Crystal Structures and Properties of a Monoprotonated Porphyrin

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A stable monoprotonated porphyrin (porphyrin monoacid) was obtained by reaction of saddle-distorted dodecaphenylporphyrin with anthracene sulfonic acids and crystal structures of its supramolecular assemblies were determined.

Porphyrins are dibasic heteroaromatic compounds to accept two protons to be diprotonated species called as porphyrin diacids.[1] The protonation of porphyrins have been investigated for a long time due to its alteration of structures and characteristics of porphyrins.[2] In the case of *meso*-substituted porphyrins, the one-step diprotonation occurs simultaneously to give diprotonated species without any detectable intermediates.[1,3] In particular, saddle-distorted dodecaphenyl-porphyrin (H_2DPP)[4] facilitates its protonation by the out-of-plane orientation of the lone pairs of its pyrroles The diprotonated species (H_4DPP^{2+}) are stabilized by its intrinsic conformational distortion derived from intramolecular steric hindrance among peripheral phenyl groups,[5] and also by forming hydrogen bonding with anionic species, which are conjugate bases of Brønstead acids, to give a supramolecular assembly.[6]

So far, many attempts have been made to detect and isolate porphyrin monoacids, which are monoprotonated species of porphyrins as intermediates in the course of the diprotonation, by protonation of porphyrins with Brønstead acid[7] or deprotonation of corresponding diacids by dilution[8] or addition of base.[9] Although the crystal structure determination of porphyrin monoacid has been made on *β*-substituted octaethylporphyrinium (H_3OEP^+),[8b,10] to date, no crystal structure determination has been made on porphyrin monoacids having substituents at the *meso* positions. Thus, porphyrin monoacids have been "missing species" for the *meso*-substituted porphyrins. The arguments on porphyrin monoacids have been limited to their formation and protonation equilibrium, and their characteristics have not been discussed due to the difficulty of their isolation and stabilization to achieve thorough characterization.

We report herein for the first time the formation and crystal structure determination of supramolecular assemblies involving a porphyrin monoacid, H_3DPP^+, and sulfonate anions that exhibit hydrogen-bonding ability due to the delocalization of negative charge on the three oxygen atoms. We also report the spectroscopic and electrochemical properties of the saddle-distorted porphyrin monoacid. Monoprotonation of H_2DPP provides a new way not only to control the electronic and redox porperties of porphyrins but also to construct supramolecular assemblies.

As shown in Scheme 1, H_2DPP can undergo two-step protonation equilibrium to give H_3DPP^+ and H_4DPP^{2+} as pro-
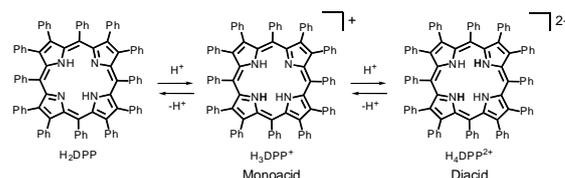
Scheme 1 Stepwise protonation of H_2DPP.

ducts of monoprotonation and diprotonation, respectively. We examined the reaction of H_2DPP and excess amount of anthracene sulfonic acid derivatives[11] to obtain porphyrin monoacid salts of H_2DPP having sulfonates as counter anions. In the case of 2-anthracene sulfonic acid (2-AN-SO$_3$H),[12] a green single crystal of [H_3DPP](2-AN-SO$_3$)•CH$_3$OH (**1**) was obtained by two-layered recrystallization with addition of CH$_3$OH on the top of the toluene solution of **1**. As for 2,6-anthracene disulfonic acid (2,6-AN-(SO$_3$H)$_2$),[12] the diacid reacted with the two molecules of H_2DPP to give a 2:1 salt, [H_3DPP]$_2$(2,6-AN-(SO$_3$)$_2$)•(CH$_3$OH)$_2$ (**2**), which was obtained as green crystals by two-layered recrystallization with addition of CH$_3$OH on the top of the CH$_2$Cl$_2$ solution of **2**. The selective crystallization of **1** and **2** should be ascribed to the better crystallinity of the monoacid salts than that of the corresponding diacid salts and that causes equilibrium shift to afford the monoacid salts, as described in Scheme 1.

