

Polar Effect on the Stacking Interaction between a Zinc Complex of an Anionic Porphyrin and Anionic Aromatics

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Although 2-anthracenesulfonate did not interact with a zinc complex of 5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphyrin (ZnTPPS), anthraquinone-2-sulfonate (AQS) and -2,6-disulfonate (AQDS) formed stable molecular complexes with ZnTPPS in aqueous solution. Such results suggest the polar effect on the stacking interaction between aromatic compounds. Molecular complexation of ZnTPPS was further studied using mono-substituted benzoate anions as the partners by means of ^{1}H NMR spectroscopy. The electron-withdrawing groups of the benzoates stabilized the complexes, while the electron-donating groups restrained the complexation. These results suggest that a reduction of the electrostatic repulsion by electron-withdrawing group(s) is important to form stable molecular complexes of ZnTPPS and anionic aromatics via the London dispersion force. A similar mechanism could be applied to the formation of the AQS dimer, which takes a slipped edge-to-edge arrangement.

Water-soluble porphyrins tend to form stable stacked molecular complexes with various aromatics because of their well-extended π-electron system.[1] For example, a cationic porphyrin, 5,10,15,20-tetrakis[1-methylpyridinium-4-yl]porphyrin (TMPyP, 4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrakis[1-methylpyridinium]), complexes with various anionic benzoates and naphthalenesulfonates in aqueous solution through van der Waals interactions as well as Coulomb interactions.[2] Kano et al. used a system where Coulomb interaction acts as a repulsive force.[3] In spite of electrostatic repulsion, 5-phenyl-10,15,20-tris(*p*-sulfonatophenyl)porphyrin ($TPPS_3$, 4,4′,4″-(20-phenylporphyrin-5,10,15-triyl)tris[benzenesulfonate]) strongly interacts with anionic anthraquinone-2,6-disulfonate (AQDS) to form a stacked complex, the binding constant (K) being 4300 M^{-1} at 25 °C.[3] The $TPPS_3$ free base also forms π-complexes with 1- and 2-naphtharenesulfonates, 2-anthracenesulfonate (AS), and 1-pyrenesulfonate, which have no polar group, except for the sulfonato group.[4] The complexation has been assumed to be promoted by van der Waals interactions and entropic gain due to dehydration upon complexation. Cationic porphyrins also form molecular complexes with cationic aromatics, such as protonated proflavine (3,6-acridinediamine).[5] These results clearly reveal that the London dispersion force overcomes the electrostatic repulsive force.

A theoretical study on π–π interactions demonstrated that the σ–π interaction is an attractive force, while the π–π interaction is always repulsive in complexation between aromatic compounds.[6] According to this theory, a porphyrin dimer was predicted to take a slipped face-to-face arrangement. Indeed, an X-ray analysis shows the structure of a porphyrin dimer that is completely in agreement with the predicted one.[7] A T-shape benzene dimer is formed by the so-called CH–π interaction.[8] Chemical calculations as well as the experimental results show that the face-to-face arrangement becomes predominant in the case of a well-extended π-electron system, while the T-shape benzene dimer is more stable than the slipped face-to-face dimer.[8,9] Recent ab initio calculations suggest that no large difference in the stabilization energies exists between the T-shape and slipped face-to-face dimers of benzene.[10] Molecular dynamics calculations suggest that the T-shape complex is important in gas phase, while the face-to-face stacking arrangement becomes stable in the aqueous phase.[11]

Based on these findings, we can imagine the nature of the stacking interaction of aromatic compounds. Namely, aromatic compounds in aqueous solution tend to take slipped face-to-face and/or T-shape arrangements through σ–π or CH–π interactions to avoid the π–π electrostatic repulsion. Such a conclusion might generally be acceptable to complexation between aromatic molecules in aqueous solution. In the present study, we observed specific phenomena that indicate a "polar effect" in the stacking interactions. We found that AS without any polar group, except for a sulfonato group, does not form a stacked complex with a zinc complex of 5,10,15,20-tetrakis(*p*-sulfonatophenyl)porphyrin (ZnTPPS, 4,4′,4″,4‴-(porphyrin-5,10,15,20-tetrayl)tetrakis[benzenesulfonate] ion zinc complex), though AQS and AQDS having polar carbonyl groups show a relatively strong interaction with ZnTPPS. Such a result led us to the present study, which deals with the polar effects on stacking interaction between aromatic molecules. Few studies on the polar effects on the stacking interactions have been investigated. Cozzi et al. discussed the polar effect using the results with restricted rotation of two phenyl groups attached to the 1- and 8-positions of naphthalene.[12] There are a few examples where polar interactions are used to create supramolecular structures.[13,14]

