© 1991 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 64, 778—784 (1991) [Vol. 64, No. 3

Strong van der Waals Interactions in Water. Molecular Complexes of Porphyrins and Quinones in Organic and Aqueous Media

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(Received October 6, 1990)

The stability of the molecular complexes between 5,10,15,20-tetraarylporphyrins and quinones in organic solvents has been compared with that in water. 5,10,15,20-Tetrakis(mono-substituted phenyl)porphines (RTPPs) hardly form molecular complexes with *p*-benzoquinone (BQ), 2,3,5,6-tetramethyl-*p*-benzoquinone (DQ), and 2,3,5,6-tetrachloro-*p*-benzoquinone (CQ) in dichloromethane (K<10 mol^{-1} dm^3). In contrast, the stability constants (K>60 mol^{-1} dm^3) for the molecular complexes of cationic porphyrins (TMPyP and TAPP) with BQ in water are much larger than those in methanol. The thermodynamic parameters clearly indicate that complexation in water is an enthalpically favorable process, suggesting that the van der Waals interactions are the main binding forces and that hydrophobic interaction does not play an important role in complex formation in water. The larger stability of the molecular complexes in water can be interpreted in terms of the nature of water, as demonstrated by Smithrud and Diederich (D. B. Smithrud and F. Diederich, *J. Am. Chem. Soc.*, **112**, 339 (1990)). The microscopically hydrophobic porphyrin ring many hardly be hydrated and interact with BQ through the van der Waals interactions without an extensive dehydration process. The water molecules bound to BQ should be released upon complexation, and the released water molecules may be incorporated tightly into the hydrogen-bonding networks of water. Such complexation in water seems to be an enthalpically favorable process.

We have demonstrated that anionic and cationic porphyrins in water tend to form molecular complexes with guest aromatics throught van der Waals interactions.[1–5] Enthalpic (ΔH) and entropic changes (ΔS) in the complexation of water-soluble porphyrins are summarized in Table 1. In all of the cases shown in Table 1, the complexation of water-soluble porphyrins with guest aromatics is an enthalpically favorable process. This suggests that the main binding forces for molecular association in water are the van der Waals interactions. During these studies, we came to recognize that the association between anionic and/or cationic porphyrins and various aromatics, as well as the porphyrin dimerization,[5–7] is strictly suppressed in organic solvents (the results have not been published except for dimerization of a cationic porphyrin[6]). Why are the van der Waals interactions so strong in water? Answering this question is the aim of the present study.

Table 1. Enthalpic (ΔH) and Entropic Changes (ΔS) for Molecular Complex Formation of 5-Phenyl-10,15,20-tris(4-sulfophenyl)porphine Trisodium Salt (TPPS$_3$) and TMPyP in Water

Porphyrin	Guest[a)]	$-\Delta H$/kJ mol^{-1}	$-\Delta S$/J mol^{-1} K^{-1}	Ref
TPPS$_3$	AQαS	10.5	−19.1	2
TPPS$_3$	AQβS	17.7	−11.0	2
TPPS$_3$	AQDS	34.9	53.1	2
TPPS$_3$	PyS	18.9	0.2	2
TPPS$_3$	AnS	12.7	−13.0	2
TPPS$_3$	MV	22.3	19.3	2
TMPyP	PFl	29.3	34.9	3
TMPyP	PNP	46.1	99.9	4

a) AQαS; sodium 9,10-anthraquinone-1-sulfonate, AQβS; sodium 9,10-anthraquinone-2-sulfonate, AQDS; disodium 9,10-anthraquinone-2,6-disulfonate, PyS; sodium 1-pyrenesulfonate, AnS; sodium 2-anthracenesulfonate, MV; 1,1′-dimethyl-4,4′-dipyridinium dichloride, PFl; 2,6-diaminoacridinium hydrogensulfate, PNP; *p*-nitrophenol.