The crystal structure of **1** is shown in Fig. 1(a).‡ In this compound, the saddle-distorted H_3DPP^+ forms hydrogen bonding among two of N-H protons of pyrroles and two of oxygen atoms in the sulfonate group of the 2-AN-SO$_3^-$ anion in the interatomic distances of 2.867(7) and 2.89(1) Å (see ESI Fig. S1(a)).† On the other side, a methanol molecule is hydrogen-bonded asymmetrically, showing interatomic distances of 2.911(5) and 2.862(6) Å (see ESI Fig. S1(a)).† The anthracene moiety was settled in a cleft formed by the two phenyl groups attached to a pyrrole tilted up toward the anthracene part, forming π-π interaction with the phenyl
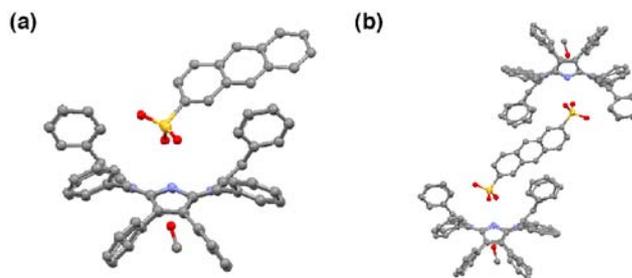
Fig. 1 Crystal structures of **1** (a) and **2** (b). Gray carbon, blue nitrogen, red oxygen, yellow sulfur. Hydrogen atoms and solvent molecules of crystallization are omitted for clarity.

groups (see ESI Fig. S2(a)).†

In the crystal of **2**, the two H_3DPP^+ units are linked by the 2,6-AN-$(SO_3^-)_2$ dianion as shown in Fig. 1(b).‡ Both of the sulfonate groups in 2,6-AN-$(SO_3^-)_2$ bind to the N-H protons of pyrroles of H_3DPP^+ with hydrogen bonding in the distances of 2.733(4) and 2.853(4) Å (see ESI Fig. S1(b)).† For the two H_3DPP^+ moieties, the oxygen atom in the CH_3OH molecule is bound to the two of pyrrole nitrogen atoms in H_3DPP^+ via hydrogen bonding in the distances of 2.844(6) and 2.860(4) Å (see ESI Fig. S1(b)).† As well as in the case of **1**, the anthracene moiety was placed in the cleft of the two phenyl groups in each H_3DPP^+ (see ESI Fig. S2(b)).†

As a comparison, we also conducted the reaction of H_2DPP with 2-anthracene carboxylic acid (2-AN-COOH).[11] A green single crystal of the diacid salt, $[H_4DPP](2\text{-}AN\text{-}COO)_2$ (**3**), was obtained by the same method as that for **1** (see ESI Fig. S3).†‡ Each 2-AN-COO^- anion binds to the H_4DPP^{2+} dication via two-point hydrogen bonding in the distances of 2.637(4) and 2.688(3) Å from one side and 2.725(4) and 2.660(3) Å from the other side of the porphyrin plane (ESI Fig. S1(c)),† respectively, as observed in $[H_4DPP][Zn(OPPc)(4\text{-}pyridine\text{-}carboxylate)]_2$ (H_2OPPc = octaphenylphtahlocyanine).[6]

The displacement of each atom from the least-squares mean plane of 24 atoms of the porphyrin cores in **1** - **3** indicated saddle distortion and the extent of distortion of H_3DPP^+ was comparable to that of H_4DPP^{2+} (see ESI Fig. S4).† .

The titration of H_2DPP by 2-anthracene sulfonic acid (2-AN-SO_3H) in benzonitrile (PhCN) allowed us to observe clearly distinguishable two-step spectral changes as shown in Fig. 2(a) with showing isosbestic points in each step. The equilibrium constants of the two-step protonation of H_2DPP by 2-AN-SO_3H were determined to be $K_1 = 8.1 \times 10^5$ mol^{-1} dm^3 and $K_2 = 4.2 \times 10^5$ mol^{-1} dm^3, respectively.[13] As can be seen in the inset of Fig. 2(a), the absorbance change at 470 nm is saturated at the point where 1 eq of 2-AN-SO_3H is added. This clearly indicates the formation of H_3DPP^+ in solution.[14] The same spectrum was observed for the solution of the single crystals of **1** in PhCN, indicating that the monoacid is stable in solution in the presence of the sulfonate anion (see ESI Fig. S5(a)).† In addition, the spectrum of the single crystals of **2** also showed the same spectrum as that of **1** (see ESI Fig. S5(b)).† In sharp contrast, one-step spectral change observed in the course of the titration with 2-AN-COOH, with showing isosbestic points, as shown in Fig. 2(b). The equilibrium constant for 2-AN-COOH was determined to be 3.8×10^{11} mol^{-2} dm^{6}.[13] In the case of 2-AN-COOH, the addition of 2 eq of the acid is required to observe the saturation of absorption change as depicted in the inset of Fig. 2(b), indicating that the simultaneous diprotonation occurs.

