

Specific binding of iodide ion to N-confused tetraphenylporphyrin (NC-TPP) at the air–water interface

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Halide recognition by a porphyrin aggregate at the air–water interface has been studied. π -A Isotherms and UV reflection spectra of mixed monolayers of 5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin, trivial name 'N-confused tetraphenylporphyrin' (NC-TPP), with methyl octadecanoate were measured in 1 mmol dm⁻³ NaX aqueous solution (X = F, Cl, Br, I). π -A Isotherms of NC-TPP alone were extracted from those of the mixed monolayers at various mixing ratios. Among the anions investigated, only the I⁻ containing subphase gave a more condensed π -A isotherm and a shifted UV reflection spectrum. The Soret band showed a red shift (465 nm) in NaI solution and blue shifts (425 nm) in pure water and in the other salt solutions, and these shifts were attributed to the occurrence of two different aggregation modes, J-like aggregate and H aggregates, respectively. X-Ray photoelectron spectroscopy (XPS) also demonstrated the incorporation of iodine but no other halogen atoms in the LB films. Loss of counterions (F⁻, Cl⁻, Br⁻) in concurrence with deprotonation during LB transfer apparently induced formation of the J-like aggregate of free-base NC-TPP in the transferred films. In contrast, iodide was kept in the film upon LB transfer, because the aggregation mode of NC-TPP remained unchanged. The important role of the modes of porphyrin aggregation in the anion recognition is discussed.

Introduction

Cation recognition has been widely studied with a variety of hosts such as crown ether,¹ cyclophane,² spherand³ and calixarene.^{4,5} In contrast, examples of anion recognition are limited, despite the fact that simple anions play important roles in biological systems.⁶ Most of the reported examples are based on polymers and liquid films that contain lipophilic ion exchangers such as quaternary ammonium and phosphonium salts.⁷⁻⁹ These membrane transports obey the Hoffmeister series (ClO₄⁻ > SCN⁻ > I⁻ > NO₃⁻ > Br⁻ > NO₂⁻ > Cl⁻) where hydrophobic anions show preferred partition coefficients between aqueous and membrane phases.¹⁰ Anion selectivity different from the Hoffmeister series has been reported for cyclic cations,^{11,12} molecules with specific cavities,^{13,14} hosts with Lewis-acidic sites,¹⁵⁻¹⁷ hydrogen donors^{18,21} and metal porphyrins with anion co-ordination sites.²²⁻²³

In addition to these designed host molecules, specific assemblies of rather simple molecules might be useful for construction of anion recognition sites that do not obey the Hoffmeister series. In order to develop such an anion recognition system, we investigated the monolayer property of 5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin, trivial name 'N-confused tetraphenylporphyrin' (NC-TPP), in subphases containing various halide ions. NC-TPP, in which one of the four pyrrole rings is linked through its α - β' axis instead of the conventional α - α' linkage, is a novel isomer of conventional tetraphenylporphyrin (TPP).^{24,25} NC-TPP is a suitable anion receptor because it exists as a mono-protonated form in the neutral pH region and thus requires a counteranion.²⁴ Like other dyes,²⁶⁻²⁹ porphyrins are known to show specific spectral changes in the Soret band depending on their aggregation modes.³⁰ The inter-plane distance and the extent of face-to-face overlapping affect the exciton coupling interaction³¹⁻³⁴ in the aggregates, and specific blue and red shifts are induced by formation of H aggregate and J-like aggregate, respectively. Anion binding to aggregated porphyrins may induce a consequent change in the mode of aggregation and spectral characteristics. Here, we report specific I⁻ recognition by mixed

monolayers of NC-TPP and methyl octadecanoate. To our knowledge, this is the first example of 'aggregation-mediated' anion recognition on the monolayer.