Published on the web October 15, 2003; DOI 10.1246/bcsj.76.2027

Results

Interactions of AQS, AQDS, and AS with ZnTPPS. Kano et al. reported that AQS, AQDS, and AS form stacked complexes with the $TPPS_3$ free base, the K values being 1.05×10^4, 4.3×10^3, and 8.6×10^2 $dm^3\,mol^{-1}$ for AQS, AQDS, and AS, respectively, in 0.05 $mol\,dm^{-3}$ phosphate buffer at pH 8.0.[4] In the present study, we determined the K values for the complexation of AQS, AQDS, and AS with ZnTPPS under the same conditions. The absorption spectral changes of ZnTPPS (1.0×10^{-5} $mol\,dm^{-3}$) in 0.05 $mol\,dm^{-3}$ phosphate buffer at pH 8.0 upon the addition of AQS are shown in Fig. 1. The [AQS]-dependent changes in the optical densities at 553, 572, and 611 nm were simultaneously fitted with a K value using a non-linear least-squares method (damping Gauss-Newton method) developed by Professor Y. Kuroda at Kyoto Institute of Technology. The determined K value is shown in Table 1. The same method afforded the K value for the AQDS–ZnTPPS system (Table 1). The K value for the AQDS complex is much smaller than that for the AQS one, which is the same tendency as the $TPPS_3$ free base shows.[4] The complexes of ZnTPPS are less stable than those of $TPPS_3$. Destabilization seems to be ascribed to a steric hindrance due to a water molecule bound to the zinc ion as an axial ligand.[1] Meanwhile, no evidence for complexation with ZnTPPS was obtained with AS that does not have any polar group, except for the sulfonato group. No absorption spectral change was observed with AS upon the addition of ZnTPPS.

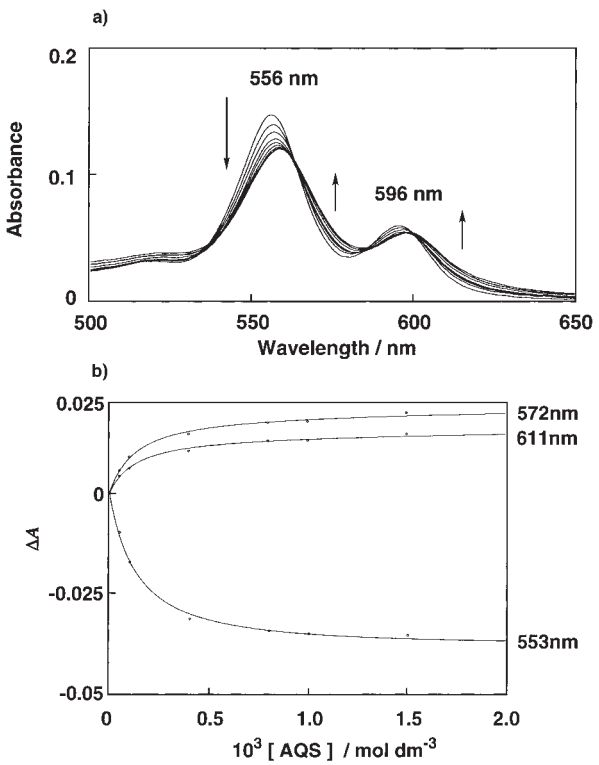


Fig. 1. (a) Absorption spectral changes of ZnTPPS (1×10^{-5} $mol\,dm^{-3}$) upon addition of AQS ($0–1.5 \times 10^{-3}$ $mol\,dm^{-3}$) in 0.05 $mol\,dm^{-3}$ phosphate buffer at pH 8.0 and 25 °C and (b) curve-fitting analysis of the data by the equation for 1:1 complex formation.

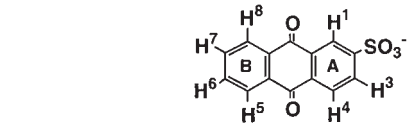
Table 1. Binding Constants for Complexation of AQS, AQDS, and AS with ZnTPPS and $TPPS_3$ in Aqueous Solution[a)]

System	K/$dm^3\,mol^{-1}$	Ref.
AQS–ZnTPPS	7800 ± 400	This work
AQDS–ZnTPPS	1500 ± 190	This work
AS–ZnTPPS	not determined	This work
AQS–$TPPS_3$	10500 ± 1100	4
AQDS–$TPPS_3$	4300 ± 300	4
AS–$TPPS_3$	860 ± 30	4

a) The absorption spectral changes of ZnTPPS (1×10^{-5} $mol\,dm^{-3}$) were measured as a function of the concentration of AQS, AQDS, or AS in 0.05 $mol\,dm^{-3}$ phosphate buffer at pH 8.0 and 25 °C.

In the case of the $TPPS_3$ free base, AS forms a molecular complex, though the K value (860 $dm^3\,mol^{-1}$) for the AS–$TPPS_3$ complex is much smaller than those for the AQS (1.05×10^4 $dm^3\,mol^{-1}$) and AQDS complexes (4.3×10^3 $dm^3\,mol^{-1}$).[4] A charge-transfer interaction was assumed to stabilize the complex of $TPPS_3$ and the anthraquinones, though a further study was not carried out.[4]

In order to determine the structure of the complex of AQS and ZnTPPS, ^{1}H NMR spectral changes of AQS in D_2O were measured as a function of [ZnTPPS]. The results are shown in Fig. 2. The signals of the protons at a hydrophobic ring (ring B) of AQS remarkably shift to higher magnetic fields, and are broadened upon the addition of ZnTPPS. Meanwhile, the signals of the protons at a hydrophilic ring (ring A) shift to higher