On the contrary, in dimethyl sulfoxide (DMSO), the titration of H_2DPP by 2-AN-SO_3H showed only one-step spectral change, which was assignable to monoprotonation and the equilibrium constant of this process was determined to be 1.4×10^3 mol^{-1} dm^3. The addition of 2-AN-COOH into the DMSO solution of H_2DPP gave rise to one-step spectral change and the equilibrium constant was determined to be 6.2×10^6 mol^{-2} dm^6. In comparison with spectral change observed in PhCN, we assigned the spectrum obtained in the
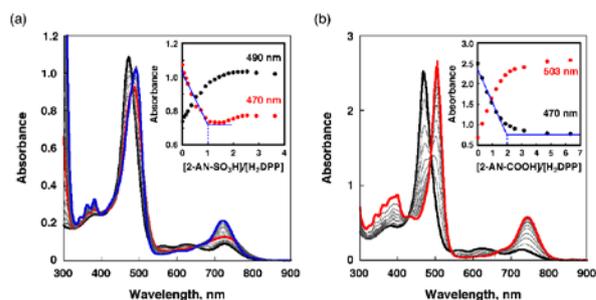

Fig. 2 Absorption spectral change in the course of titration of H_2DPP with 2-AN-SO_3H and 2-AN-COOH in PhCN at room temperature: (a) 0 - 4 eq of 2-AN-SO_3H (inset: absorbance change at 470 nm (red) and 490 nm (black)) and (b) 2-AN-COOH (inset: absorbance change at 503 nm (red) and 470 nm (black)). The concentration of H_2DPP were 6.7×10^{-6} mol dm^{-3} for 2-AN-SO_3H and 1.7×10^{-5} mol dm^{-3} for 2-AN-COOH.

reaction of H_2DPP with 2-AN-SO_3H to that of H_3DPP^+ and that for the reaction of H_2DPP with 2-AN-COOH to H_4DPP^{2+}, although the absorption maxima were not the same as those in PhCN (see ESI Fig. S6).† In DMSO, the solvent molecule is expected to bind strongly to the pyrrole N-H with hydrogen bonding and to inhibit the hydrogen binding of the weak conjugate base. ^1H NMR spectra in the course of the titration with 2-AN-COOH in DMSO-d_6 exhibited line-broadening, probably due to the restriction of molecular motion by hydrogen bond formation of the stronger conjugate base, 2-AN-COO^-, with H_4DPP^{2+} formed (see ESI Fig. S7).† In sharp contrast, ^1H NMR spectra for the titration with 2-AN-SO_3H showed no line-broadening and no change in chemical shifts of its signals, indicating no hydrogen bond formation.

The fluorescence spectrum of **1** was measured in PhCN with photoexcitation at 450 nm to exhibit the emission maximum at 796 nm ($\phi = 0.033$) with 1 eq of 2-AN-SO_3H and 786 nm ($\phi = 0.058$) with 2 eq of 2-AN-SO_3H, which were blue-shifted in comparison with that of H_2DPP (810 nm, $\phi = 0.006$) and in much higher quantum yields (see ESI Fig. S8).† The fluorescence spectrum of **3** was also obtained under the same conditions to exhibit the emission maximum at 808 nm ($\phi = 0.011$) with 2 eq of 2-AN-COOH, which was only slightly blue-shifted form that of H_2DPP.

The redox behavior of H_3DPP^+ was irreversible in cyclic voltammograms in PhCN and DMSO. Therefore, by measuring differential pulse voltammograms (DPV) of H_2DPP with the addition of 2-AN-SO_3H in PhCN (0.1 M [(n-butyl)$_4$N]PF_6 as an electrolyte), we could observe a new peak at –0.70 V relative to SCE as 0 V up to the addition of 1 eq of 2-AN-SO_3H (see ESI Fig. S10).†[15] The potential was higher than that of H_2DPP (–1.20 V) and lower than that of H_4DPP^{2+} (–0.45 V). This also lends credence to the formation of H_3DPP^+. In DMSO in the presence of 0.1 M of [(n-butyl)$_4$N]PF_6 as an electrolyte, we could observe only one peak at –0.85 V by the addition of 2-AN-SO_3H and –0.76 V by the addition of 2-AN-COOH, exhibiting anodic shift compared to that of H_2DPP in DMSO (–1.26 V).