Results and discussion

π -A Isotherms

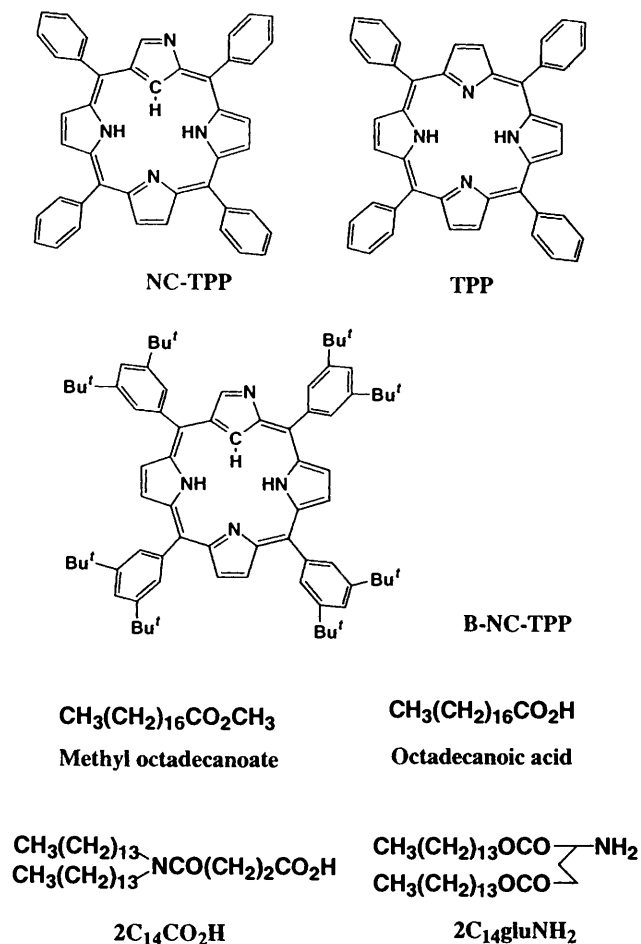
The porphyrins and lipids used in this study are summarized in Scheme 1. In a preliminary experiment, NC-TPP alone was spread on a pure water subphase. Its π -A isotherm showed a very small molecular area (<0.1 nm²) and a poor reproducibility that suggests formation of collapsed NC-TPP layers. Therefore, NC-TPP was diluted with monolayer-forming lipids (matrix lipids) in the stock solution and then spread on water. π -A Isotherms of mixed monolayers of NC-TPP and neutral methyl octadecanoate (NC-TPP:lipid = 0.034–0.089) have satisfactory reproducibility. Their π -A isotherms on pure water are shown in Fig. 1 where the x-axis represents a molecular area per methyl octadecanoate molecule. Two-step collapse behaviour is clearly observed, suggesting that the two components are phase-separated. The molecular area increased with increasing NC-TPP content, indicating a contribution of NC-TPP molecules to the total area.

The porphyrin component in the π -A isotherm can be estimated according to the following procedure.³⁵ When the two components are sufficiently phase-separated the total area, *A*, occupied by a mixed monolayer should be a simple sum of the areas of NC-TPP and the matrix lipid (methyl octadecanoate) as shown in eqn. (1) where *A_m*, *N_m*, *A_p* and *N_p*

$$A = A_m N_m + A_p N_p \quad (1)$$

are the molecular area of the matrix lipid, the number of matrix lipid molecules, the molecular area of NC-TPP and the number of NC-TPP molecules, respectively. Eqn. (2) is derived from eqn. (1); according to eqn. (2), the slope in the plot of *A/N_m* vs.

$$\frac{A}{N_m} = A_m + A_p \frac{N_p}{N_m} \quad (2)$$



Scheme 1 Structures of porphyrins and lipids used in this research

N_p/N_m is equal to the molecular area of NC-TPP, A_p . The data in Fig. 1(a) plotted at 5 mN m^{-1} intervals show satisfactory linearities at all the pressures as shown in Fig. 1(b), confirming the suitability of this method. The A_p values were calculated from the slope by a least-squares method at 0.5 mN m^{-1} intervals with good correlation coefficients (> 0.990). Now, it is possible to calculate a hypothetical π -A isotherm for NC-TPP alone by plotting A_p data points obtained at 0.5 mN m^{-1} intervals. Fig. 2 summarizes such π -A isotherms for NC-TPP in 1 mmol dm^{-3} NaX ($X = \text{F, Cl, Br, I}$). The isotherms (except for NaI) gave very similar shapes: surface pressures start to rise at *ca.* 1 nm^2 , and the presence of both expanded and condensed phases are seen with collapse pressures at *ca.* 32 mN m^{-1} . The limiting areas obtained by extrapolation of the condensed phase are *ca.* 0.5 nm^2 in these cases. Miller *et al.*³⁶ estimated the molecular area of TPP to be *ca.* 2 nm^2 for the porphyrin ring oriented parallel to the surface and *ca.* 0.5 nm^2 when oriented perpendicular to the surface. Our data are essentially identical to the latter, and NC-TPP in the monolayer is probably oriented perpendicular to the water surface. The π -A isotherm on 1 mmol dm^{-3} NaI shows a steeper curve with a lower collapse pressure, although the limiting area is virtually the same as those of the other salts. Clearly NaI exerted a specific effect on the NC-TPP monolayer.