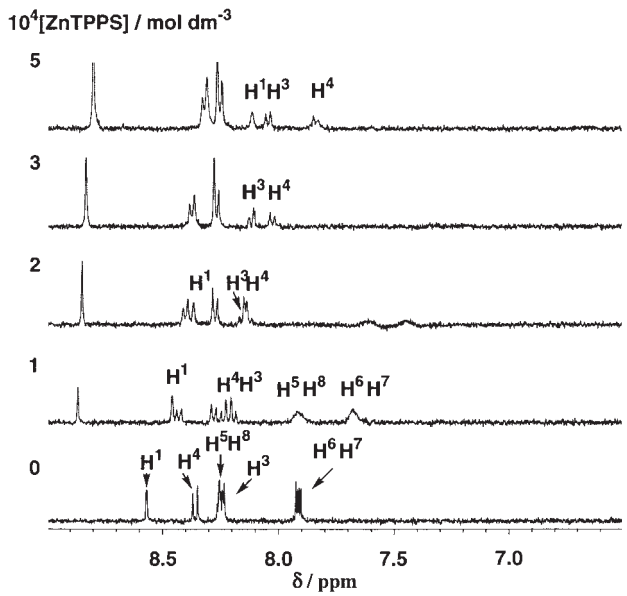


Fig. 2. ^{1}H NMR spectral changes of AQS (5×10^{-4} $mol\,dm^{-3}$) upon addition of ZnTPPS in D_2O at pD 8.0 and 25 °C.

magnetic fields more gently as compared with those at ring B. No remarkable broadening was observed with the H^1, H^3, and H^4 protons at ring A. The saturated complexation-induced shifts of AQS ($\Delta\delta_{sat}$), which mean the changes in the chemical shifts when all AQS molecules form the complex with ZnTPPS, are shown in Fig. 3. The $\Delta\delta_{sat}$ values were calculated from the K value; the results are shown in Fig. 2.[15] The $\Delta\delta_{sat}$ values for the protons at ring B are much larger than those at ring A, indicating that the hydrophobic ring B is located on the porphyrin ring, while the hydrophilic ring A is settled in the area where the ring-current effects due to the porphyrin ring are relatively weak. If the AQS molecular plane is aligned parallel to the porphyrin ring, the signals of H^1, H^3, and H^4 should be broadened. In addition, since the sulfonato group should be placed in the aqueous bulk phase to avoid the contact with the porphyrin plane, the protons at ring A need to be located at a deshielding area of the porphyrin ring. In such a case, the signals due to H^1, H^3, and H^4 are expected to shift to lower magnetic fields. The experimental results disagree with this assumption. The results shown in Figs. 2 and 3 strongly suggest that the AQS molecule sits on the porphyrin ring in a tilted form, as drawn in Fig. 4a. A hydrophilic part of AQS is located farthest from the hydrophobic porphyrin ring to take a tilted arrangement. Therefore, the protons at ring A are affected by the ring-current effects due to the porphyrin ring much more weakly compared with the protons at ring B.

The ^{1}H NMR spectral changes of AQDS upon the addition of ZnTPPS are shown in Fig. 5. There is no hydrophobic aromatic ring in AQDS. The proton signals due to H^1, H^3, and H^4 appear at the same range as those of AQS. The $\Delta\delta_{sat}$ val-

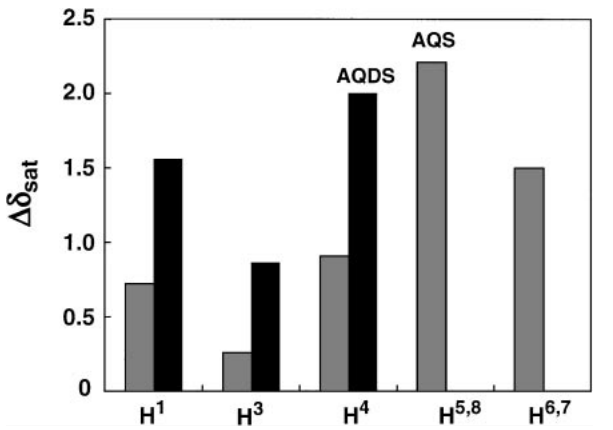


Fig. 3. Saturated complexation-induced shifts ($\Delta\delta_{sat}$) of AQS and AQDS complexed with ZnTPPS in D_2O at pD 8.0 and 25 °C.