Finally, we considered the effect of hydrogen bonding between protonated species of H_2DPP and conjugate base of acid employed. As described above, an acid involving strongly hydrogen-bonding conjugate base such as carboxylic acids gives rise to diprotonation, while an acid involving
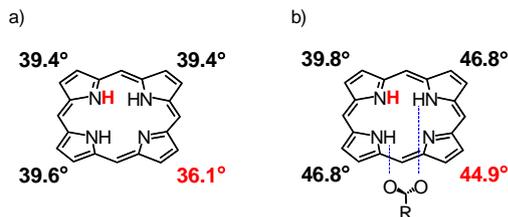
Fig. 3 Schematic description of DFT-optimized structures of H$_3$DPP$^+$ (a) and that hydrogen-bonded with 2-AN-COO$^-$ (b). Values described in the figure are dihedral angles relative to each porphyrin mean plane. The phenyl groups of H$_3$DPP$^+$ are omitted for clarity. R in (b) stands the 2-anthryl moiety.

poorly hydrogen-bonding conjugate base such as sulfonic acids affords step-wise protonation to provide the monoacid. We conducted DFT calculations on H$_3$DPP$^+$ and that hydrogen-bonded with 2-AN-COO$^-$ at the B3LYP/6-31G level of theory.[16] As for the porphyrin monoacid, the dihedral angles of pyrroles relative to the H$_3$DPP$^+$ mean plane were estimated as shown in Fig. 3(a). The non-protonated pyrrole showed the dihedral angle of 36.1°. On the other hand, the hydrogen-bonded monoacid exhibited the dihedral angles as demonstrated in Fig. 3(b) and a larger dihedral angle (44.9°) was obtained for the non-protonated pyrrole. This result suggests that the non-protonated pyrrole in the hydrogen-bonded porphyrin monoacid is more subject to be protonated than the counterpart. Thus, the second protonation should be enhanced to give the corresponding diacid.

In summary, we succeeded in the isolation and crystal structure determination of a *meso*-substituted porphyrin monoacid derivative with saddle distortion by controlling hydrogen-bonding ability of conjugate base of the Brϕnstead acid used for protonation. Weakly hydrogen-bonding conjugate base such as sulfonates gave the porphyrin monoacid in the crystal as well as in solution, however, strongly hydrogen-bonding conjugate base such as carboxylates afforded the porphyrin diacid. The sulfonate anions are not interacting in solution with the monoacid, however, they can form two-point hydrogen bonding with the N-H protons of pyrroles in the saddle distorted monoacid in the crystal. The intrinsic saddle distortion of H$_2$DPP may contribute to the stabilization of the porphyrin monoacid, allowing us to reveal its characteristics. The results reported herein will provide clear and precise description of a "missing species" in porphyrin chemistry and a new standpoint to develop novel supramolecular assemblies based on porphyrin monoacids.

Notes and references

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13   For two-step equilibrium: $(A - A_0)/(A_\infty - A) = K_1([H^+]_0 - \alpha[H_2DPP]_0)$ ($\alpha = (A - A_0)/(A_\infty - A_0)$), for $K_1 = [H_3DPP^+]/[H_2DPP][H^+]$. Similarly, $K_2 = [H_4DPP^{2+}]/[H_3DPP^+][H^+]$ was determined by assuming that the 1 eq addition of the acid gave H$_3$DPP$^+$ quantitatively, where $[H^+]_0 = [2-AN-SO_3H]$ or $[H^+]_0 = 2[2,6-AN-(SO_3H)_2]$. For one-step equilibrium: $(A - A_0)/(A_\infty - A) = K([2-AN-COOH]_0 - 2\alpha[H_2DPP]_0)^2$ ($\alpha = (A - A_0)/(A_\infty - A_0)$) for $K = [H_4DPP(2-AN-COO)_2]/[H_2DPP][2-AN-COOH]^2$.

14   The titration of H$_2$DPP with 2,6-AN-(SO$_3$H)$_2$ also exhibited saturation behavior by the addition of 0.5 eq of the diacid. See ESI Fig. S9.

15   We could observe a peak at –0.45 V due to H$_4$DPP^{2+} by the addition of less amount of 2-AN-SO$_3$H, however, this is probably due to the conditions for DPV measurements as represented by the presence of a large amount of PF$_6^-$ involved as an electrolyte. The presence of a large amount of PF$_6^-$ anion may induce diprotonation based on hydrogen bond formation as described in ref 5c.

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Graphical Abstract

A stable monoprotonated porphyrin (porphyrin monoacid) was obtained by reaction of saddle-distorted dodeca-phenylporphyrin with anthracene sulfonic acids and crystal structures of its supramolecular assemblies were determined.