Subsequently, the effect of pH on the π -A isotherm was measured (NaOH and H_2SO_4 were used to adjust pH) in the presence and absence of 1 mmol dm^{-3} NaX. The methyl octadecanoate monolayer alone showed no detectable pH dependency. In contrast, π -A isotherms of NC-TPP/methyl octadecanoate clearly showed pH dependency. As in the previous case, the NC-TPP component of the isotherm was estimated and is demonstrated in Fig. 3(a) for pH 3, 7 and 11. The pH dependency is pronounced. In order to understand the

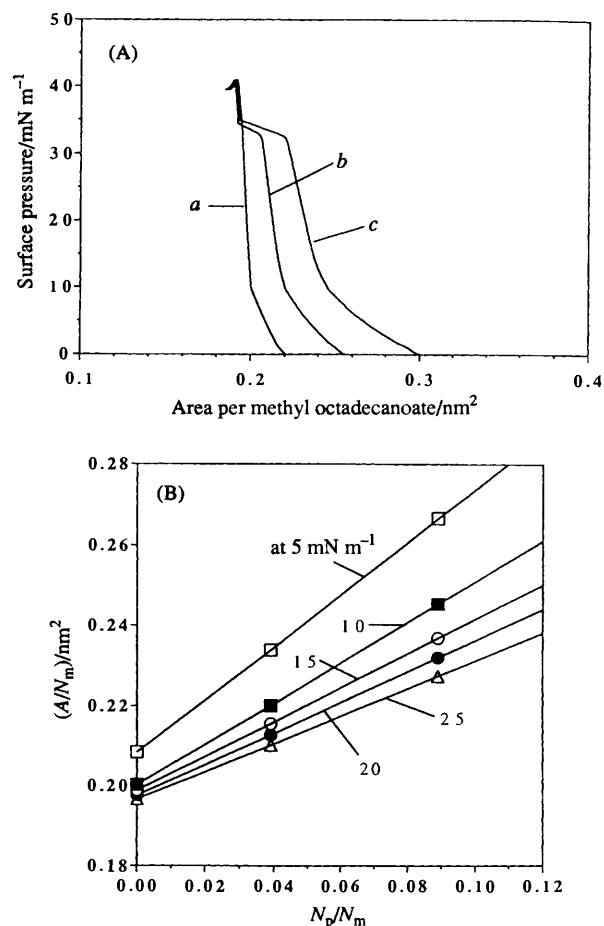


Fig. 1 (a) π -A Isotherms of monolayers of NC-TPP and methyl octadecanoate in pure water at 20°C ; x-axis represents area per methyl octadecanoate molecule. NC-TPP/methyl octadecanoate (molar ratio): a, 0; b, 0.039; c, 0.089. (b) Plots of A/N_m vs. N_p/N_m obtained from Fig. 1(a) at 5 mN m^{-1} intervals [see eqn. (2) in the text].

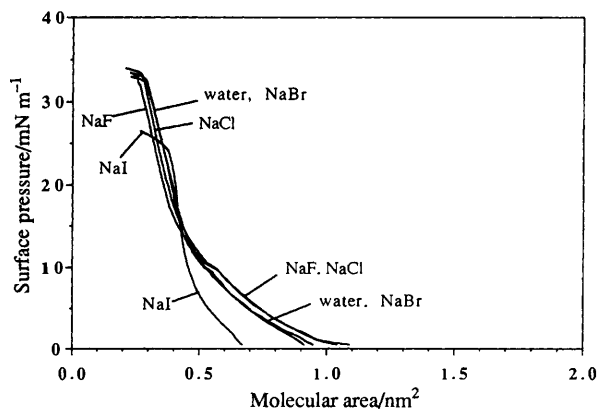


Fig. 2 π -A Isotherms of NC-TPP alone in 1 mmol dm^{-3} aqueous NaX and in pure water at 20°C . The curves are calculated from π -A isotherms of the mixed monolayer of NC-TPP and methyl octadecanoate according to the method described in the text.

mechanism of the observed pH dependency the π -A isotherms of the mixed monolayer were extensively measured for numerous subphase conditions (pH, salt). The calculated molecular areas of NC-TPP at a fixed surface pressure of 25 mN m^{-1} are plotted as a function of subphase pH of 2 to 12, as shown in Fig. 3(b). The molecular areas (except for that on NaI) give essentially the same pH profile with two inflection points at around pH 3 and 9.5. It is reported that NC-TPP dissolved in an aqueous micelle of sodium dodecyl sulfate gives two $\text{p}K_a$ values (3.27 and 8.35) that correspond to conversion of the di-protonated to mono-protonated form and of the mono-