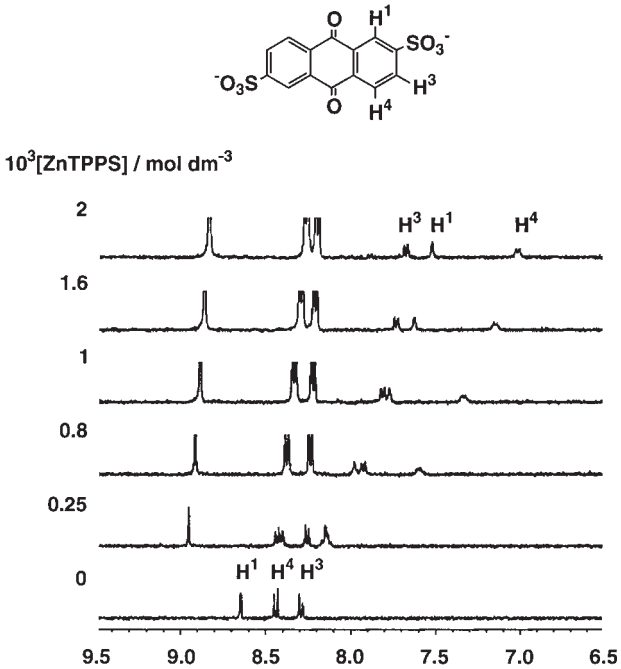


Fig. 5. ^{1}H NMR spectral changes of AQDS (5×10^{-4} mol dm^{-3}) upon addition of ZnTPPS in D_2O at pD 8.0 and 25 °C.

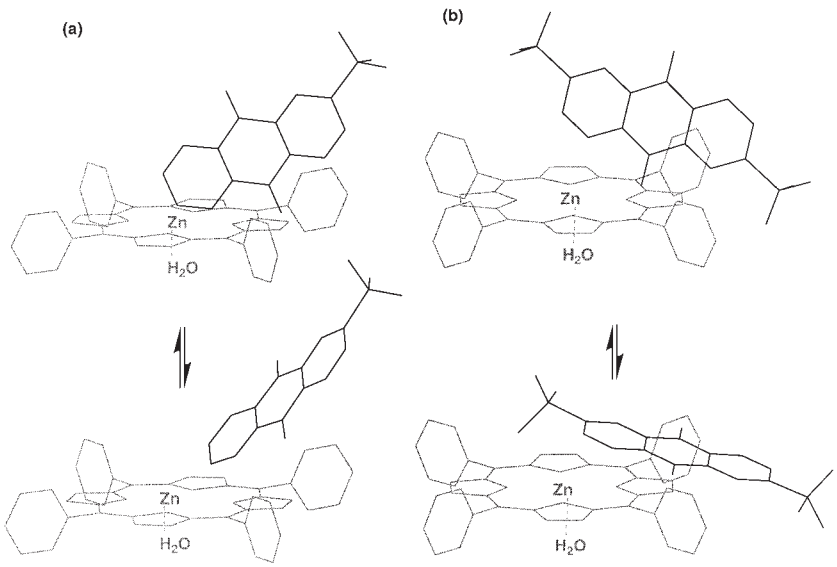


Fig. 4. Plausible structures of (a) AQS–ZnTPPS and (b) AQDS–ZnTPPS complexes. Only skeletons of AQS, AQDS, and ZnTPPS are drawn and the SO_3^- groups of ZnTPPS are omitted for clarity.

ues for the protons of AQDS are exhibited in Fig. 3. The $\Delta\delta_{sat}$ values of AQDS are significantly larger than those of the protons at ring A of AQS. The protons of AQDS correspond to the protons at ring A of AQS. Different from the case of AQS, the hydrophilic part of AQDS should be located on the porphyrin ring, yielding large upfield shifts of the H^1, H^3, and H^4 protons. The most plausible structures are shown in Fig. 4b, which can explain the ^{1}H NMR results reasonably. The assumption that a half part of the AQDS molecule sits on the porphyrin ring is supported by the fact that the $\Delta\delta_{sat}$ of the H^1 and H^4 protons of AQDS are comparable to those of the $H^{5,8}$ and $H^{6,7}$ protons of AQS. Although the 2D NMR spectra of the AQS– and AQDS–ZnTPPS systems were measured, no distinct correlation peak was observed.

Self-aggregation of AQS and AQDS. We accidentally found the self-aggregation of AQS and AQDS in aqueous solution. The concentration-dependent ^{1}H NMR spectral changes were measured with AQS in D_2O (Fig. 6). As the concentration of AQS increased, all of the proton signals of AQS shifted to higher magnetic fields. Such a result suggests the self-association of AQS. At first, we assumed the dimer formation. The association constant for dimerization can be evaluated by using the method of Bangerter and Chan.[16] The chemical shift of a proton in the sample (δ) is expressed by

$$\delta = \{1 + 4K_2[S]_t - (1 + 8K_2[S]_t)^{1/2}\}(\delta_2 - \delta_1)(4K_2[S]_t)^{-1} + \delta_1, \quad (1)$$

where K_2 is the association constant for dimerization, $[S]_t$ is the total concentration of AQS, δ_1 is the chemical shift of the monomer, and δ_2 is the chemical shift of the dimer. The

