Although the selectivity of acid **2** would not be perfect for anion recognition, we believe that the methodology would be simpler and more powerful for practical anion recognition.

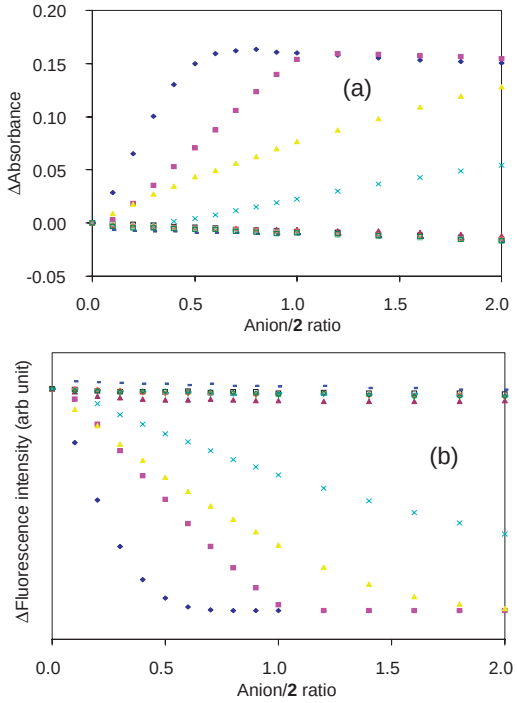


Figure 3. Absorbance and fluorescence intensity changes monitored at 349 nm (a) and 410 nm (b), respectively, upon titrations of acid **2** (2.0×10^{-5} mol/L) with $(TBA)_2HPO_4$ (◆), $(TBA)_2SO_4$ (■), (TBA)F (▲), $(TBA)H_2PO_4$ (×), $(TBA)HSO_4$ (−), $(TBA)ClO_4$ (▲), $(TBA)BF_4$ (□), $(TBA)PF_6$ (□), (TBA)Br (◇), (TBA)Cl (—), and $(TBA)NO_3$ (+) in CH_3CN. Excitation wavelength: 350 nm.

References and Notes

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1 For example, see: a) J. L. Sessler, P. A. Gale, W.-S. Cho, *Anion Receptor Chemistry*, Royal Society of Chemistry, Cambridge, **2006**. b) T. Nabeshima, T. Saiki, J. Iwabuchi, S. Akine, *J. Am. Chem. Soc.* **2005**, *127*, 5507. c) C. Lin, V. Simov, D. G. Drueckhammer, *J. Org. Chem.* **2007**, *72*, 1742. d) H. Maeda, Y. Kusunose, Y. Mihashi, T. Mizoguchi, *J. Org. Chem.* **2007**, *72*, 2612. e) E. Quinlan, S. E. Matthews, T. Gunnlaugsson, *J. Org. Chem.* **2007**, *72*, 7497.

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4 K. Kobiro, Y. Inoue, *J. Am. Chem. Soc.* **2003**, *125*, 421.

5 D. D. Perrin, *Ionization Constants of Inorganic Acids and Bases in Aqueous Solution*, 2nd ed., Pergamon, Oxford, **1982**.

6 The value was cited from CA database registry No.19694-02-1.

7 Commercially available acetonitrile was used without further purificaion. Complexation phenomena can be affected by water content of the acetonitrile.

8 A carboxylate anion of acid **2** and a complex between resulting $H_2PO_4^-$ and acid **2** would be formed during the titration till 0.5 equiv. addition of HPO_4^{2-}, while we supposed that the carboxylate and the complex would not be separated fully by solvent to afford a complete ionic species, but would form a pair of the carboxylate and the complex through hydrogen bonding in CH_3CN; see Ref. 2.

9 *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill, New York, **1985**.

10 The relatively large K_1 value of acid **2** for F^- may be attributed to the strong hydrogen bonding property of F^- to carboxylic acid.

11 1-Naphthoic acid and 2-naphthoic acid were also used as reference compounds of acid **2**. For detail, see Supporting Information, which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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