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Formation of supramolecular hetero-triads by controlling hydrogen bonding of conjugate bases with a diprotonated porphyrin based on electrostatic interaction†

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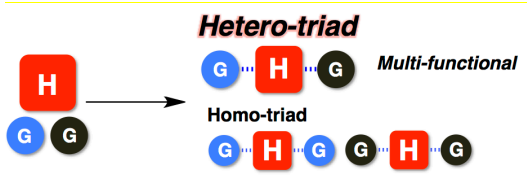
Thermodynamic stability of diprotonated saddle-distorted dodecaphenylporphyrin ($H_4DPP^{2+}(X^-)_2$) was controlled by hydrogen-bonding strength of conjugate bases (X^-) of strong acids (HX) or acids (R^+-COOH) having positively charged moieties. The thermodynamic control of $H_4DPP^{2+}(X^-)_2$ made it possible to achieve selective formation of supramolecular hetero-triads, $H_4DPP^{2+}(X^-)(Cl^-)$.

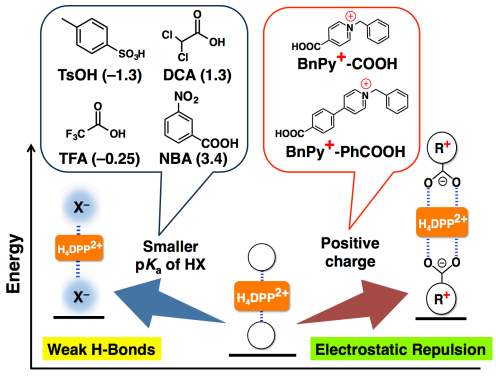
Hydrogen bonding is one of the most important non-covalent interactions in enzymes[1,2] and artificial supramolecular systems[3] to construct highly organized supramolecular functional assemblies. A great advantage of hydrogen-bonded supramolecules lies in the structural flexibility and diversity because of the tunable hydrogen-bonding strength composed of several factors such as atomic N(–H)•••O separation and charge delocalization of proton donors and acceptors related to electrostatic interaction.[4] The regulation of hydrogen-bonding strength is essential for selective formation of aimed supramolecular structures together with destabilization of undesired ones. In this context, selective formation of supramolecular hetero-triads composed of three different components (Scheme 1) would be expected to construct a multi-functional system such as Photosystem II in a photosynthetic reaction centre. Although supramolecular hetero-triads have been reported only in the solid states,[3] the selective formation of hydrogen-bonded supramolecular hetero-triads in solution has yet to be reported.



Scheme 1 Selective formation of a supramolecular hetero-triad (H: Host molecule, G: Guest molecules)

Porphyrins have been widely recognized as photofunctional and redox-active molecules as seen in photoinduced electron transfer reactions.[5-7] As further modification of their functions, protonation of free-base porphyrin (H_2P) is effective to form diprotonated porphyrin ($H_4P^{2+}(X^-)_2$) with hydrogen-bonded conjugate bases (X^-) of acids (HX),[8] although the excess amount of HX is necessary for diprotonation of H_2P.[9] On the other hand, protonation of dodecaphenylporphyrin (H_2DPP) by HX such as carboxylic acids resulted in quantitative formation of diprotonated $H_4DPP^{2+}(X^-)_2$ due to the higher basicity derived from the saddle distortion of H_2DPP.[10] However, systematic investigation on thermodynamic stability control of $H_4DPP^{2+}(X^-)_2$ by changing the hydrogen-bonding strength of X^- has yet to be reported. The strategy to regulate the hydrogen-bonding strength based on the properties of conjugate bases should be applicable to form more complicated supramolecular systems such as porphyrin-based hydrogen-bonding hetero-triads, $H_4DPP^{2+}(X^-)(Y^-)$ by controlling thermodynamic stability of $H_4DPP^{2+}(X^-)_2$.