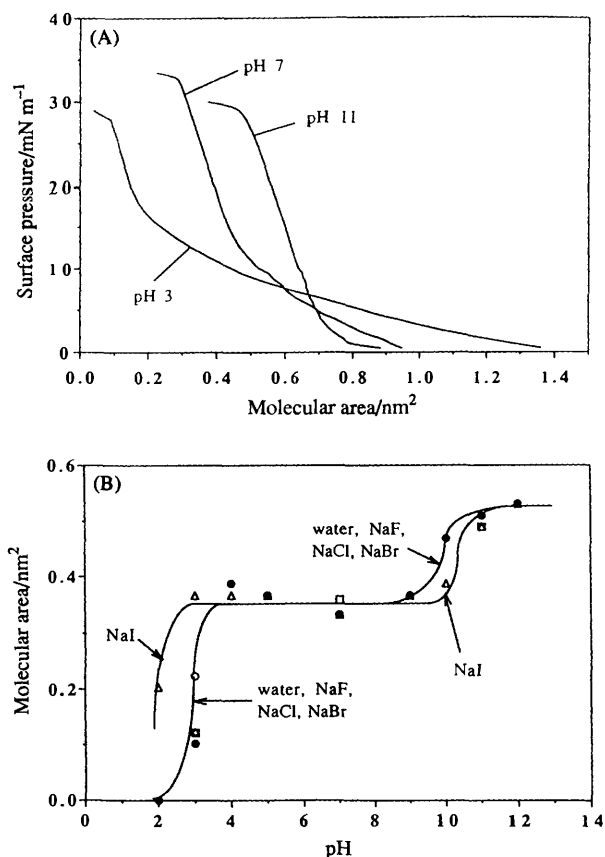


Fig. 3 (a) π -A Isotherms of NC-TPP alone at pH 3, 7 and 11 in the absence of halogen ions (20 °C). (b) The pH profiles of the molecular area of NC-TPP at 25 mN m⁻¹ in pure water (●), in 1 mmol dm⁻³ NaF (○), in 1 mmol dm⁻³ NaCl (◇), in 1 mmol dm⁻³ NaBr (□) and in 1 mmol dm⁻³ NaI (△). Molecular areas in NaF, NaCl and NaBr were measured only at pH 3, 7 and 11.

protonated to free-base form, respectively.²⁴ Therefore, NC-TPP in the micelle exists as a mono-protonated form from pH 4 to pH 8. In the same vein, NC-TPP molecules in the monolayer should also exist as a mono-protonated form in the neutral pH region. As shown in Fig. 3(a), the π -A isotherm at pH 3 was significantly expanded at low surface pressures but is much condensed at high pressures. Apparently, di-protonation of NC-TPP at pH 3 induces formation of a significantly expanded phase due to charge repulsion, but this species may be dissolved in the acidic subphase by compression. The π -A isotherm at pH 11 showed a condensed phase only and its limiting area observed at pH 11 was larger than that at pH 7. This observation suggests that the free-base NC-TPP might form an aggregated structure with a large tilt angle. It is interesting to note that the shape of the π -A isotherm at pH 11 was similar to that observed in 1 mmol dm⁻³ NaI at neutral pH.

In accordance with the specific effect on the π -A isotherm of Fig. 2, NaI displayed a specific effect on the pH profile. The inflection points are shifted to pH 2 and 10.5, and the pH region for the mono-protonated NC-TPP is expanded. The mono-protonated NC-TPP might be stabilized through a specific interaction with I⁻.

UV reflection spectra of the monolayer

The Soret band of porphyrin derivatives at around 400–430 nm is intense and is sensitive to aggregate formation. Thus, this band is useful in monitoring the aggregation behaviour of NC-TPP monolayers. Prior to UV measurement at the air–water interface, we examined solution spectra of NC-TPP in dichloromethane with trifluoroacetate as a counter anion.²⁴ The spectra showed a significant dependency on the protonation state of NC-TPP. The observed λ_{max} values of the

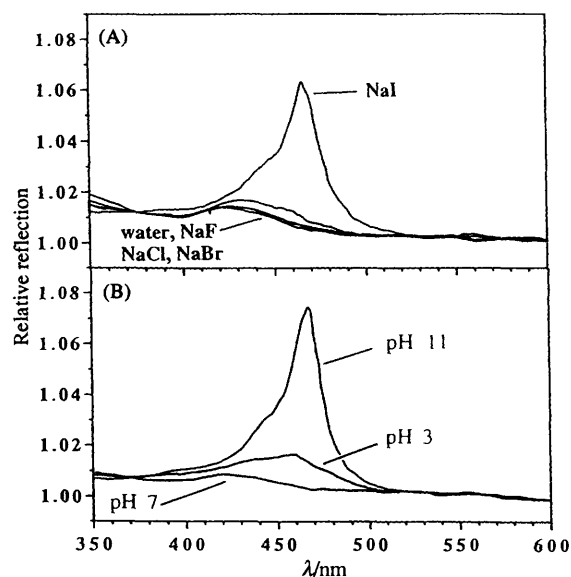


Fig. 4 UV reflection spectra of the mixed monolayer of NC-TPP and methyl octadecanoate (NC-TPP/methyl octadecanoate = 0.039 mol/mol) at ca. 25 mN m⁻¹ and 20 °C. (a) Spectra in 1 mmol dm⁻³ aqueous NaX at neutral pH; (b) those in pure water at pH 3, 7 and 11.

Soret band are 438 nm for the free base, 450 nm for the mono-protonated species and 465 nm for the di-protonated species. The mono-iodide salt of NC-TPP obtained by equimolar mixing of NC-TPP and HI also showed λ_{max} around 450 nm in dichloromethane.