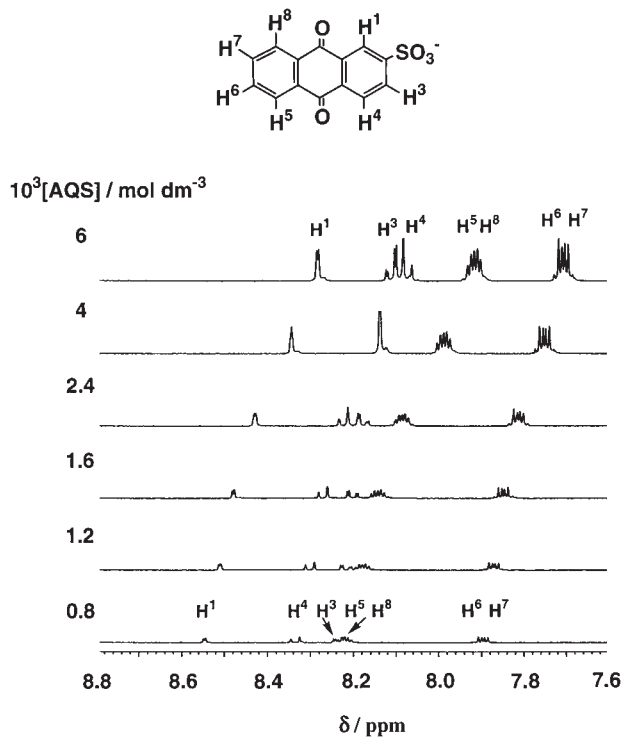


Fig. 6. Concentration-dependent ^{1}H NMR spectral changes of AQS in D_2O at pD 8.0 and 25 °C.

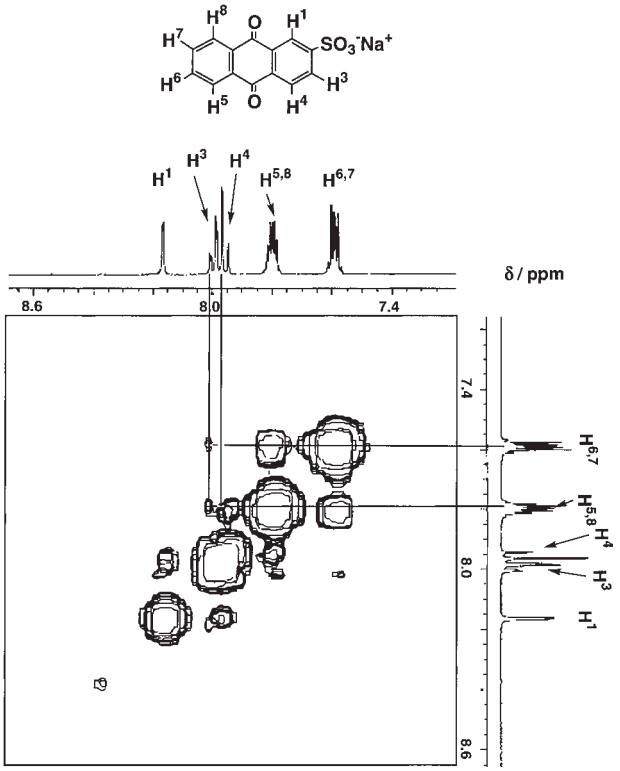


Fig. 7. NOESY spectrum of 6×10^{-3} mol dm^{-3} solution of AQS in D_2O at pD 8.0 and 25 °C. The mixing time for the NOESY measurement was 600 ms.

data shown in Fig. 6 were computed by curve fitting using a commercially available software (KaleidaGraph, HULINKS). Good fitting of the data to Eq. 1 suggests the formation of the AQS dimer. The K value for the dimerization of AQS was evaluated to be 72 ± 4 dm^3 mol^{-1}. The NOESY spectrum of the 6×10^{-3} mol dm^{-3} AQS solution is shown in Fig. 7, where correlation peaks between H^3 and H^6 and/or H^7, H^3 and H^5 and/or H^8, and H^4 and H^5 and/or H^8 were detected. It is noteworthy that there is no correlation between H^1 and H^5. If the dimer takes a face-to-face arrangement (Fig. 8a), the correlation should exist between H^1 and H^5. In addition, the electrostatic repulsion between two AQS molecules should be largest for this arrangement. The plausible structures, which explain the NMR data, are shown in Figs. 8b–d. The NOESY spectrum suggests the formation of a slipped edge-to-edge dimer, as shown in Fig. 8b. Assuming the cross peaks between H^3 and H^5 and H^3 and H^6, the structure shown in Fig. 8b is derived for the AQS dimer. The space-filling molecular model indicates that the H^3 proton is placed close to both H^5 and H^6 protons. The structure shown in Fig. 8c is profitable for interpreting the upfield shifts of the H^1, H^8, and H^7 protons and the cross peaks between H^3 and H^7 and H^4 and H^8. Although the structure shown in Fig. 8d is also plausible, no evidence was obtained for such a type of dimer. In any case, the slipped edge-to-edge dimer of AQS seems to be formed. Such an edge-to-edge aggregate is called a J-aggregate. The J-aggregates of diprotonated TPPS[17] and cyanine dyes[18] have been known.