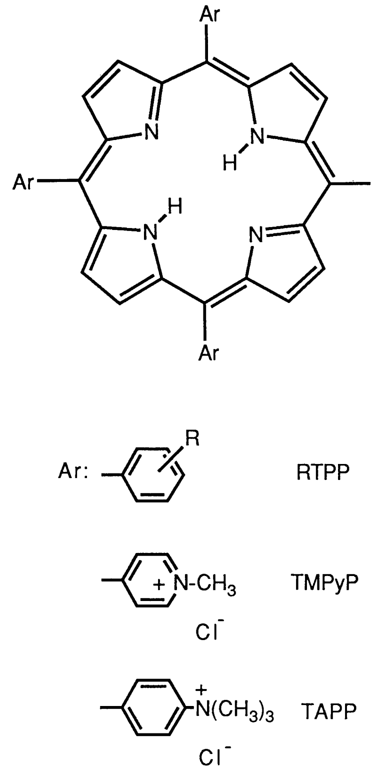
At first, in order to known the extent of the van der Waals interactions in an organic solvent, we investigated the complex formation of 5,10,15,20-tetrakis(mono-substituted phenyl)porphines (RTPPs) with quinones, such as *p*-benzoquinone (BQ), 2,3,5,6-tetramethyl-*p*-benzoquinone (DQ), and 2,3,5,6-tetrachloro-*p*-benzoquinone (CQ), in dichloromethane (CH_2Cl_2). The quinones were chosen as guests because ground-state complexes can be detected easily by measuring the static fluorescence quenching of prophyrins by quinones. The substituents (R) attached to the phenyl groups at the meso positions seem to alter the electron density of the porphyrin ring. It is expected, therefore, that the substituent effects on the formation of molecular complexes with quinones through the van der Waals interactions can be studied. We also presumed that a charge-transfer interaction may act as an cooperative force for forming stable molecular complexes, since porphyrin and quinone can behave as an electron donor and acceptor, respectively. Moreover, some tetrakis(*o*-substituted phenyl)porphines have a possibility to bind with quinones through hydrogen bonding.

Second, the stability of the molecular complexes of cationic porphyrins, such as 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphine tetrachloride (TMPyP) and 5,10,15,20-tetrakis[4-(trimethylammonio)phenyl]-porphine tetrachloride (TAPP), and BQ in methanol was compared with that in water. Although the experiments were limited due to the solubilities of porphyrins and quinones in organic and/or aqueous media, we expected to obtain information about the specialty of water as a solvent for molecular complex formation through van der Waals interactions.

Experimental

RTPPs (R=*o*-, *m*-, *p*-OH, *o*-, *m*-, *p*-CH_3, *o*-, *m*-, *p*-OCH_3, *o*-NH_2, *o*-$NHCOCH_3$, *o*-, *m*-, *p*-Cl, *o*-Br, *o*-, *p*-NO_2, *p*-$COOCH_3$, *p*-CN) were prepared according to the procedures described in the literatures.[8] The TMPyP[7] and TAPP[5] employed were previously described. BQ, DQ, CQ, and 1,4-naphthoquinone (NQ) were purchased from Nacalai Tesque (Kyoto) and purified by sublimation in vacuo.

The absorption and fluorescence spectra were measured on a Shimadzu UV-2100 spectrophotometer and a Hitachi 650-60 spectrofluorometer (uncorrected, band width=5 nm), respectively, whose cell holders were thermostated. The 400 MHz ^1H NMR spectra in $CDCl_3$ were recorded with a JEOL GX-400 spectrometer at 23±0.5 °C using TMS as an internal standard. The fluorescence lifetimes of RTPPs were determined by an Ortec-PRA single-photon counting apparatus, as described previously.[7] The cyclic voltammograms (CV) of RTPPs were taken in CH_2Cl_2 containing tetrapropylammonium perchlorate as a supporting electrolyte at 10 °C with a CV-1B voltammograph manufactured by Bioanalytical Systems. Platinum and silver-silver chloride electrodes were used as the working and reference electrodes, respectively. All samples containing both porphyrin and quinone were prohibited from exposure to room light.



Results and Discussion

Substituent Effects on ^1H NMR and CV of RTPPs. The complexation of porphyrin with quinone through van der Waals and/or charge-transfer interactions should be affected by the electron density of the porphyrin ring. Worthington et al.[9] have determined the reduction potentials ($E_{1/2}{}^{\mathrm{r}}$) of various RTPPs in DMSO and found that the electron density on the porphyrin ring is slightly affected by the substituent attached to the phenyl group at the meso position.