UV reflection spectra of the mixed monolayer of NC-TPP and methyl octadecanoate in 1 mmol dm⁻³ NaX are shown in Fig. 4(a). NaI again produces a unique effect. The mixed monolayer in 1 mmol dm⁻³ NaI showed a strong absorption at around 465 nm, while the spectra for the other salts gave weak, broad peaks around 420–430 nm. NaI in the subphase induced a red shift and the others induced blue shifts compared to the λ_{max} value in organic solvents (ca. 450 nm). The same spectral change was observed over a wide range of NaI concentrations (0.01–10 mmol dm⁻³).

Porphyrins are known to form aggregates in monolayers with consequent spectral changes.^{30,37–40} The blue and red shifts in the Soret band are considered to be attributed to H-aggregate and J-like aggregate formation, respectively. The observed red shift in NaI and the blue shifts in the other NaX solutions can then be ascribed to formation of J-like aggregates and H-aggregates of mono-protonated NC-TPP, respectively, because NC-TPP in the monolayer exists as the mono-protonated form at neutral pH as shown in the pH profile of Fig. 3(b). Di-protonated NC-TPP also has a λ_{max} value at around 465 nm without forming any aggregate.²⁴ It is possible that di-protonation of NC-TPP is the origin of the red-shifted spectra observed on NaI. However, the pH dependency of the π -A isotherms and the observed Q band (NC-TPP monolayer on aqueous NaI, $\lambda_{\text{max}} = 745$ nm; free base in CH₂Cl₂, 725 nm; mono-protonated in CH₂Cl₂, 800 nm; di-protonated in CH₂Cl₂, 825 nm) deny the possibility of di-protonation of NC-TPP in 1 mmol dm⁻³ NaI.† Therefore, we conclude that the observed red-shifted behaviour of NC-TPP in NaI probably originates in the J- aggregate formation of mono-protonated NC-TPP.

The above data imply that the iodide ion in the subphase exerts a specific effect on the monolayer organization. This presumption was also confirmed by the following experiments. When NaI was replaced with NH₄I, the same red shift was

† Although the Q band of porphyrins is known to be hardly affected by aggregation because of weak exciton coupling interactions,^{39,40} the Q band observed in the monolayer with NaI was different from that of NC-TPP in organic solvents in any protonated state.

Table 1 Elemental composition and absorption maximum of mixed monolayers

Subphase (1 mmol dm ⁻³)	Elemental composition				(X - Na)/N (mol/mol)	UV spectra λ_{\max} /nm	
	C (%)	N (%)	X (%)	Na (%)		LB film	Water ^a
NC-TPP							
Pure water	96.45	3.55		0.00		465	425 465 ^b
NaF	96.35	3.65	0.01	0.02	0 ^c		428
NaCl	96.25	3.66	0.04	0.05	0 ^c	460	425
NaBr	96.22	3.63	0.04	0.12	0 ^c		425
NaI	94.74	3.00	2.11	0.15	0.672	465	467
B-NC-TPP							
Pure water	96.11	3.89		0.00	—		445
NaF	95.29	3.59	1.03	0.09	0.262		442
NaCl	94.46	4.02	1.39	0.13	0.314	442	442
NaBr	94.96	3.48	1.07	0.49	0.166		442
NaI	90.81	3.93	4.14	1.12	0.750	442	445

^a Data from Fig. 4 and Fig. 6. ^b At pH 11. ^c The simple calculation gave a negative value because of experimental error.

observed. On the other hand, when NaClO₄, NaNO₃ and Na₂SO₄ were used, both UV spectra and π -A isotherms were identical to those observed in pure water. As ClO₄⁻ and SO₄²⁻ are the first and the last species in the Hoffmeister series,¹⁰ the partition of anions between aqueous and lipid phases could not be the key factor in anion binding to NC-TPP.

Competitive experiments were conducted in order to examine the efficiency of iodide binding. When the other salt (1 mmol dm⁻³ NaX, X = F, Cl, Br) was added to 1 mmol dm⁻³ NaI in the subphase, UV spectra were identical to those observed in 1 mmol dm⁻³ NaI alone. In the same vein, π -A isotherms of NC-TPP/methyl octadecanoate in 1 mmol dm⁻³ NaI + 1 mmol dm⁻³ NaX were similar to that in 1 mmol dm⁻³ NaI. All these data strongly suggest that I⁻ binds to NC-TPP more specifically than do the other halogen ions.