The proton signals of AQDS also shifted to higher magnetic fields as the concentration of AQDS increased, though the shift

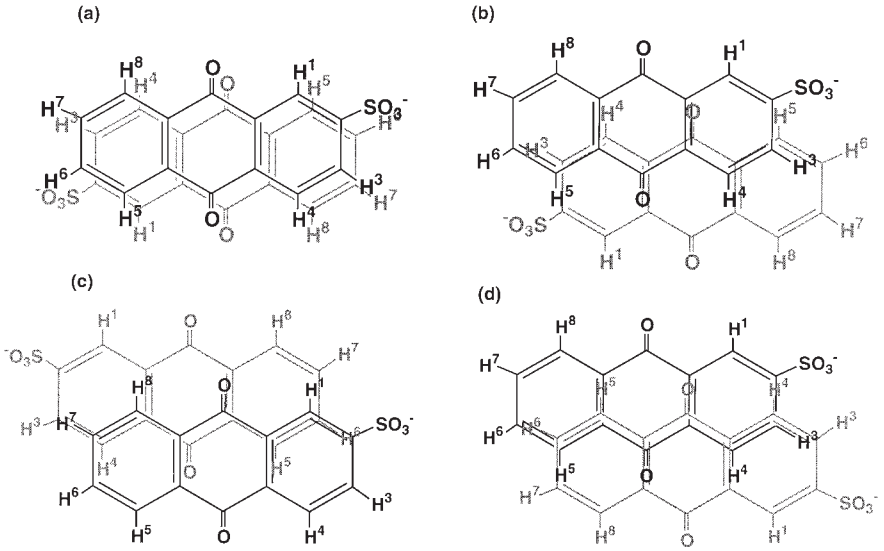


Fig. 8. Structures of the AQS dimer. (a) Irrelevant face-to-face and (b) relevant slipped edge-to-edge dimers of AQS.

in each chemical shift was much smaller than in the case of AQS. In addition, the concentration-dependent NMR spectral changes could not be analyzed by the equation applied for dimer formation. Presumably, higher self-aggregates are formed in the case of AQDS. No self-aggregation was observed with AS. The polar carbonyl groups are also essential for the dimerization of AQS and the self-aggregation of AQDS.

Interactions of Benzoate Anions with ZnTPPS. In order to confirm the polar effects on the molecular complexation of ZnTPPS, the interactions of ZnTPPS with mono-substituted benzoate anions, which are the original species used to discuss the electronic effects on chemical phenomena of aromatic molecules, were investigated. Schneider and Wang also used various benzoate anions to investigate the interactions between cationic porphyrins and anionic aromatics.[2] In their case, however, an electrostatic attractive force makes the story complex.

The ^{1}H NMR signals of the benzoate anion (5×10^{-4} mol dm^{-3}) without any substituent appeared at 7.480 (*meta*-H), 7.549 (*para*-H), and 7.872 ppm (*ortho*-H) in D_2O at pD 8.0 (0.05 mol dm^{-3} phosphate buffer). These signals shifted to higher magnetic fields by ca. 0.01 ppm upon the addition of 3×10^{-3} mol dm^{-3} ZnTPPS. The complexation-induced shifts in the chemical shifts (CIS, $\Delta\delta$) were too small to evaluate K value. Very slight upfield shifts of the ^{1}H NMR signals were also observed with the *p*-hydroxy- and *p*-methylbenzoate anions. No change in the UV–vis absorption spectrum of ZnTPPS was observed upon the addition of these benzoate anions. Meanwhile, the addition of ZnTPPS to the benzoate anions having electron-withdrawing groups, such as *p*-NO_2, *m*-NO_2, *p*-CN, *m*-CN, *p*-$COCH^3$, *p*-CHO, *p*-F, *p*-Cl, and *p*-I, caused marked upfield shifts of the ring protons of the benzoate anions. As a typical example, the ^{1}H NMR spectral changes of the *p*-acetylbenzoate anion are shown in Fig. 9. A curve-fitting analysis[19] afforded the K value for each system; the results are summarized in Table 2. There is a rough linear-relationship between the K values for the complexation of *p*-substituted benzoates having electron-withdrawing groups and Hammett's σ values. The data for *meta*-derivatives deviate from this relationship. The linear relationship predicts that the K value for the benzoate anion, itself, is ca. 60 dm^3 mol^{-1}. However, the experiment indicated that the K value for the benzoate–ZnTPPS system is almost zero. Cozzi et al. found a linear relationship between the $\Delta G^{\ddagger}$ values for rotation of the substituted phenyl groups of 1-(*o*-methylphenyl)-8-(*p*-substituted phenyl)naphthalenes and the Hammett's σ values.[12a] The electron-withdrawing groups at the *para*-positions of the substituted phenyl groups at the 8-position of naphthalene cause a restriction of the rotation of the substituted phenyl groups. They called such an effect "polar/π inter-

