Tetra(*p*-*t*-butyl)thiacalix[4]arenetetrol Forms 4:1 Complex with Tetrakis(1-methyl-4-pyridinio)porphyrin

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A liquid–liquid extraction of cationic porphyrin (tetrakis(1-methyl-4-pyridinio)porphyrin, TMPyP) by tetra(*p*-*t*-butyl)thiacalix[4]arenetetrol (TCA) from an aqueous phase to a dichloromethane phase was performed. TCA stoichiometrically formed 4:1 complexes with TMPyP in dichloromethane phase within a few seconds. On the other hand, tetra(*p*-*t*-butyl)calix[4]arenetetrol did not form the complex with TMPyP.

To construct multi-molecular systems, a spontaneous complex formation between host–guest molecules by the molecular recognition ability of a host molecule should be a convenient method. Calixarene, which is cyclic phenol connected through methylene bridges and its derivatives (Figure 1), have been noticed in molecular recognition chemistry.[1–4] The molecular recognition ability of calixarene is based on two functions: one, a ligand effect by the hydroxy groups,[1–4] and the other, an inclusion of a guest molecule into the cyclic phenol.[1–9] The ability can be modified by replacing the bridge methylene groups of calixarene with heteroatoms. For example, tetra(*p*-*t*-butyl)thiacalix[4]arenetetrol (TCA, Figure 1)[9–12] of which the linking units are epithio groups has a higher affinity for transition-metal ions by the flexible epithio bridges than tetra(*p*-*t*-butyl)calix[4]arenetetrol (CA, Figure 1).[11] Such abilities of TCA are thought to apply to a molecular architecture through non-covalent bonding. The flexible framework of TCA should be especially effective for an inclusion of a large organic compound. In this paper, we investigated the complex formation between tetrakis(1-methyl-4-pyridinio)porphyrin tetra(*p*-toluenesulfonate) (TMPyP, Figure 1) and TCA. The complex formation ability of TCA was compared with that of CA.

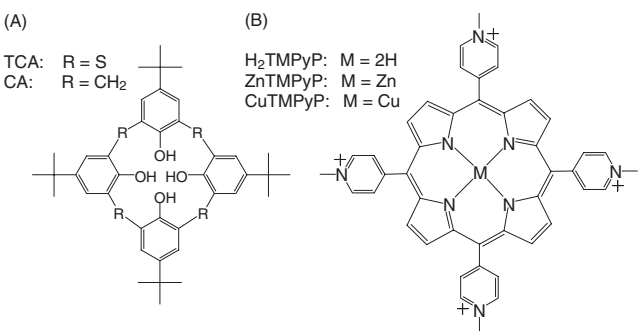

Figure 1. Structures of TCA, CA, and TMPyPs.

Samples of TCA and CA were supplied by the Cosmo Research Institute.[10] TMPyPs (H_2TMPyP, ZnTMPyP, and CuTMPyP) were synthesized according to the literature.[13] Dichloromethane (spectra grade, Dojin Chem. Ins.) was purchased and used for the solvent as received. The complex formation was performed as a liquid–liquid extraction of TMPyPs by TCA from an aqueous phase to a dichloromethane phase. The TCA or CA solution was pre-treated with potassium hydroxide (shaken with 2 M of an aqueous solution) to ionize the hydroxy groups. After that, 10 mL of the aqueous solution of TMPyPs (initial concentration: $[\mathrm{TMPyP}]_0 = 2.8 \times 10^{-5}$ mol dm^{-3}) and 10 mL of the dichloromethane solution of TCA or CA (0, 2.8, 5.6, 8.4, 11.2, and 14.0×10^{-5} mol dm^{-3}) were mixed and shaken in a 30 mL vial. The concentration of extracted TMPyPs from the aqueous phase to the dichloromethane phase was estimated from UV–vis absorption spectra.