We measured ^1H NMR in $CDCl_3$ and the oxidation potentials ($E_{1/2}{}^{\mathrm{o}}$) in CH_2Cl_2 in order to determine the effects of the substituents (R) on the electron density of the porphyrin ring. The chemical shifts of the β-protons of pyrrole, as well as of the N–H protons of RTPPs, are expected to be the measures of the π-electron density on the porphyrin ring. The chemical shifts of the β-protons (δ_{CH}) and the N–H protons (δ_{NH}) and the first ($E_{1/2}{}^{\mathrm{o}}(1)$) and second oxidation potentials ($E_{1/2}{}^{\mathrm{o}}(2)$) of RTPPs are listed in Table 2.

Although δ_{CH} tends to shift to a lower magnetic field upon increasing the electron-donating ability of R, no clear relationship has been found between δ_{CH} as well as δ_{NH} and Hammett's σ-values. Figure 1 shows a plot of $E_{1/2}{}^{\mathrm{o}}(1)$ vs. Hammett's σ-values. A linear relationship was found ($E_{1/2}{}^{\mathrm{o}}(1)=0.38\sigma+1.05$, $R=0.980$), suggesting that the substituent at the phenyl group of RTPP regularly alters the electron density on the porphyrin ring.

Molecular Complexes of RTPPs with Quinones in Organic Solvents. It has been well-known that the fluorescent states of the porphyrins and their metal complexes are quenched by quinones and that an electron transfer from photoexcited porphyrin to quinone can be accounted for by a quenching mechanism.[10] For dynamic fluorescence quenching, a

Table 2. Chemical Shifts (δ_{CH}, δ_{NH}) and Oxidation Potentials ($E_{1/2}{}^{\mathrm{o}}$) of RTPPs

R	δ_{CH}/ppm	δ_{NH}/ppm	$E_{1/2}{}^{\mathrm{o}}(1)$/V	$E_{1/2}{}^{\mathrm{o}}(2)$/V
H	8.85	−2.78	1.05	1.26
o-OH			0.85	1.29
m-OH	8.91	−2.99	0.83	1.28
p-OH	8.89	−2.89	0.90	1.15
o-CH_3	8.66	−2.68	1.07	1.40
m-CH_3	8.85	−2.79	1.03	1.24
p-CH_3	8.85	−2.78	1.05	1.30
o-OCH_3	8.72	−2.63	1.06	1.20
m-OCH_3	8.89	−2.80	1.07	1.28
p-OCH_3	8.86	−2.76	0.92	1.07
o-NH_2	8.90	−2.73	1.03	1.22
o-Cl	8.69	−2.67	1.20	
m-Cl	8.87	−2.89	1.19	
p-Cl	8.84	−2.87	1.14	1.28
o-Br	8.67	−2.63		
p-CN	8.80	−2.83	1.30	
o-NO_2	8.62	−2.57		
m-NO_2	8.82	−2.81		

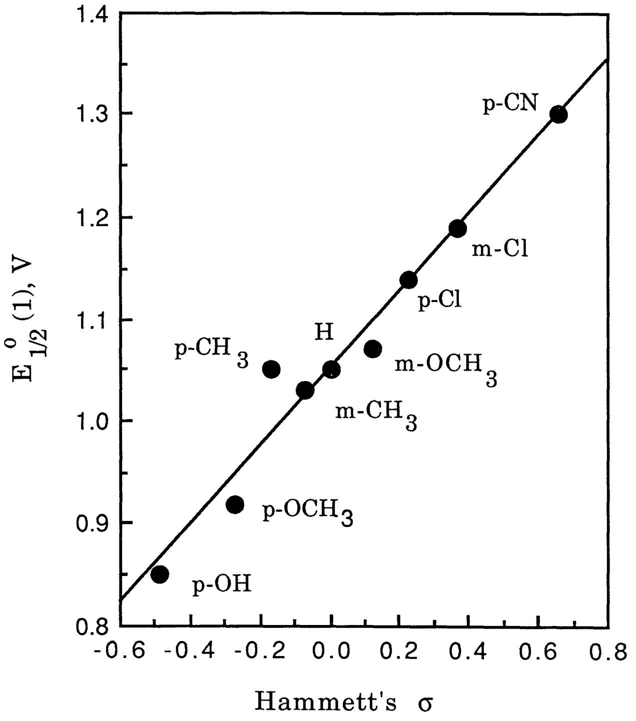


Fig. 1. Plot of $E_{1/2}^{o}$ (1) of RTPPs in CH_2Cl_2 vs. Hammett's σ.