The pH dependency of the UV spectra of NC-TPP in methyl octadecanoate monolayer was investigated at pH 3, 7 and 11 in the absence of halogen anions and is shown in Fig. 4(b). The UV spectrum at pH 7 showed a blue-shifted peak relative to that observed in organic solvents, indicating the H-aggregate formation of the monoprotonated NC-TPP as described above. The UV spectrum at pH 3 gave a broad peak centered at around 460 nm. This λ_{\max} value, as well as the spectral pattern, is almost the same as those observed for di-protonated NC-TPP in organic solvents. Apparently, the di-protonated NC-TPP did not form aggregates due to charge repulsion even in the monolayer. The peak intensity decreased as the surface pressure increased, probably due to partial dissolution of NC-TPP into the water during compression. This observation agrees with the too small a molecular area found for the mixed monolayer at high surface pressures and pH 3 [Fig. 3(a)]. Fig. 4(b) also shows that the UV peak is intense at pH 11 with λ_{\max} around 465 nm. NC-TPP is in the free-base form in the subphase of this pH. This λ_{\max} is clearly red-shifted compared to λ_{\max} in isotropic solution (440 nm). This red shift may indicate a preferred formation of J-aggregate from the free base in the monolayer. The π -A isotherm of the NC-TPP monolayer at pH 11 in Fig. 3(a) also points to a large tilt angle of aggregated molecules in the form of the free base.

Characterization of LB films of NC-TPP

Although π -A isotherms and UV reflection spectra indicate a specific interaction between I⁻ and NC-TPP, they are not direct proof of strong binding between NC-TPP and I⁻. More direct evidence would be provided by elemental analyses by X-ray photoelectron spectroscopy (XPS). NC-TPP/methyl octadecanoate monolayers were transferred from various subphases onto gold-covered glass plates and characterized by XPS (Table 1). The amount of halogen ions bound to NC-TPP was evaluated from the elemental ratio of nitrogen and halogen. The

contribution of non-specifically adsorbed NaX onto LB films can be corrected by subtracting the amount of Na (derived from non-specific adsorption) from the observed halogen content. Thus, the values of (X - Na)/N reflect the amount of X bound to NC-TPP.

The (X - Na)/N value is essentially zero for films transferred from 1 mmol dm⁻³ NaX (X = F, Cl, Br). Halogen atoms (F, Cl, Br) are absent in these LB films, in spite of the fact that NC-TPP exists as a mono-protonated form under the conditions used and requires a counteranion. The λ_{\max} values of the UV spectra of the LB films are also summarized in Table 1. Although the monolayer of NC-TPP in 1 mmol dm⁻³ NaX (X = F, Cl, Br) and pure water showed blue-shifted λ_{\max} values, the corresponding LB films show red-shifted λ_{\max} values at around 460–465 nm. These UV spectra are almost identical to that of the free-base NC-TPP monolayer. Apparently, loosely-bound counterions (F⁻, Cl⁻ and Br⁻ or OH⁻ in the absence of added NaX) are lost simultaneously with deprotonation of NC-TPP during the transfer process onto gold plates. The resulting LB films contain J-aggregated NC-TPP that is characteristic of the LB film of free-base NC-TPP.

In contrast, the situation is totally different for the LB film transferred from 1 mmol dm⁻³ NaI. A large (X - Na)/N value was observed, endorsing the specific binding of I⁻ toward NC-TPP. The observed atomic ratio of I:N is close to 3:4. This value suggests binding of the I₃⁻ species⁴¹ to NC-TPP. We suspect that I⁻ anion was oxidized to I₃⁻ during the transport process *via* photosensitization by NC-TPP. The observed UV spectra of the LB film showed a red-shifted peak with λ_{\max} 467 nm, in agreement with that of the corresponding monolayer. In both the monolayer and the LB film, NC-TPP molecules formed J-like aggregates in the presence of I⁻. The tightly-bound iodide species is not lost during LB transfer and the aggregation mode of NC-TPP remains unchanged. The preservation of iodide ion in the LB film is clearly related to the stability of the aggregation mode of NC-TPP.

Comparison with other porphyrin derivatives and the effect of matrix lipids

The importance of aggregation on anion selectivity was further corroborated by comparison with other porphyrin compounds and an investigation of the effect of matrix lipids.

π -A Isotherms of the mixed monolayer of TPP with methyl octadecanoate were measured on 1 mmol dm⁻³ NaX. The limiting areas of all the calculated isotherms (0.1–0.2 nm²) are much smaller than the cross-sectional area of TPP, 0.5 nm², in the perpendicular orientation.³⁶ It is clear that TPP cannot form a stable monomolecular layer on water. The monolayer must readily collapse⁴² even in a mixture with methyl octadecanoate. UV reflection spectra of the monolayers on

1 mmol dm⁻³ NaX showed strong absorption peaks at around 435 nm, independent of the halogen ions used. The observed λ_{\max} value on the water surface was red-shifted by 20 nm compared to that observed in toluene solution. These spectral shifts and π -A isotherms clearly indicate that TPP on water formed a collapsed structure with J-like aggregate characteristics. Anion selectivity was not found.