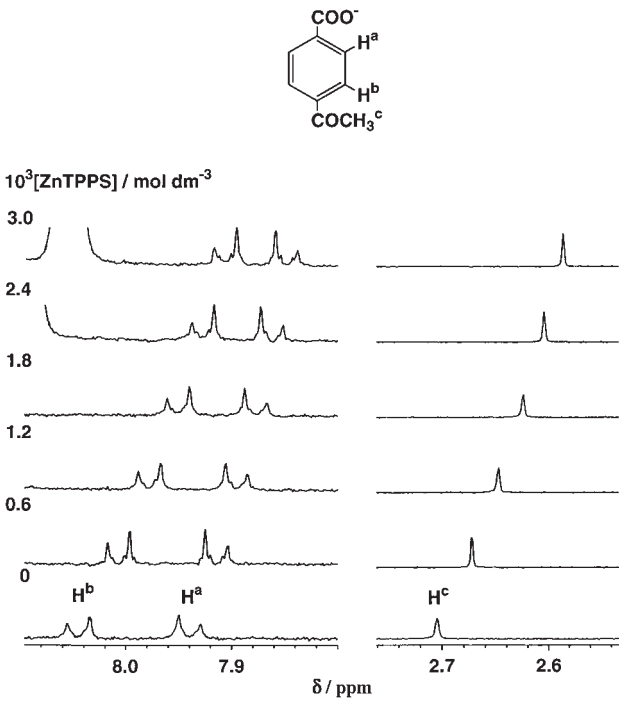


Fig. 9. ^{1}H NMR spectral changes of the *p*-acetylbenzoate anion (5×10^{-4} mol dm^{-3}) upon addition of ZnTPPS in D_2O at pD 8.0 and 25 °C.

Table 2. Binding Constants for Complexation of the Mono-Substituted Benzoate Anions with ZnTPPS in D_2O[a] and Hammett's σ Values

Benzoates	σ	K/dm^3 mol^{-1}
p-NO_2	0.78	180 ± 6
m-NO_2	0.71	60 ± 10
p-CN	0.66	120 ± 8
m-CN	0.56	20 ± 10
p-$COCH_3$	0.50	140 ± 10
p-CHO	0.43	120 ± 6
p-I	0.18	100 ± 10
p-Cl	0.23	90 ± 10
p-F	0.06	130 ± 10
H	0	too small
p-OH	−0.37	too small
p-CH_3	−0.17	too small

a) The $\Delta\delta$ values of the protons of the benzoate anions (5×10^{-4} mol dm^{-3}) were measured as a function of [ZnTPPS] in D_2O at pD 8.0 (0.05 mol dm^{-3} phosphate buffer) and 25 °C.

Table 3. Binding Constants for Complexation of 4-Fluoro-, 3,5-Difluoro-, and 3,4,5-Trifluorobenzoate Anions with ZnTPPS in D_2O[a]

Benzoate Anion	K/dm^3 mol^{-1}
4-Fluorobenzoate	130 ± 10
3,5-Difluorobenzoate	160 ± 15
3,4,5-Trifluorobenzoate	220 ± 10

a) The $\Delta\delta$ values of the protons of the benzoates (5×10^{-4} mol dm^{-3}) were measured as a function of [ZnTPPS] in D_2O (0.05 mol dm^{-3} phosphate buffer) at pD 8.0 and 25 °C.

action". The present finding is similar to that reported by Cozzi et al.[12]

The polar effect on the stacking interaction was further verified by the results given in Table 3, where the K values for the complexation of mono-, di-, and tri-fluorinated benzoates with ZnTPPS are listed. The lower is the π-electron density of the benzoate anion, the more stable is the molecular complex with ZnTPPS.

Discussion

It has been well known that dyes, such as Acridine Orange and cyanines, in aqueous solutions tend to aggregate spontaneously despite an electrostatic repulsion between the dye molecules.[20] Such a molecular association has been explained simply in terms of van der Waals interactions. In the case of the molecular association of aromatic compounds, the term "π–π interaction" has often been used without careful consideration. However, Hunter and Sanders warned that π–π interactions between aromatic molecules are always repulsive (repulsive Coulomb interactions), and that σ–π and/or CH–π interactions essentially act as attractive forces (attractive Coulomb interactions).[6] The structure of a porphyrin dimer energy-minimized according to this theory takes a slipped face-to-face arrangement, where one-fourth of the porphyrin ring overlaps another in the dimer unit.[6] We found that a porphyrin having alkyl chains at the meso-positions takes such an arrangement in its crystalline state, and that the average distance between the porphyrin planes is 0.36 nm.[7] In the case of 5,10,15,20-tetraphenylporphyrin (TPP), whose meso-positions are occupied by the bulky phenyl groups, the average distance between the porphyrin planes in the crystalline form is 0.65 nm.[7] A Monte Calro simulation carried out by Jorgensen and Severance suggested that the Coulomb interactions between arene molecules are attractive in a T-shape arrangement, while it is repulsive in a stacked arrangement.[8] A preferential arrangement of a molecular complex is dominated by the sum of the Coulomb and London dispersion energies (ΔH_t). The London dispersion force of a well-extended π-electron system in a stacked form is larger than that of a small π-electron system. Since ΔH_t for the benzene–anthracene pair in the stacked form is smaller than that in the T-shape form, because of a large dispersion energy for the stacked form, this pair is expected to take the stacked form. Meanwhile, since the Coulomb repulsive force between two benzene molecules is relatively large, as compared with the London dispersion force in the stacked form, the benzene dimer takes the T-shape arrangement.[8] Wilcox and co-workers claimed that the London dispersion force is the most important factor, even for the CH–π interaction, and that the Coulomb interaction is less important.[21] Meanwhile, distinct polar effects on the interaction between the arene moieties at the 1- and 8-positions of naphthalene were experimentally observed by Cozzi et al.[12]