Stern–Volmer linear relationship can be applied:

$$I_0/I = \tau_0/\tau = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q], \qquad (1)$$

where I_0 and I are the fluorescence intensities in the absence and the presence of a quencher (Q), respectively; K_{SV} is the Stern–Volmer constant, k_q is the rate constant for fluorescence quenching, and τ_0 and τ are the fluorescence lifetimes in the absence and the presence of Q, respectively. If static quenching due to the formation of nonfluorescent ground-state complex competes with a dynamic type, the Stern–Volmer equation is modified as[11]

$$I_0/I = (1 + K(\varepsilon_2/\varepsilon_1)[Q])(1 + K_{SV}^{\tau}[Q]), \qquad (2)$$

where K is the binding constant of the ground-state complex, K_{SV}^{τ} is the Stern–Volmer constant for dynamic quenching, and ε_1 and ε_2 are the extinction coefficients of fluorophore and complex at the excitation wavelength, respectively. In the case where Eq. 2 can be applied, the absorption spectral change should be observed. When the fluorophore is excited at an isosbestic point, Eq. 2 can be simplified as

$$I_0/I = (1 + K[Q])(1 + K_{SV}^{\tau}[Q]). \qquad (3)$$

The fluorescence quenching technique is very convenient for determining molecular complex formation as well as the binding constant, K, when a Benesi–Hildebrand plot[12] for an absorption spectral change cannot be applied for reasons such as a small change in the optical density upon complexation.

Table 3. Fluorescence Quenching of RTPPs by DQ, BQ, and CQ in Dichloromethane at 10 °C

R	τ_0/ns	$10^{-9}\,k_q/\mathrm{mol^{-1}\,dm^3\,s^{-1}}$		
		DQ	BQ	CQ
H	7.1	5.1	16.0	31.7
o-NH_2	3.9	6.7	30.8	45.1
o-OH	5.4	10.0	26.0	25.9
m-OH	5.1	13.0	31.0	35.3
p-OH	9.0	8.3	22.0	31.0
o-CH_3	5.0	5.0	23.0	36.0
m-CH_3	6.5	5.8	17.0	28.6
p-CH_3	4.1	8.5	26.0	44.4
o-Cl	3.3	6.1	20.0	40.6
m-Cl	4.4	4.2	15.0	29.1
p-Cl	2.9	8.4	23.0	46.9
o-OCH_3	7.1	3.2	13.0	25.4
m-OCH_3	7.5	3.2	14.0	24.8
p-OCH_3	6.8	4.9	16.0	27.6
p-NO_2	5.4	0.6	8.7	26.3
p-$COOCH_3$	5.2	3.7	14.0	28.8
p-CN	5.2	2.5	11.0	36.2

We initially sought RTPP–quinone pairs which form molecular complexes in an organic solvent by using the 17 RTPPs listed in Table 3 as well as BQ, DQ, and CQ. Dichloromethane (CH_2Cl_2) was used as an organic solvent. The $E_{1/2}^{r}(1)$ of DQ, BQ, and CQ determined using a cyclic voltammograph are −1.08, −0.72, and −0.10 V, respectively, at 10 °C. Contrary to expectations, linear Stern–Volmer plots were obtained for all cases when the fluorescence emissions from RTPPs ($4\times10^{-5}\,\mathrm{mol\,dm^{-3}}$) were quenched by the quinones at concentrations below $1\times10^{-2}\,\mathrm{mol\,dm^{-3}}$. This indicates that only dynamic fluorescene quenching takes place and that no appreciable amounts of the ground-state complexes of RTPPs with quinones are formed at the concentration range of the quinone below $1\times10^{-2}\,\mathrm{mol\,dm^{-3}}$. The results of fluorescence quenching are shown in Table 3. Of course, no absorption spectral change was measured under the same conditions as those for fluorescence quenching. In the cases of DQ and BQ, the k_q value tends to increase with decreasing $E_{1/2}^{o}(1)$ of RTPP. This should be ascribed to fluorescence quenching via an electron transfer from photoexcited RTPP to the quinone. Meanwhile, no correlation was observed between k_q and $E_{1/2}^{o}(1)$ in fluorescence quenching by CQ. This result can be interpreted as meaning that the fluorescence quenching by CQ proceeds at a diffusion-controlled rate because of the large electron affinity of this quinone.