Herein, we would like to report the thermodynamic control to destabilize $H_4DPP^{2+}(X^-)_2$ by lowering pK_a values of HX to form weaker hydrogen bonding between H_4DPP^{2+} and



Scheme 2 Strategies for thermodynamic destabilization of supramolecular homo-triad of H_4DPP^{2+}

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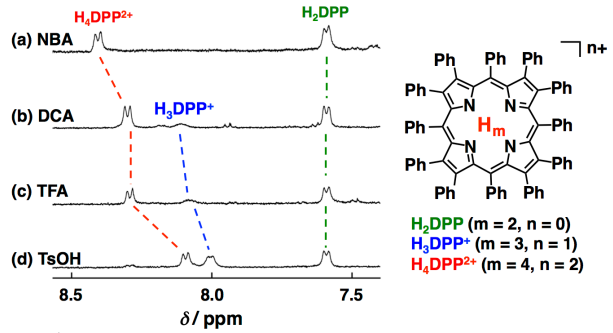

Fig. 1 ^{1}H NMR spectra of H_2DPP with 1 eq of HX in acetone-d_6 at 298 K; HX = (a) NBA, (b) DCA, (c) TFA, and (d) TsOH.

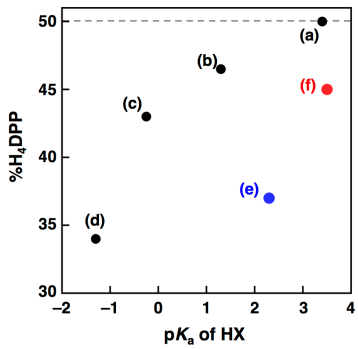

Fig. 2 Plots of %H_4DPP *vs.* pK_a of HX in acetone-d_6 at 298 K; HX = (a) NBA, (b) DCA, (c) TFA, (d) TsOH, (e) $BnPy^+$-COOH, and (f) $BnPy^+$-PhCOOH.

conjugate bases (X^-) of HX. In addition, destabilization of H_4DPP^{2+} have been also achieved by using electrostatic repulsion between the positive charge of the H_4DPP^{2+} and that of conjugate bases (R^+-COO^-) having a positively charged moiety for destabilization of $H_4DPP^{2+}(R^+\text{-}COO^-)_2$ (Scheme 2). These strategies are critical for the selective formation of hydrogen-bonded supramolecular hetero-triads ($H_4DPP^{2+}(X^-)(Y^-)$ and $H_4DPP^{2+}(R^+\text{-}COO^-)(Y^-)$) by destabilizing supramolecular homo-triads, $H_4DPP^{2+}(X^-)_2$ or $H_4DPP^{2+}(R^+\text{-}COO^-)_2$.

First, to investigate the effect of pK_a of acids (HX) on the thermodynamic stability of supramolecular homo-triads, $H_4DPP^{2+}(X^-)_2$, ^{1}H NMR spectra were measured in an acetone-d_6 solution containing H_2DPP and 1 eq of HX at 298 K. When we employed *m*-nitrobenzoic acid (NBA = NO_2PhCOOH, pK_a = 3.4 in H_2O)[11a] as HX, $H_4DPP^{2+}(NO_2PhCOO^-)_2$ was formed selectively, judging from a ^{1}H NMR signal assigned to the *ortho*-protons of the *meso*-phenyl groups that should appear in the range of 8.4 ppm (Fig. 1a) In contrast, protonation of H_2DPP by *p*-toluenesulfonic acid (TsOH, pK_a = –1.3 in H_2O)[11b] resulted in appearance of the signals attributable to the *ortho*-protons of monoprotonated $H_3DPP^+(TsO^-)$ at 8.0 ppm in addition to those due to H_2DPP at 7.6 ppm and $H_4DPP^{2+}(TsO^-)_2$ at 8.1 ppm as shown in Fig. 1d.[12] The formation yield (%H_4DPP)[13] of $H_4DPP^{2+}(X^-)_2$ was determined to be 34% on the basis of the relative integral value of the *ortho*-protons of $H_4DPP^{2+}(TsO^-)_2$ to 1,4-dioxane as an internal standard. In the case of other HX such as trifluoroacetic acid (TFA, pK_a = –0.25 in H_2O)[9e] and dichloroacetic acid (DCA, pK_a = 1.3 in H_2O)[9e], %H_4DPP values were determined to be 43% and 46%, respectively. As shown in Fig. 2, together with the decrease of the %H_4DPP values in accordance with lowering the pK_a values of HX, a stronger acid destabilizes $H_4DPP^{2+}(X^-)_2$ to afford $H_3DPP^+(X^-)$ favorably.[10a, 12]

