

Proof of Partial Flattening of Meso Substituents in Tetracationic Porphyrin at a Mica/Solution Interface

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A free base tetracationic porphyrin (TMPyP) was adsorbed at a mica/aqueous solution interface. Atomic force microscopy (AFM) in liquid revealed that the porphyrin rings lie flat on the mica surface with their meso substituents partially rotated toward planarity. Optical waveguide spectroscopy elucidated a bathochromic shift of the Soret band, suggesting extension of π -conjugation by partial inclusion of pyridinium rings.

The bottom-up fabrication of molecular assemblies on surfaces or interfaces is an important and challenging theme in view of connecting supramolecular chemistry to the macroscopic world for potential applications in the field of organic devices.¹ Porphyrins are versatile building blocks for the production of supramolecular architectures that exhibit ample electronic and optical properties.² In recent years, porphyrin assemblies on clay surfaces (porphyrin–clay complexes) have attracted specific attention because of their great photochemical interest.³ The tetracationic 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphine (TMPyP; chemical structure is shown in the inset in Figure 2b) is the representative dye used in these studies. In the TMPyP–clay (e.g., vermiculite or saponite) complexes, the porphyrin Soret band shows a large bathochromic shift compared to the free monomer but the reasons have been the subject of some debate; for example, protonation or aggregation of TMPyP can cause the red shift of the Soret band⁴ whereas the meso substituent methylpyridinium (MePy) rotation (or flattening) toward the porphyrin ring can be the different origin.⁵ Aggregation of TMPyP on clay surfaces is generally found to be negligible as deduced from the excited singlet lifetime meas-

urements.⁶ Very recently, it has been proposed that the flattening of cationic MePy moieties is the most probable reason on the basis of spectroscopic and theoretical studies;^{5,6} however, there is still no direct evidence on the geometry of TMPyP regarding the MePy rotation due to the lack of in situ observations of the target molecules. In the present study, to obtain more information on the geometry of TMPyP on clay minerals, we examined the adsorption behaviors of TMPyP at a mica/aqueous solution interface by mostly using atomic force microscopy (AFM) in liquid. It is well known that mica (muscovite) is a typical clay substrate having a highly negatively charged and atomically flat surface.⁷ On the basis of the in situ AFM observations at the mica/solution interfaces, we demonstrate a partial flattening of the meso substituent MePy groups in TMPyP on mica.

Determination of an adsorption isotherm of TMPyP (Sigma-Aldrich Chemical) on mica (Nilaco) gives us helpful information on the experimental conditions for the AFM measurements. We then prepared a series of initial amounts of finely ground mica flakes (15–2 mg) in centrifuge tubes containing the same concentration of the aqueous TMPyP solution (10 μ M), followed by the measurements of absorption spectra for the supernatant solution to estimate the dye adsorption capacity onto mica.⁸ As a consequence, the amount of TMPyP adsorbed per unit mass of mica flakes increased first with the initial concentration of TMPyP, then reached a plateau value at ca. 8.0 μ M (Langmuir-like behavior) that represented the monolayer saturation of the active sites on the mica surface (that is, approximately 100% versus CEC of mica, where CEC denotes the cation-exchange capacity for TMPyP).⁹ On this basis, we conducted the AFM measurements at [TMPyP] = 1.0 and 10 μ M.

Tapping mode AFM topographic images were obtained in liquid (Nanoscope IIIa). Figures 1a and 1b show the AFM

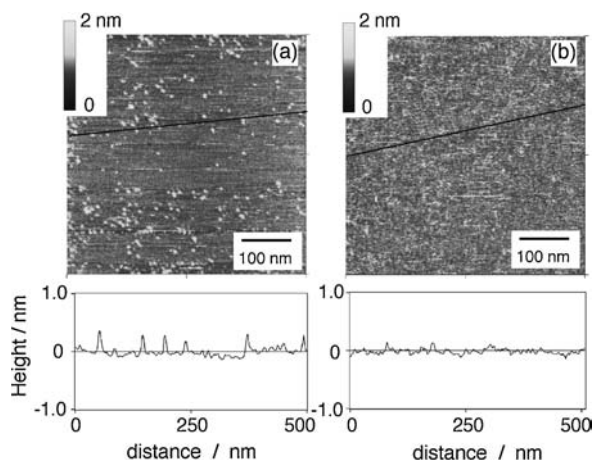


Figure 1. AFM images of TMPyP at the mica/aqueous solution interface: (a) [TMPyP] = 1.0 μ M, (b) [TMPyP] = 10 μ M. (Top) Topographic images. (Bottom) Cross-sectional profiles along the lines.

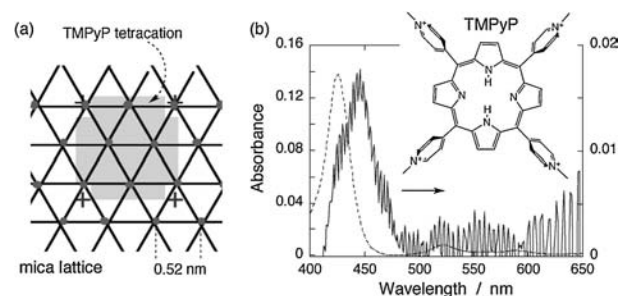


Figure 2. (a) Top view of an example of TMPyP adsorption on a mica lattice. The gray circles represent anionic sites on mica that can bind to the cationic MePy moieties. The porphyrin is depicted as a square. (b) Absorption spectrum of TMPyP at the vicinity of the mica/solution interface (solid). The spectrum was obtained via optical waveguide spectroscopy. Absorption spectrum of TMPyP in bulk aqueous solution is also shown (dashed). [TMPyP] = 1.0 μ M.