At BQ concentrations above $1\times10^{-2}\,\mathrm{mol\,dm^{-3}}$, however, the absorption spectra of the several RTPPs regularly changed upon addition of BQ. An example is shown in Fig. 2, which shows the absorption

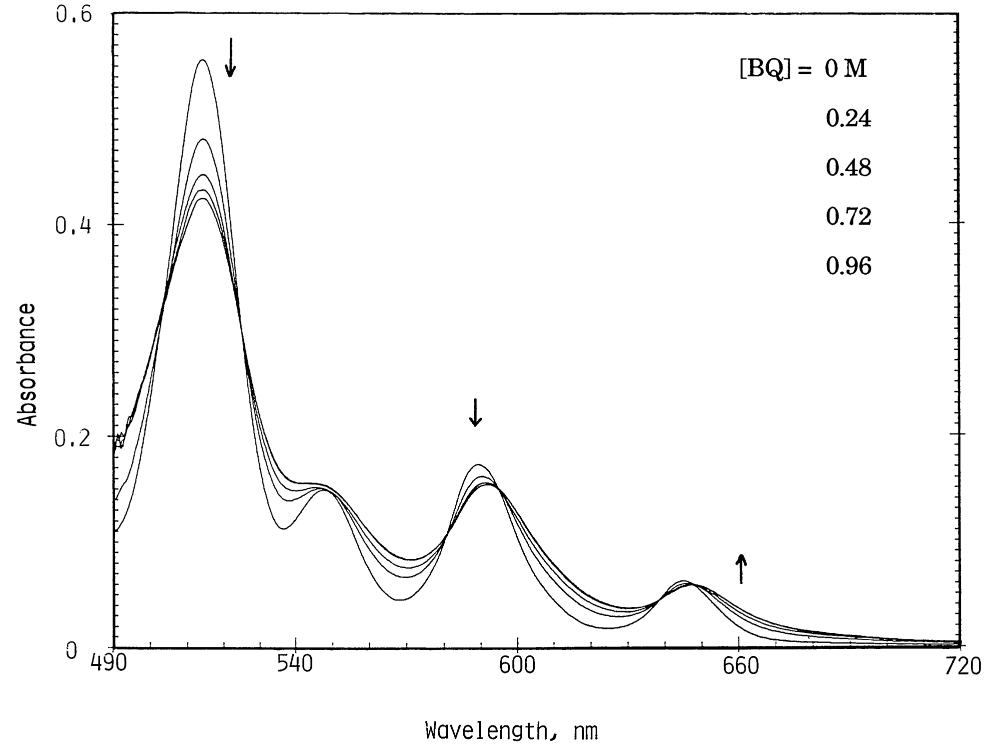


Fig. 2. Absorption spectral change of o-$NHCOCH_3TPP$ (4×10^{-5} mol dm^{-3}) in CH_2Cl_2 upon addition of BQ at 7 °C.