The monolayer property of a bulky NC-TPP derivative, B-NC-TPP, which has four 3,5-di(*tert*-butyl)phenyl groups instead of four unsubstituted phenyl groups, was subsequently investigated. π -A Isotherms of B-NC-TPP are greatly expanded compared to those of NC-TPP, and they gave positive surface pressures even at molecular areas of more than 2.0 nm². This indicates that the molecular packing is disturbed because of bulky side chains. UV reflection spectra of the mixed monolayer measured in 1 mmol dm⁻³ NaX had λ_{\max} values close to those observed for a toluene solution of the mono-protonated species, and are independent of the halogen ions used. Therefore, bulky B-NC-TPP did not form specific aggregates even in the presence of halogen ions. XPS measurements showed that all of the halogen ions were detected in the LB films of B-NC-TPP (Table 1), while only iodine was incorporated in the case of NC-TPP. These results lead to one of the most important conclusions in this study: NC-TPP derivatives cannot show anion selectivity without specific aggregation, *i.e.* 'aggregation-mediated' ion recognition.

It is probable that the behaviour of NC-TPP is affected by the nature of the matrix monolayers. A mixed monolayer of NC-TPP with octadecanoic acid gave a condensed phase and showed a λ_{\max} shift from 455 to 465 nm upon compression. This is attributed to formation of J-like aggregates from the mono-protonated NC-TPP. The mixed monolayer of NC-TPP/2C₁₄CO₂H showed an expanded behaviour in the isotherm and the λ_{\max} value at 451 nm did not vary over the whole range of surface pressure. NC-TPP remained in a randomly dispersed, mono-protonated form in expanded 2C₁₄CO₂H matrix even at high surface pressures.

Dialkylamine-type matrix lipid, 2C₁₄gluNH₂, provides a basic microenvironment for NC-TPP, keeping it in the free-base form. π -A Isotherms of this mixed monolayer clearly showed transitions from expanded to condensed phases at 10–20 mN m⁻¹. The λ_{\max} value observed at low surface pressures is similar to that of free-base NC-TPP in organic solvents (*ca.* 440 nm), but it shifts to 465 nm on further compression. The red shift to 468 nm apparently originates from J-like aggregate formation of free-base NC-TPP.

The results presented above show that the red shift to 465 nm in the UV spectra of the NC-TPP monolayers can be reproduced by changing the matrix lipid and surface pressure, and that the presence of iodide is not required for the same spectral shift. Thus, the most intrinsic factor in the 'iodide recognition' is not iodide binding itself, it is the J-like aggregation of NC-TPP.

Mechanism of iodide recognition by NC-TPP

The mechanism of specific iodide binding by the NC-TPP monolayer is summarized in this section. Fig. 5 illustrates a unified mechanism for the mode of aggregation and iodide binding. The NC-TPP molecule has a non-symmetric structure with two kinds of nitrogen in different environments. Therefore, this compound possesses two separate pK_a values, and exists as a mono-protonated form in the neutral pH region. Iodide ion in the subphase induces UV red-shifts with J-like aggregate formation, while blue-shifted spectra are observed with the other halogen ions by H-aggregate formation. It was also noted that free-base NC-TPP at pH 11 formed J-like aggregates. The situation is different for the transferred films. UV spectra showed that NC-TPP in the transferred films formed J-like aggregates in all cases. XPS analyses confirmed

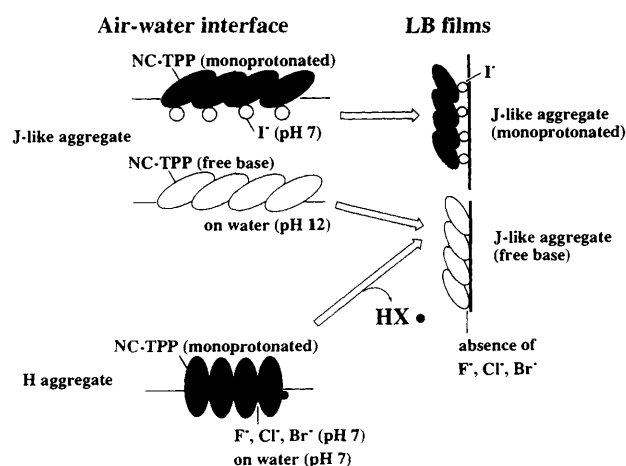


Fig. 5 A proposed mechanism for halide recognition by NC-TPP monolayer

the loss of counterions in the case of F⁻, Cl⁻ and Br⁻, in concurrence with deprotonation during the LB transfer, and J-like aggregate formation of the resulting free-base species. In contrast, iodide was not lost in the films upon LB transfer and the aggregation mode of NC-TPP remained unchanged.

As explained above, the specific binding of iodide by the NC-TPP monolayer is based on the difference in the aggregation mode of NC-TPP, and is not connected to a simple affinity enhancement between NC-TPP and iodide. To our knowledge, this is the first example of 'aggregation-mediated' anion recognition on the monolayer. It should have fundamentally different aspects from simple stoichiometric recognition systems, because the aggregate structure is affected by many parameters such as combination of components, mixing ratio, surface pressure, and so on. Changes in these parameters may lead to varied selectivity and strength in molecular recognition.