TCA extracted TMPyPs (H_2TMPyP, ZnTMPyP, and CuTMPyP) from aqueous phase to dichloromethane phase, whereas no change was observed in the case of CA. CA could not extract TMPyPs, even though an excess amount (2.8×10^{-3} mol dm^{-3}) of CA was used. This extraction completed within a few seconds. The absorption spectra of extracted TMPyPs in dichloromethane were red-shifted and broadened compared to those in an aqueous phase (Figure 2A and Table 1). In the case of CuTMPyP, spectral broadening was observed and the peak did not red-shift. These spectral changes suggested a π–π interaction between the porphyrin ring of TMPyPs and the phenol ring of TCA in the complex.[14–17] Under this condition, TCA was not detected in the aqueous phase, indicating that water-soluble complexes were not formed. Since TMPyPs monomer was separated from the complex by extraction of the dichloromethane phase with purified water (Figure 2B), this complex formation is a reversible process.

The concentration of TMPyPs decreased in the aqueous phase and increased in the dichloromethane phase in proportion to the concentration of TCA ([TCA]) as shown in Figure 3. To determine the composition of the complex, we carried out the following analysis. The complex formation can be expressed by the equilibrium eq 1 as a reversible reaction:

$$\mathrm{TMPyP} + n\mathrm{TCA} \rightleftharpoons \mathrm{Complex} \quad (1)$$

This complex and TCA were soluble in dichloromethane phase (dcm) and these species could not be detected in aqueous phase (aq). TMPyPs, water-soluble porphyrins, are not soluble in dichloromethane. Therefore, the apparent equilibrium constant (K) can be expressed as follows:

$$K = \frac{[\mathrm{Complex}]_{\mathrm{dcm}}}{[\mathrm{TMPyP}]_{\mathrm{aq}}[\mathrm{TCA}]_{\mathrm{dcm}}{}^{n}} = \frac{[\mathrm{TMPyP}]_0 - [\mathrm{TMPyP}]_{\mathrm{aq}}}{[\mathrm{TMPyP}]_{\mathrm{aq}}\{[\mathrm{TCA}] - n([\mathrm{TMPyP}]_0 - [\mathrm{TMPyP}]_{\mathrm{aq}})\}^{n}} \quad (2)$$

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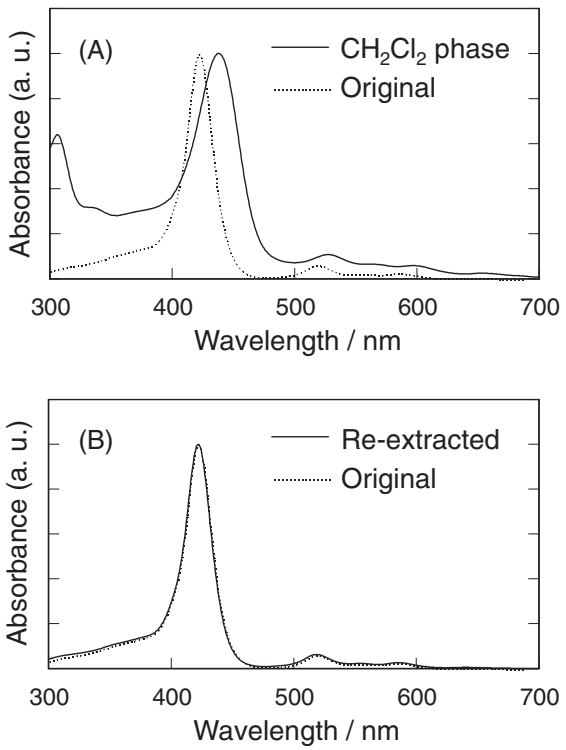

Figure 2. Absorption spectra of H_2TMPyP in aqueous phase (dotted) and its complex with TCA in dichloromethane phase (solid) (A). The spectrum of H_2TMPyP (solid) separated from the complex coincided with that of the original H_2TMPyP in aqueous phase (dotted) (B).