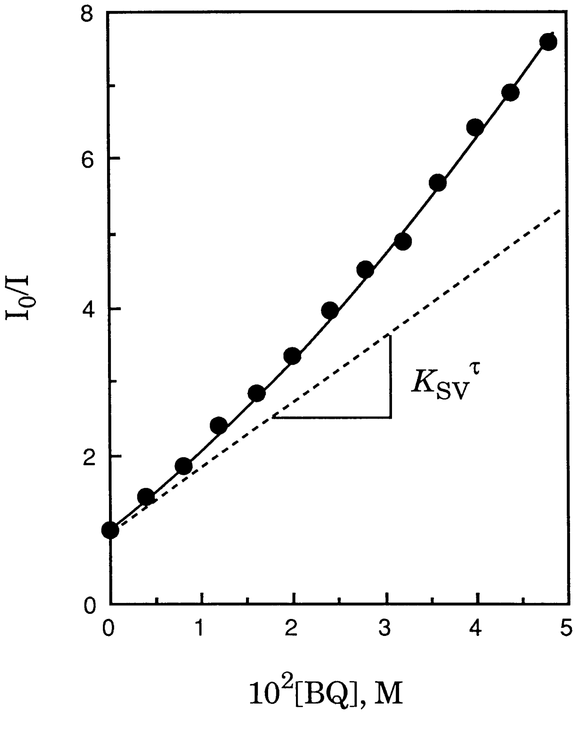


Fig. 3. Stern–Volmer plot for the fluorescence quenching of o-$NHCOCH_3TPP$ (4×10^{-5} mol dm^{-3}) by BQ in CH_2Cl_2 at 7 °C. The porphyrin was excited at 581 nm and the fluorescence intensities were followed at 652 nm.

Table 4. Binding Constants (K) for Complexation of RTPPs with BQ in Organic Solvents

R	Solvent	Temperature/°C	K/mol^{-1} dm^3
H	CH_2Cl_2	15	0.6
o-$NHCOCH_3$	CH_2Cl_2	7	7.8
o-$NHCOCH_3$	CH_3CN	15	4.1
o-OH	CH_3CN	15	3.2
m-OH	CH_3CN	15	2.4
o-NH_2	CH_3CN	15	0.02

spectral change of o-$NHCOCH_3TPP$ in CH_2Cl_2 upon addition BQ at 7 °C. The spectra are of the differential type obtained by substracting the BQ contribution. The Stern–Volmer plot for the fluorescence quenching deviates upward from a straight line, as predicted by Eq. 2 (Fig. 3). These results clearly indicate the formation of a ground-state complex of o-$NHCOCH_3$-TPP and BQ. The binding constant, K, determined by a Benesi–Hildebrand plot for the absorption spectral change is 7.8 mol^{-1} dm^3 at 7 °C (Table 4). HTPP (5,10,15,20-tetraphenylporphine) also shows a similar behavior (K=0.6 mol^{-1} dm^3 at 15 °C). A molecular complex with a very small K has also been reported for the p-CH_3TPP–BQ system in acetone (K=0.5 mol^{-1} dm^3 at 25 °C).[13]

In order to evaluate the contribution of a charge-transfer interaction to complexation, CH_2Cl_2 was replaced by an aprotic polar solvent, acetonitrile. The results obtained for *o*-$NHCOCH_3$TPP, *o*-OHTPP, and *m*-OHTPP are shown in Table 4. Since the *K* value (4.1 $mol^{-1}\,dm^3$ at 15 °C) for the *o*-$NHCOCH_3$-TPP–BQ system in acetonitrile is almost the same as that in CH_2Cl_2, a charge-transfer interaction may not play an important role in complexation. *o*-$NHCOCH_3$-TPP, *o*-OHTPP, and *o*-NH_2TPP were used to study the possibility for the formation of hydrogen-bonded complexes between these porphyrins and BQ. However, no appreciable difference was observed for the *K* values between these ortho-substituted porphyrins and HTPP and *m*-OHTPP. The *K* value for the *o*-OHTPP–BQ system was too small to be determined accurately. It, therefore, seems that the hydrogen bonding as well as the charge-transfer interaction scarcely participate in the complex formation of organic solvents. Therefore, it may be reasonable to assume that the main binding forces for the unstable complexes of RTPPs with quinones are van der Waals interactions.