Since protonation of H_2DPP proceeded to give H_4DPP^{2+} quantitatively even in the case of NBA as shown in Fig. S1 in the ESI†, the protonation-deprotonation equilibrium of HX could be excluded as a cause of the relationship depicted in Fig. 2. Therefore, the change of %H_4DPP values should be derived from the difference of hydrogen-bonding strength of conjugate bases (X^-) due to the difference of electrostatic interaction between H_4DPP^{2+} and X^-. The thermodynamic stability of $H_4P^{2+}(X^-)_2$ decreased by using X^- bearing delocalized negative charge such as ClO_4^-.[14] In this work, an acid showing a lower pK_a value such as TsOH should form a supramolecule ($H_4DPP^{2+}(TsO^-)_2$) with weaker hydrogen bonding than that using NBA. This trend was reflected on redox potentials of $H_4DPP^{2+}(X^-)_2$ in acetone containing 0.1 M $TBAPF_6$ as an electrolyte (Fig. S2 in the ESI†). In the case of TsOH, the reduction potential (E_{red}) of $H_4DPP^{2+}(TsO^-)_2$ was determined to be –0.76 V *vs.* Fc/Fc^+, which was the most positive among HX. When NBA was employed as an HX, the reduction of $H_4DPP^{2+}(NO_2PhCOO^-)_2$ was observed at the most negative potential (E_{red} = –0.98 V *vs.* Fc/Fc^+) (Table S1 in the ESI†). As shown in Fig. S3 in the ESI†, the relationship between %H_4DPP and E_{red} was almost the same as that between %H_4DPP and pK_a values of HX in Fig. 2. The most positive reduction potential of $H_4DPP^{2+}(TsO^-)_2$ indicates that electrostatic attraction between TsO^- and H_4DPP^{2+} was weakest in the series of X^-, in stark contrast to the case of NBA. This weak electrostatic interaction resulted in the destabilization of hydrogen-bonded supramolecular assemblies, $H_4DPP^{2+}(TsO^-)_2$. Thus, the hydrogen-bonding strength between protonated porphyrin and X^- based on electrostatic attraction plays a crucial role to control the thermodynamic stability of $H_4DPP^{2+}(X^-)_2$.

Next, as another strategy to destabilize $H_4DPP^{2+}(X^-)_2$, we applied electrostatic repulsion between the positive charge of the protonated porphyrin and conjugate bases with a cationic moiety. *N*-benzyl-4-carboxypyridinium ($BnPy^+$-COOH) salt and *N*-benzyl-4-carboxyphenylpyridinium ($BnPy^+$-PhCOOH) salt were synthesized as carboxylic acids with cationic pyridinium moieties to protonate H_2DPP (Fig. S4 and S5 in the ESI†).[15] The pK_a values of $BnPy^+$-COOH and $BnPy^+$-PhCOOH were determined to be (2.29 ± 0.06) and (3.46 ± 0.02), respectively (Fig. S6 and S7 in the ESI†), acidic enough for quantitative diprotonation of H_2DPP (Fig. S8 in the ESI†).

On the basis of ^{1}H NMR measurements of H_2DPP in acetone-d_6 containing 1 eq of $BnPy^+$-COOH, %H_4DPP could be calculated to be 36% at 298 K (Fig. S9a in the ESI†). The value was much smaller than that of TFA (43%) with a smaller pK_a value (–0.25) than that of $BnPy^+$-COOH (2.29) as shown in Fig. 2. In the case of $BnPy^+$- PhCOOH, the %H_4DPP was calculated to be 45% (Fig. S9b in the ESI†), which is also smaller than that of DCA (46%) but larger than that of $BnPy^+$-COOH (36%). These results were attributable to the destabilization of $H_4DPP^{2+}(R^+\text{-}COO^-)_2$ by electrostatic repulsion between H_4DPP^{2+} and positively charged conjugate bases. According to