Experimental

Materials

Octadecanoic acid (Gasukuro Kogyo, analytical standard), methyl octadecanoate (Wako Pure Chemicals; analytical standard) and tetraphenylporphyrin (TPP; Wako Pure Chemicals) were commercially available and used without further purification. Inorganic salts used here are commercially available (Merck and Wako Pure Chemicals) in more than 99.5% purity. Water used for the subphase was deionized and doubly distilled by a Nanopure II-4P and Glass Still D44 System (Barnstead). The subphase pH was adjusted by 1 mol dm⁻³ aqueous NaOH and 0.5 mol dm⁻³ sulfuric acid (Wako, for volumetric analysis), when necessary. Spectroscopic grade toluene was used as a spreading solvent. Gold (99.999%) and chromium (99.99%) used for surface modification of substrates were purchased from Soekawa Chemicals.

Syntheses of monolayer-forming lipids, 2C₁₄CO₂H⁴³ and 2C₁₄gluNH₂,⁴⁴ are described elsewhere. NC-TPP was synthesized by the acid-catalysed condensation of pyrrole and benzaldehyde according to the reported procedure.²⁴ Similarly, bulky analogue B-NC-TPP⁴⁵ was synthesized from pyrrole and 3,5-di-*tert*-butylbenzaldehyde.⁴⁶

B-NC-TPP. (Found: C, 84.8; H, 8.8; N, 5.1. Calc. for C₇₆H₉₄N₄·0.5H₂O: C, 85.1; H, 8.9; N, 5.2%); δ_{H} (300 MHz, CDCl₃) – 5.11 (1 H, s, 'confused pyrrole' β -H), – 2.52 (2 H, br s, NH), 1.63 (72 H, m, Bu'), 7.81 (2 H, s, *p*-Ph), 7.85 (2 H, s, *p*-Ph), 7.87 (2 H, s, *p*-Ph), 8.06 (4 H, s, *o*-Ph), 8.21 (2 H, s, *o*-Ph), 8.26 (2 H, s, *o*-Ph), 8.67 (4 H, m, pyrrole), 8.87 (1 H, s, 'confused pyrrole' α -H), 8.96 (1 H, d, *J* 5.1 Hz, pyrrole), 9.05 (1 H, d, *J* 4.8 Hz, pyrrole).

π -A Isotherms and LB films

π -A Isotherms were measured with a computer-controlled film balance system FSD-50 (USI System, Fukuoka). Compression was started 30 mins after spreading of a toluene solution containing ca. 0.05 mg cm⁻³ porphyrin and 0.5 mg cm⁻³ matrix lipids at a rate of 30 mm² s⁻¹. The temperature of the subphase was kept at 20 ± 0.2 °C.

The substrate for LB transfer was prepared as follows. Slide glass (pre-cleaned, 176 × 26 × 1 mm, Iwaki Glass) was immersed in a detergent solution overnight (Dsn90, Bokusui Brown Co. LTD.). The glass was washed with a large excess of ion-exchanged water to remove the detergent completely and subjected to sonication in fresh ion-exchanged water several times. After the glass had been dried under vacuum for 1 h, chromium and gold thin layers were consecutively formed by the vapour-deposition method (500 Å Au/50 Å Cr/slide glass) with a vapour-deposition apparatus VPC-260 (ULVAC Kyushu). LB transfer was carried out at 20 mN m⁻¹ with an FSD-21 instrument (USI System, Fukuoka) by the vertical dipping method. The dipping speeds were 20 mm min⁻¹ (for down stroke) and 5 mm min⁻¹ (for up stroke).

Characterization of monolayers and LB films

Reflection-absorption UV spectra of monolayers were measured with a computer-controlled, photodiode array-equipped spectrometer (Otsuka Electronics, Model MCPD-100). The tip of an optical fibre was fixed vertically ca. 5 mm above the water surface. A black light trap was placed in the trough below the optical fibre to absorb all the light transmitted through the surface. Therefore, only the light reflected from the surface was detected. A xenon lamp was used as the incident light source, and the spectra were obtained at wavelengths from 350 to 600 nm at 20 ± 0.2 °C.

X-ray photoelectron spectra of the LB films on Au/Cr/glass were measured with a Perkin-Elmer PHI 5300 ESCA. The X-ray source was MgK α (300 W). Repeated scans over the same region of surface at a take off angle of 45° gave reproducible spectra. The elemental composition was obtained by dividing the observed peak area by the intrinsic sensitivity factors of each element. UV spectra of the LB films (30 layers) on quartz plates were measured with a UV/VIS/NIR spectrometer V-570 (JASCO Corp.).

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