Molecular Complexes of TMPyP and TAPP with BQ in Organic and Aqueous Media. In spite of the electrostatic repulsion, both cationic porphyrins, TMPyP and TAPP, associate with a cationic dye, 2,6-diaminoacridinium hydrogensulfate (PFl), in water to form relatively stable molecular complexes (*K* for TMPyP=2161 $mol^{-1}\,dm^3$ at 25 °C, *K* for TAPP=800 $mol^{-1}\,dm^3$ at room temperature).[3,5] *p*-Nitrophenol (PNP) can also act as a guest molecule in complexation with TMPyP in water (K=550 $mol^{-1}\,dm^3$ at 25 °C).[4] On the basis of the thermodynamic parameters determined for these systems (see Table 1), we have claimed that the van der Waals interactions are the main binding forces.[4,5]

We initially expected that relatively stable molecular complexes of these cationic porphyrins should be formed in organic solvents, as long as van der Waals interactions are the binding forces. We then compared the stability of the TMPyP- and TAPP–BQ complexes in methanol and water. The determined *K* values are listed in Table 5. The *K* values in methanol were evaluated from Benesi–Hildebrand plots for the absorption spectral changes, and those in water were determined from data regarding fluorescence quenching using Eq. 3. We confirmed that both methods can provide almost the same *K* values. For example, the *K* values evaluated from the Benesi–Hildebrand plots for the TMPyP–BQ and TAPP–BQ systems at 20 °C are 79 and 151 $mol^{-1}\,dm^3$, respectively, and are in good agreement with the *K* values determined from the fluorescence quenching (see Table 5).

Table 5. Binding Constants (*K*) for Complexation of TMPyP and TAPP with BQ and NQ in Methanol and Water

Porphyrin	Quinone	Solvent	Temperature/°C	K/$mol^{-1}\,dm^3$
TMPyP	BQ	CH_3OH	20	4.0
TAPP	BQ	CH_3OH	20	2.7
TMPyP	NQ	CH_3OH	20	7.6
TAPP	NQ	CH_3OH	20	13.0
TMPyP	BQ	H_2O	20	73
TMPyP	BQ	H_2O	25	70
TMPyP	BQ	H_2O	30	67
TMPyP	BQ	H_2O	35	63
TAPP	BQ	H_2O	20	147
TAPP	BQ	H_2O	25	85
TAPP	BQ	H_2O	30	84
TAPP	BQ	H_2O	35	80

As Table 5 indicates, complexes formed in water are much more stable than those formed in methanol. The *K* values in methanol are comparable to those of the RTPP–BQ systems in CH_2Cl_2 or acetonitrile. NQ, which has a more expanded π-conjugated system compared with BQ, also shows small *K* values. From these results it can be concluded that the cationic porphyrins, as well as RTPPs, cannot form stable molecular complexes with quinones in organic solvents through van der Waals interactions. Meanwhile, the *K* values in water are much larger than those in methanol. The van't Hoff plots for the data shown in Table 5 provide ΔH and ΔS for complexation of TMPyP and TAPP with BQ in water, ΔH and ΔS being $-28\,kJ\,mol^{-1}$ and $-56\,J\,mol^{-1}\,deg^{-1}$, respectively, for TMPyP and $-34\,kJ\,mol^{-1}$ and $-73\,J\,mol^{-1}\,deg^{-1}$, respectively, for TAPP. It is clear that the complex formation of these cationic porphyrins with BQ in water is the enthalpically favorable process. This finding is the same as that obtained for other systems investigated previously (see Table 1). If we define that complexation through hydrophobic interaction is favorably dominated by an entropy term, it can be concluded that the hydrophobic interaction does not contribute to the complexation of these cationic porphyrins with BQ in water. The charge-transfer, hydrophobic, and, in some special cases, hydrogen-bonding interactions can be excluded from the main binding forces. The van der Waals interactions may mainly participate in the complexation of cationic porphyrins with BQ in water. However, in order to conclude that the van der Waals interactions are the main binding forces, we have to explain the reason why these interactions are so strong in water compared with in organic solvents.

Quite recently, Smithrud and Diederich[14] reported the solvent effects on complex formation of a macrocyclic cyclophane host and a pyrene guest and found a linear relationship between $-\Delta G^\circ$ for complexation and Dimroth's $E_T(30)$ values of the solvents. They explained the largest binding constant in water in terms of such water properties as low molecular polarizability and a high cohesive interaction that promote the strongest van der Waals interactions between an apolar host and an apolar guest in water. A similar explanation may be possible

Table 6. Average Molecular Polarizabilities (α)

Molecule	α (calcd)/Å^3	α (exp)/Å^3	Ref
H_2O	1.47	1.45	15
CH_3OH	3.28	3.26	15
CH_3CN	4.86		This work
CH_2Cl_2	6.38	6.48	15
HTPP	74.9		This work
TMPyP^{4+}[a)]	75.4		This work
BQ	10.7		This work

a) The α value was calculated for the cation (TMPyP^{4+}) and no contribution of Cl^- was considered.

for our systems.