In the present study, we subordinately found the self-aggregation of AQS. It has been known that 1-amino-4-alkylaminoanthraquinone-2-sulfonates dimerizes in aqueous solution.[22] Based on the ^{1}H NMR spectral data, we postulate the structures of the AQS dimers as shown in Figs. 8b–d, which are the slipped edge-to-edge dimers. A quite similar structure was measured with a crystal of Acridine Orange (*N*,*N*,*N*′,*N*′-tetramethyl-3,6-acridinediamine) by means of X-ray crystallography.[23] If the structures shown in Figs. 8b–d are correct, we can discuss the polar effect on the molecular association of aromatic compounds. The carbonyl groups at the 9- and 10-positions withdraw the π-electrons on the anthraquinone ring. Especially, the π-electrons located between fused sp^2 carbons are drawn strongly. Therefore, the electrostatic repulsion between electron-poor C–C double and electron-rich carbonyl double bonds may not be serious in the dimer arrangements shown in Figs. 8b–d. The structure shown in Fig. 8a is a face-to-face dimer whose π–π repulsion is maximally large. Based on the fact that AS without an electron-withdrawing group does not form a self-aggregate, it can be concluded that the polar carbonyl groups contribute to diminish the Coulomb repulsive interaction between the AQS molecules, and that the London dispersion force gathers the AQS molecules, thus affording the slipped edge-to-edge dimer.

A polar effect on the stacking interaction was clearly observed for interactions of ZnTPPS with mono-substituted benzoate anions. Namely, the electron-withdrawing groups stabilize the stacked complexes, while the electron-donating groups involving hydrogen completely inhibit the stacking interaction between the benzoates and ZnTPPS (Table 2). No correlation was found between the calculated polarizabilities (α) of the

benzoates[24] and the K values. Meanwhile, a rough linear relationship exists between the K values for complexation of the *para*-substituted benzoates having the electron-withdrawing groups and the Hammett's σ values. Our results are consistent with those obtained by Cozzi et al.[12] However, the results that the benzoate anion without any substituent and the *p*-methyl- and *p*-methoxybenzoate anions do not interact with ZnTPPS are hardly explained by a simple polar effect. Although the detailed mechanism for the interaction between ZnTPPS and mono-substituted benzoate anions has not been clarified, it may be concluded that the electron-withdrawing groups in the benzoates diminish the π–π repulsive interaction to make the London dispersion force effective for stacking. The van't Hoff plot provided the enthalpy (ΔH^0) and entropy changes (ΔS^0) for the association of the *p*-cyanobenzoate anion and ZnTPPS to be -27.6 ± 2.4 kJ mol^{-1} and -53.5 ± 8.0 J mol^{-1} K^{-1}, respectively.[25] These thermodynamic parameters suggest the van der Waals interaction to be the main binding force as previously discussed for the complexation of the cationic porphyrin free bases with *p*-benzoquinone.[26]

^{1}H NMR data suggest the structure of the ZnTPPS–AQS complex as shown in Fig. 4a. In order to avoid a steric hindrance due to the sulfonatophenyl groups at the meso-positions of ZnTPPS, the AQS molecule should tilt against the porphyrin plane. In such a structure, the stacking interaction of ZnTPPS mainly occurs with hydrophobic ring B. There are two possible arrangements for the tilted arrangement, the face-to-face type and the T-shape type (see Fig. 4). We could not verify which arrangement is more stable.

As a consequence, the present study suggests the important contribution of the polar effect to stacking interactions between aromatic molecules, which have been demonstrated by Kano et al.[4] and Cozzi et al.[12]

Experimental

ZnTPPS was prepared by reacting TPPS (Tokyo Kasei, $-SO_3H$ form) with zinc oxide in boiling water.[27] After the reaction, the reaction mixture was filtered using a membrane filter, and the filtrate was passed through an ion-exchange region column (DOWEX HCR-W2, 20–50 mesh) to obtain Na salt. ZnTPPS in water was purified by gel-filtration (Sephadex^{TM} G-25 Fine). An elemental analysis indicated the formation of ZnTPPS$\cdot$7H$_2$O. Anal. Calcd for $C_{44}H_{26}N_4Na_4O_{12}S_4Zn\cdot 7H_2O$: C43.52; H, 3.32; N, 4.61%; found: C, 43.02, H, 3.17; N, 4.35%. The AS sodium salt was prepared by the reduction of AQS sodium salt (Nacalai) with zinc powder in 28% aqueous ammonia.[28] The reaction mixture was filtered and the filtrate was treated with active carbon. Crude AS was repeatedly recrystallized from water. The AQDS disodium salt purchased from Tokyo Kasei was recrystallized from water. The benzoic acids (reagent grades) were purchased and used without further purification.

The absorption spectra were measured on a Shimadzu UV-2100 spectrophotometer. The ^{1}H NMR spectra (400 MHz) were taken on a JEOL GX-400 spectrometer using 3-trimethylsilyl[2,2,3,3-d_4]propionate (TSP, Aldrich) as an external standard.

This work was supported by a Grand-in-Aid for Scientific Research B (KAKENHI 14340224) from the Ministry of Education, Culture, Sports, Science and Technology.

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