images of the surface with scan size of $500 \times 500 \text{ nm}^2$ at $[\text{TMPyP}] = 1.0$ and $10 \mu\text{M}$, respectively. Typical cross-sectional profiles are also shown. At $[\text{TMPyP}] = 1.0 \mu\text{M}$, grain-shaped domains with height ranging from 0.2 to 0.4 nm were observed, and the average height of the grains was calculated to be 0.31 nm statistically. The lateral size of the grains was 5–10 nm, close to the probe size of the AFM tip, so the grains can consist of 1–ca. 50 TMPyP molecules. At $[\text{TMPyP}] = 10 \mu\text{M}$, which would correspond to the region in the full dye coverage, a very flat surface with the mean roughness of 0.04 nm was detected. The roughness is almost the same as that of a bare mica/water interface (mean roughness of 0.05 nm in our measurement), suggesting that TMPyP molecules are densely adsorbed in a uniform manner at the mica/solution interface.

Using the dimensions of the TMPyP molecule (ca. 1.4 nm for the maximum distance between the two adjacent MePy substituents, ca. 0.18 nm for the flattened porphyrin ring thickness, and ca. 0.42 nm for the thickness with the dihedral angle of 90° between the porphine ring and the peripheral MePy moieties), TMPyP should adsorb on the mica surface monomolecularly with a parallel orientation with respect to the substrate in water at $[\text{TMPyP}] = 1.0 \mu\text{M}$. The result can be explained in terms of the four-point binding through positively charged MePy groups to the negatively charged substrate, providing the limitation of molecular orientation.^{10,11} Furthermore, in regard to the orientation of the MePy moieties, they are “partially” flattened with respect to the porphyrin ring in view of the mean height of the adsorbed porphyrin molecules ($=0.31 \text{ nm}$). This conclusion would be reasonable because (i) a significant rotation of the MePy substituents toward planarity induces a concomitant strain of the porphyrin ring, so that a partial twisting would be favorable;¹² (ii) the size-matching effect, which is based on the matching of the distance between the cationic sites on the porphyrins and that between anionic sites on clay surfaces, is somewhat insufficient. This effect is proposed to contribute to the preferential orientation of the adsorbed tetracationic porphyrins on clay minerals.⁶ On the mica surface, the anionic sites are hexagonally arranged with a lattice constant of 0.52 nm.⁸ Considering the distances (1.09 nm) between adjacent cationic sites in TMPyP,⁶ a two-point matching is successful but other sites are slightly deviated as shown in Figure 2a. In any case, we can conclude that the adsorbed TMPyP molecules present a smaller dihedral angle (Φ) between the porphyrin ring and the MePy substituents compared to the free TMPyP with Φ of ca. 90° .⁵

At $[\text{TMPyP}] = 1.0 \mu\text{M}$, we proposed a feasible geometry of TMPyP molecules adsorbed on a mica surface from an AFM image.¹³ To examine the correlation between the spectroscopic properties and molecular planarity, we next measured the absorption spectrum at the vicinity of the mica/solution interface in a total-internal-reflection (TIR) (or optical waveguide) configuration at that concentration. In the TIR configuration, a trapezoid prism (quartz) was contacted with a homemade cell composed of mica/solution/PMMA-plate using *cis/trans*-decalin as the index-matching oil.⁸ The penetration depth of the evanescent field was ca. 89 nm at a wavelength of 500 nm.⁸ Figure 2b shows the TIR absorption spectrum at $[\text{TMPyP}] = 1.0 \mu\text{M}$, together with that of the bulk solution. While the peak of the Soret band in aqueous bulk solution appeared at ca. 425 nm, that at the mica/solution interface was red-shifted to ca. 445 nm ($\Delta\lambda = 20 \text{ nm}$). Note that the superimposed sinus-

oidal oscillations in the spectrum were caused by the interference of a cleaved mica sheet. This bathochromic shift behavior was quite similar with that observed for a TMPyP–saponite complex,^{6,10} and thus has been rationally explained in terms of a flattening of the porphyrin molecule on the mica (clay) sheet; namely, four MePy moieties rotate toward parallel orientation to the porphyrin ring, which cause the extension of π -conjugation by partial inclusion of pyridinium rings.^{5,6} It should be noted that protonation of the porphyrin ring nitrogens may bring about the red shift of the Soret band;¹⁴ however, it is unlikely because the mica surface is chemically inert⁷ and the peak attributed to protonated TMPyP (ca. 591 nm) was not detected.⁴ In conclusion, in situ AFM observations revealed that the TMPyP molecules adsorbed flat at the mica/solution interface with their meso substituents partially rotated toward planarity, yielding a bathochromic shift of the Soret band.

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- 9 a) The mica flakes were prepared by grinding a mica sheet in a small blade mill for 10 min with water or water/ethanol mixture, followed by complete drying under vacuum. The size of the flakes ranged from about 1 to 10 μm . b) The adsorption isotherm may be influenced by the edge/step sites on small mica flakes, yielding an overestimation for the adsorption capacity. However, the measurements would give us semi-quantitative considerations on the adsorption behavior of TMPyP on a flat mica surface.
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- 13 At $[\text{TMPyP}] = 10 \mu\text{M}$, the AFM image (Figure 1b) exhibited a featureless flat surface, so that definitive geometry identification of the adsorbed species was not, unfortunately, possible.
- 14 At $[\text{TMPyP}] = 1.0 \mu\text{M}$, aggregation (or π - π stacking) of TMPyP did not occur at the mica/solution interface as judged from the mean height of the adsorbed molecules obtained by AFM.