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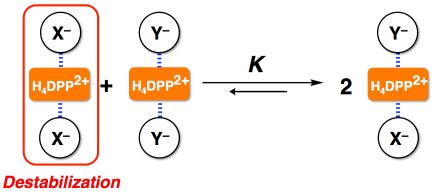
the Coulomb's law, the degree of electrostatic repulsion between positive charges should depend on the distance between the two positive charges. The distances (r) between mean planes of the diprotonated porphyrins hydrogen-bonded with conjugate bases and the centres of positive charge (nitrogen atoms) on the conjugate bases were estimated to be 7.51 Å for $BnPy^+$-COOH and 11.8 Å for $BnPy^+$-PhCOOH, respectively, by DFT calculations at the B3LYP/6-31G** level of theory (Fig. S10 in the ESI†). Considering the difference of pK_a values between $BnPy^+$-COOH (2.29) and $BnPy^+$-PhCOOH (3.46), difference of $\%H_4DPP$ values ($\Delta\%H_4DPP$) between a positively charged acid and a neutral acid with a comparable pK_a value, $BnPy^+$-COOH *vs*. DCA (pK_a = 1.3) and $BnPy^+$-PhCOOH *vs*. NBA (pK_a = 3.4), were used to elucidate distance dependence on the formation of H_4DPP^{2+} with elimination of influence of the acidity. In the case of $BnPy^+$-COOH, $\Delta\%H_4DPP$ (= $\%H_4DPP$(DCA) – $\%H_4DPP$($BnPy^+$-COOH)) was calculated to be 10%, while it was only 5% in the case of $BnPy^+$-PhCOOH relative to NBA ($\%H_4DPP$(NBA) – $\%H_4DPP$($BnPy^+$-PhCOOH)) = 5%) (Table S1 in the ESI†). These results indicate that positive charge of conjugate bases in a shorter distance to the diprotonated porphyrin causes stronger electrostatic repulsion to destabilize $H_4DPP^{2+}(X^-)_2$. Therefore, electrostatic repulsion between the positive charge on a diprotonated porphyrin and that on conjugate bases is an effective way to destabilize H_4DPP^{2+}, allowing us to control the thermodynamic stability of $H_4DPP^{2+}(X^-)_2$.



Scheme 3 A strategy for selective formation of supramolecular hetero-triads based on destabilization of supramolecular homo-triads

The concept of destabilization of supramolecular homo-triads ($H_4DPP^{2+}(X^-)_2$) could be applied to selective formation of supramolecular hetero-triads, $H_4DPP^{2+}(X^-)(Y^-)$ in the presence of two kinds of homo-triads ($H_4DPP^{2+}(X^-)_2$ and $H_4DPP^{2+}(Y^-)_2$) as shown in Scheme 3. Thus, we chose TsOH and R^+-COOH as acids for selective formation of $H_4DPP^{2+}(X^-)(Y^-)$ because of the lower thermodynamic stability of supramolecular homo-triads, $H_4DPP^{2+}(X^-)_2$, as described above.

When $CDCl_3$ solutions of $H_4DPP^{2+}(TsO^-)_2$ (0.4 mM) and $H_4DPP^{2+}(Cl^-)_2$ (0.4 mM) were mixed with 1:1 ratio at 298 K, ^{1}H NMR signals derived from *ortho*-protons of the *meso*-phenyl groups of a supramolecular hetero-triad, $H_4DPP^{2+}(TsO^-)(Cl^-)$, were observed at 7.9 ppm and 8.1 ppm (Figs. 3a and S11 in the ESI†), which was clearly different from those of $H_4DPP^{2+}(TsO^-)_2$ and $H_4DPP^{2+}(Cl^-)_2$ (Fig. 3b, 3c). The formation yield of $H_4DPP^{2+}(TsO^-)(Cl^-)$ was calculated to be 76% at 298 K; the selectivity reached to 87% at 268 K (Fig. S12 in the ESI†). The equilibrium constant (K) defined by eqn (1), to form the supramolecular hetero-triad was determined to