The London dispersion force, as well as the dipole-induced dipole interaction, becomes remarkable when host and/or guest molecules have large molecular polarizabilities. The average molecular polarizability, α, can be calculated using the following equation:[15)]

$$\alpha = (4/N)(\textstyle\sum \tau_A)^2 \ (\text{Å}^3), \qquad (5)$$

where N is the number of electrons in the molecule and τ_A is the atomic hybrid components of α for each atom in a particular hybrid configuration. The calculated polarizabilities of the molecules which were used in this study are summarized in Table 6. The molecular polarizability of H_2O is lowest amongst the solvent molecules in Table 6, which means that the van der Waals interactions between apolar solute and solvent molecules are weakest in water. Both TMPyP and TAPP are regarded as being amphiphilic molecules and the hydrophobic porphyrin rings of these porphyrins may not strongly interact with water molecules through van der Waals interactions, while the hydrophilic peripheries are extensively hydrated through an ion–dipole interaction. The association of the cationic porphyrins and BQ in water, therefore, may be a process which does not require extensive dehydration from the porphyrin rings. Since TMPyP and TAPP have large molecular polarizabilities, BQ is also polarizable and the carbonyl groups of BQ have dipoles, molecular association between these hosts and the guest seems to occur through dipole-induced dipole and London dispersion interactions in water as an enthalpically favorable process.

Meanwhile, BQ is hydrated through both hydrogen bonding and dipole–dipole interactions. Dehydration from the BQ molecules, therefore, needs to form a complex with porphyrin as an endothermic process. The water molecules released from BQ, however, may be incorporated tightly into hydrogen-bonding networks of water as an exothermic process. This strong cohesive interaction of water may compensate for any energetic disadvantage due to dehydration. Sinanoglu[18)] has developed a theory regarding solvophobic interaction. In this theory an apolar solute molecule is regarded as being a cavity. The dissolution of a solute molecule in a solvent causes an increase in the surface area of the solvent, which requires energy to work against the strong cohesive interaction of water. The association of two solute molecules, therefore, is energetically favorable since the surface area of the solvent is reduced upon complexation. Margalit and Rotenberg[19)] have applied this theory to explain the dimerization of porphyrin in water. The strong solvophobic interaction in water is ascribed to a strong cohesive interaction of this solvent, and may also participate in the complexation of the cationic porphyrins with BQ in water.

The large stability of the complexes of TMPyP with PFl and PNP[3–5)] as well as of the complexes of TPPS$_3$ with various aromatics[1,2)] in water may be interpreted in the same manner. We have claimed that TMPyP dimerizes in water, even at very low concentrations ([TMPyP]$>2\times10^{-7}$ mol dm^{-3}).[3–7)] Our dimer model for TMPyP contradicts the conclusion presented by Hambright and Fleischer[16)] as well as Pasternack and his co-workers.[17)] The novel dimerization of TMPyP can also be explained by strong van der Waals interactions which are ascribed to the nature of water, such as the low molecular polarizability and the strong cohesive interaction of water.

We believe that the stoichiometries of the complexes of TMPyP and TAPP with BQ are 2:1 and 1:1, respectively, in water while the 1:1 complexes of both porphyrins are formed in methanol. In previous papers we confirmed that TMPyP and TAPP exist as a dimer and monomer, respectively, in water under the present conditions ([porphyrin]$=4\times10^{-5}$ mol dm^{-3})[5)] and that the TMPyP dimer associates with PFl.[3)] Although we attempted to obtain a correlation between ΔG° for the complexation of TMPyP with BQ and $E_T(30)$ in aqueous methanol, we did not succeed because of the partial dissociation of the TMPyP dimer to the monomer in aqueous methanol.

This work was supported by Grant-in-Aid for Science Research on Priority Areas, "Multiplex Organic Systems" No. 01649006, from the Ministry of Education, Science and Culture.

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