Table 1. Absorption Data of TMPyPs and Their Complexes with TCA

Guest (complex)	Phase	Soret band λ_{max}/nm [fwhm[a)]]	Q band λ_{max}/nm
H_2TMPyP	H_2O	424 [1460]	518, 554, 584, 640
(complex)	CH_2Cl_2	429 [2440]	529, 568 (sh[b)]), 599, 658
ZnTMPyP	H_2O	436 [1500]	564, 606
(complex)	CH_2Cl_2	472 [3530]	588, 636
CuTMPyP	H_2O	425 [1510]	548
(complex)	CH_2Cl_2	424 [2380]	554

a) fwhm: full width at half maximum (cm^{-1}). b) sh: shoulder.

where $[Complex]_{dcm}$, $[TMPyP]_{aq}$, and $[TCA]_{dcm}$ are concentrations of the complex, free TMPyP monomers, and free TCA monomer in the corresponding phases, respectively. Since the complex formations quantitatively proceeded against the [TCA], indicating the large K value, we can write the approximated eq 3 from eq 2 by assuming a sufficiently (infinitely) large K value:

$$[TMPyP]_{aq}\{[TCA] - n([TMPyP]_0 - [TMPyP]_{aq})\}^n = \frac{[TMPyP]_0 - [TMPyP]_{aq}}{K} \approx 0 \quad (3)$$

From eq 3,

$$[TMPyP]_{aq} = [TMPyP]_0 - \frac{1}{n}[TCA] \quad (4)$$

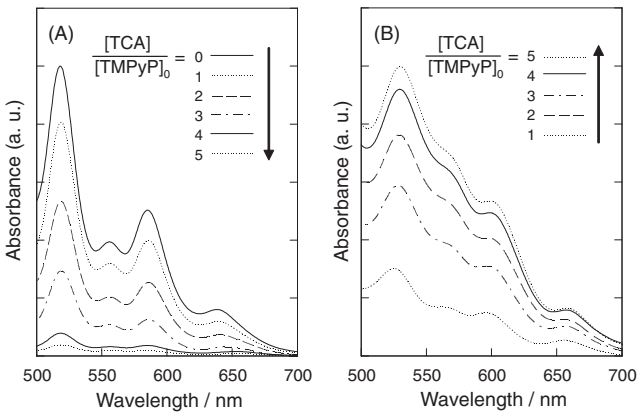

Figure 3. Absorption spectra of H_2TMPyPs in aqueous phase (A) and dichloromethane phase (B).

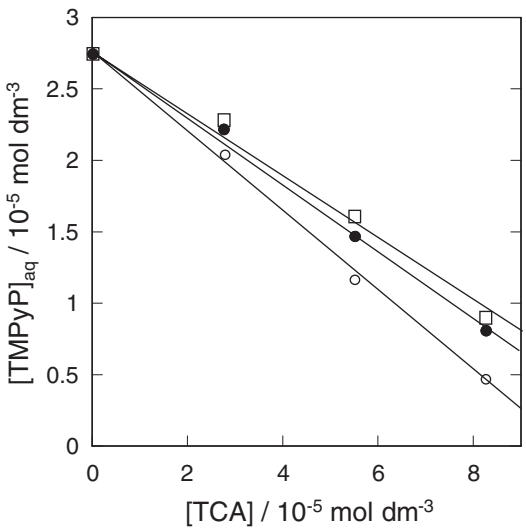

Figure 4. Dependencies of the $[TMPyP]_{aq}$ on the [TCA]. H_2TMPyP (●), ZnTMPyP (○), and CuTMPyP (□).

Table 2. Complex Formation Data of TMPyPs with TCA

Porphyrin	n	$\log K$
H_2TMPyP	4.2	23.8
ZnTMPyP	3.5	18.3
CuTMPyP	4.4	22.7

is obtained. Therefore, the n values can be estimated from the plots of Figure 4. Estimated n values from the reciprocals of the slopes in the plots are 4.2, 3.5, and 4.4 for H_2TMPyP, ZnTMPyP, and CuTMPyP, respectively. These n values almost agree with the four, which coincides with the number of cationic sites of TMPyPs (four methylpyridinio groups), indicating that one TMPyP forms the complex with four TCAs to be extracted to a dichloromethane phase. The K values were estimated by a least square curve fitting with the plots in Figure 4 using eq 2 with the estimated n values and the values of $\log K$ are listed in Table 2. The obtained values are extremely large compared with those of previously reported systems, e.g., CA/neutral organic species in non-aqueous phase