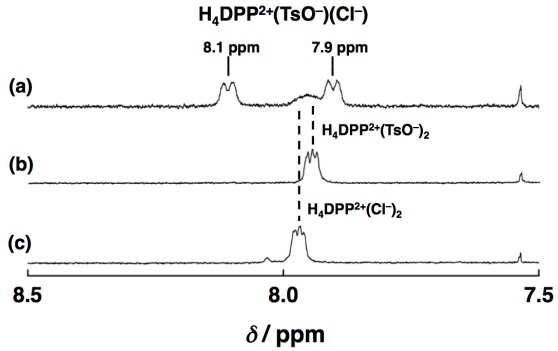


Fig. 3 ^{1}H NMR spectra of (a) a mixture of $H_4DPP^{2+}(TsO^-)_2$ solution (0.4 mM) and the solution of $H_4DPP^{2+}(Cl^-)_2$ (0.4 mM) with the ratio of 1:1, (b) $H_4DPP^{2+}(TsO^-)_2$, (c) $H_4DPP^{2+}(Cl^-)_2$ in $CDCl_3$ at 298 K.

$$K = \frac{[H_4DPP^{2+}(X^-)(Y^-)]^2}{[H_4DPP^{2+}(X^-)_2]\,[H_4DPP^{2+}(Y^-)_2]} \quad (1)$$

be 39 (Table S2 in the ESI†) at 298 K. On the other hand, mixing the solution of $H_4DPP^{2+}(NO_2PhCOO^-)_2$ (0.4 mM) and $H_4DPP^{2+}(Cl^-)_2$ (0.4 mM) resulted in the formation of $H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$ with a low yield (48%, Fig. S13 in the ESI†) and a small K value (3.5). Furthermore, the K values of $H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$ decreased with lowering temperature in contrast to the case of $H_4DPP^{2+}(TsO^-)(Cl^-)$ (Fig. S14 and Table S2 in the ESI†). Based on the formation constants of supramolecular hetero-triads, the Gibbs energy change in the formation of $H_4DPP^{2+}(X^-)(Y^-)$ was determined to be –2.1 kcal mol^{-1} for $H_4DPP^{2+}(TsO^-)(Cl^-)$ and –0.67 kcal mol^{-1} for $H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$ (Table S3 in the ESI†). These results suggest that the thermodynamic stability of $H_4DPP^{2+}(TsO^-)(Cl^-)$ is higher than those of $H_4DPP^{2+}(TsO^-)_2$ and $H_4DPP^{2+}(Cl^-)_2$; however, the stability of $H_4DPP^{2+}(NO_2PhCOO^-)(Cl^-)$ is comparable to those of the corresponding homo-triads. The improved selectivity should be derived from the thermodynamic destabilization of $H_4DPP^{2+}(TsO^-)_2$ because of weak hydrogen bonding between H_4DPP^{2+} and TsO^- in $H_4DPP^{2+}(TsO^-)_2$. The formation yield of a supramolecular hetero-triad, $H_4DPP^{2+}(Cl^-)(BnPy^+$-$COO^-)$ was also confirmed to be 77% by ^{1}H NMR spectroscopy in $CDCl_3$ at 298 K when mixing H_2DPP solution with 2 eq of $BnPy^+$-COOH and the solution of $H_4DPP^{2+}(Cl^-)_2$ with 1:1 ratio (Fig. S15a-15c in the ESI†). The K value for $BnPy^+$-COOH was determined to be 45 at 298 K to afford ΔG = –2.3 kcal mol^{-1} (298 K), which was comparable to that of TsOH. Formation of $H_4DPP^{2+}(Cl^-)(BnPy^+$-$COO^-)$ was confirmed by CSI-TOF-MS measurements in acetone at 223 K (Fig. S15d in the ESI†). Furthermore, the crystal structure of the supramolecular hetero-triad, $[H_4DPP^{2+}(Cl^-)(BnPy^+$-$PhCOO^-)](PF_6^-)$, was determined by X-ray crystallography (Fig. 4). In the crystal structure, hydrogen-bonding distance between C(O)O•••N was 2.72(8) Å, which was shorter than that in $H_4DPP^{2+}(BnPy^+$-$PhCOO^-)_2$ (2.75 Å) as estimated by DFT calculations. This result indicates that negative charge on Cl^- could suppress electrostatic repulsion between H_4DPP^{2+} and pyridinium moiety of $BnPy^+$-$PhCOO^-$, resulted in stabilization of the supramolecular hetero-triad relative to $H_4DPP^{2+}(BnPy^+$-$PhCOO^-)_2$. Thus, electrostatic repulsion to destabilize $H_4DPP^{2+}(R^+$-$COO^-)_2$ should be also effective for selective formation of supramolecular hetero-triads,