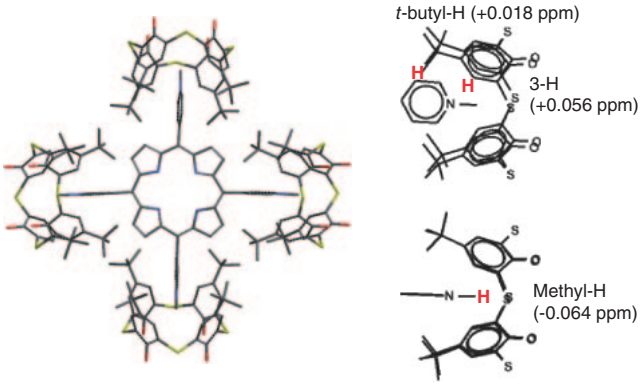

Figure 5. Proposed structure of the complex of TMPyP and TCA (left). The chemical shift changes ($\Delta\delta$) of ^{1}H NMR of TCA and the methylpyridinio moiety of H_2TMPyP (right).

($\log K = 1$–8),[3,8] CA or TCA/metal cation in aqueous phase (1–9),[3,11] and typical water–dichloromethane systems using crown ether (around 5).[3]

The experimental results showed that TCA and TMPyPs forms a 4:1 complex. Equilibrium geometry of the complex of TCA and TMPyP was calculated by molecular mechanics, suggesting the inclusion complex of methylpyridinio groups of TMPyPs by TCA (Figure 5). ^{1}H NMR measurements of the complex in chloroform-*d* showed the down-field shifts of TCA *t*-butyl-H ($\Delta\delta$ +0.018) and its 3-H ($\Delta\delta$ +0.056) through the complex formation, whereas the methyl-H of methylpyridinio moiety of H_2TMPyP showed up-field shift ($\Delta\delta$ −0.064). These results support this complex formation (Figure 5).

On the other hand, the complex formation of TMPyPs with CA was not observed, even though an excess amount of CA was used. Semiempirical calculation (MNDO) showed that the formation enthalpy change ($-\Delta H$) of this complex of TCA (434 kcal mol^{-1}) is slightly larger than that of CA (424 kcal mol^{-1}). The difference between TCA and CA may be caused by the difference in flexibility between the epithio bridge of TCA and the methylene bridge of CA.[9,10] The flexible epithio bridge of TCA is considered to make the inclusion of the methylpyridinio groups of TMPyPs possible.

In conclusion, TCA, which is a derivative of calixarene, stoichiometrically formed a 4:1 complex with cationic porphyrins, TMPyPs. For this complex formation, the flexibility of a bridge group of calixarene was considered to be an important factor. This experiment indicated the possibility of a molecular architecture using porphyrin and TCA through non-covalent bonding. A preliminary study suggested that fluorescence from the TMPyP moiety of these complexes was completely quenched through intra-complex electron transfer from TCA.[18] Relevantly, the electron transfer from a water-soluble CA to TMPyPs has been reported.[4] Thus, TCA can act as an electron donor in inclusion compounds beside being a building block.

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18 The redox potential (vs. SCE) of one-electron oxidation of TCA (0.98 V),[19] H_2TMPyP (>1.30 V),[20] and ZnTMPyP (1.18 V)[21] supported that the intra-complex electron transfer is possible from an energetic point of view. Further, HOMO energies of TCA and TMPyPs were calculated by ab initio molecular orbital calculations at the Hatree–Fock/3-21G level utilizing Spartan 06'. The calculated HOMO energy of TCA is −8.44 eV and higher than that of TMPyPs (H_2TMPyP: −14.94 eV, ZnTMPyP: −14.66 eV, CuTMPyP: −12.46 eV), suggesting that the electron transfer from TCA to photoexcited TMPyPs is energetically possible.
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