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in addition to the use of strong acids affording weak conjugate bases to form weak hydrogen bonds with H_4DPP^{2+}.

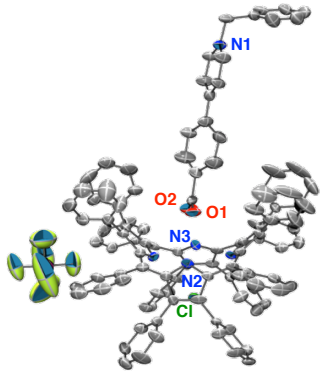

Fig. 4 An ORTEP drawing of $[H_4DPP^{2+}(Cl^-)(BnPy^+\text{-}PhCOO^-)]\text{-}(PF_6^-)$ with 50% probability thermal ellipsoids. Hydrogen atoms were omitted for clarity.

In conclusion, we have revealed the impact of conjugate bases (X^-) of acids (HX) on the thermodynamic stability of $H_4DPP^{2+}(X^-)_2$ toward the selective formation of hydrogen-bonded supramolecular hetero-triads. The strength of hydrogen bonding between H_4DPP^{2+} and X^- controls the thermodynamic stability of $H_4DPP^{2+}(X^-)_2$. Then, the weak conjugate base such as TsO^- form weak hydrogen bonds with H_4DPP^{2+}, resulting the destabilization of $H_4DPP^{2+}(TsO^-)_2$. Furthermore, electrostatic repulsion between H_4DPP^{2+} and zwitterionic conjugate bases ($R^+\text{-}COO^-$) with positive charge also destabilized $H_4DPP^{2+}(R^+\text{-}COO^-)_2$. In addition, selective formation of supramolecular hetero-triads, $H_4DPP^{2+}(X^-)(Y^-)$ was successfully achieved in solution by destabilizing $H_4DPP^{2+}(X^-)_2$. To the best of our knowledge, this is the first example to demonstrate the selective formation of hydrogen-bonded supramolecular hetero-triad in solution. This strategy should be effective to control formation of multicomponent supramolecular assemblies based on electrostatic interaction including hydrogen bonding toward the development of multifunctional supramolecular assemblies.

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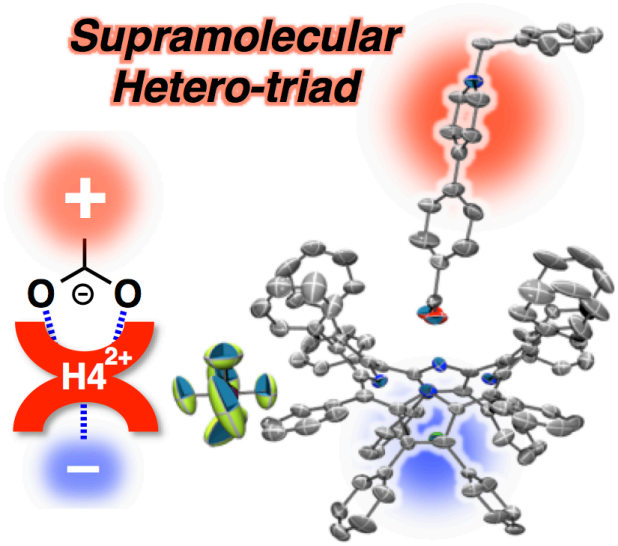

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