# The Orientation Control of Dicationic Porphyrins on Clay Surfaces by Solvent Polarity

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The orientations of cationic porphyrins on a clay surface were found to be successfully controlled by solvent polarity. The orientational change was directly observed with the interface spectrometer equipped with a quartz waveguide system. Tetracationic porphyrins on the clay surface in water are oriented with the plane of the rings parallel to the silicate layer, while in the case of dicationic porphyrins (*cis*-type), the porphyrin plane stood up against the clay surface on addition of less polar water-miscible solvent.

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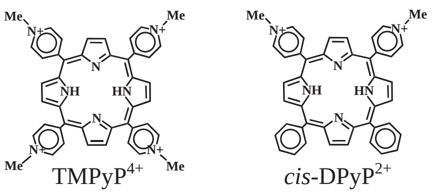
Recently, hybrids between clays and organic molecules have been studied intensively. In particular, clay–porphyrin complexes attract much interest from the viewpoint of materials chemistry.[1–4] These materials could be useful for electro-responsive and photo-responsive devices. Thus far, we have reported an interesting porphyrin–clay hybrid in which the porphyrin molecules adsorb on the clay sheets as densely packed monolayers, without discernible aggregation.[5] The average center-to-center distance between porphyrins was controlled to be 2.4 nm, which is based on the matching of the distance between the cationic sites on the porphyrins and the distance between anionic sites on the clay surfaces. We have termed this the "size-matching effect."[5]

In this paper, the first example of controlling the porphyrin orientation (angle with respect to the clay substrate) with the choice of solvent composition will be reported. A tetracationic porphyrin (tetrakis(1-methylpyridinium-4-yl)porphyrin (TMPyP)) and a dicationic porphyrin ((*cis*-bis(*N*-methylpyridinium-4-yl)-diphenylporphyrin (*cis*-DPyP)) were used as the cationic porphyrins in this study (Figure 1). Smecton SA (Kunimine), well characterized synthetic clay was used.[5]

The orientation of the porphyrin molecule on the clay surface was examined by use of two types of measurements. First, the absorption maximum ($\lambda_{\max}$) of the porphyrin Soret band, which reflects the molecular structure of the porphyrin (described below), was observed. When the porphyrin molecule adsorbs on the clay surface with a parallel orientation, the $\lambda_{\max}$ should shift to longer wavelength by ca. 30 nm compared to that in water, without clay, in the case of TMPyP.[4,5] A co-planarization of the porphyrin ring with respect to the *meso*-substituted pyridinium groups is believed to induce the bathochromic shift of the Soret band.[4,5] Parallel adsorption onto the clay surfaces, induced by the strong electrostatic attractive interaction between the positive charges on the porphyrins and the negative charges on the clay surfaces, should force the porphyrins to be coplanar by rotating the pyridinium planes, while adsorption with a standing orientation with respect to the clay surface should allow the porphyrins to have a structure similar to that in water. In the non-parallel orientation, for example, in which the two positive charges of *cis*-DPyP cling to the negative charges on the clay surfaces, and the remainder is free from this restriction, the pyridinum groups should be tilted back again versus the porphyrin plane. Thus, the absorption maximum of the porphyrin Soret band provides useful information with which to discuss the orientation (parallel vs non-parallel to the clay surface). In the preparation of the sample, the clay sheets ($2.0 \times 10^{-5}$ equiv. L$^{-1}$) were exfoliated, and the porphyrin molecules ($5.0 \times 10^{-7}$ mol L$^{-1}$) were adsorbed on the clay sheets in water. The $\lambda_{\max}$ values of the porphyrin Soret band were 450 and 455 for TMPyP and *cis*-DPyP on the clay surfaces, respectively. The values in aqueous solution without clay, however, were 420 and 418 nm for TMPyP and *cis*-DPyP. The bathochromic shift of the Soret band for the porphyrin on the clay surface clearly indicates that the adsorbed porphyrin molecule has a parallel orientation.

Second, the orientational changes of the porphyrin were observed directly by polarized absorption spectroscopy[6] by the use of an interface spectrometer equipped with a quartz waveguide system (System Instruments, SIS-50BS). Because the absorbance is amplified dozens of times in the waveguide, even a monolayer of clay–porphyrin complexes on the quartz glass can be measured with sufficient absorbance. Samples were prepared as follows. The aqueous dispersion of the clay–porphyrin complex was cast onto the quartz waveguide. The area on the quartz waveguide covered with the complex was around 1.5 cm$^2$. According to the number of clay sheets in the solution droplet used to cast the film, the resulting clay layer can be controlled so as to form a monolayer. The monolayer formation was confirmed by AFM measurements, i.e., that the clay sheets are aligned on the quartz in a parallel (flat) orientation, as schematically depicted in the experimental setup (Figure 2).



TMPyP$^{4+}$ *cis*-DPyP$^{2+}$

**Figure 1.** Structures of the cationic porphyrins.

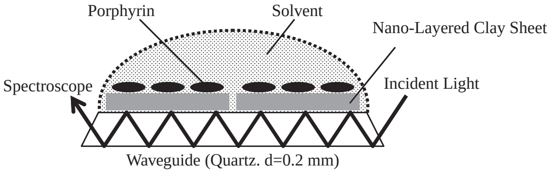


**Figure 2.** Experimental setup of the surface-interface spectrometer with quartz waveguide.

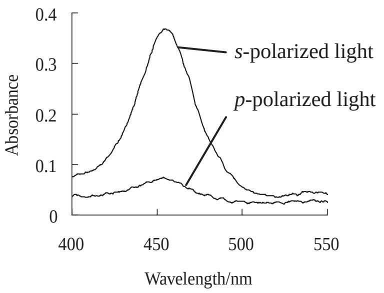


**Figure 3.** Absorption spectra obtained with *s*- and *p*-polarized light for TMPyP on the quartz waveguide in water.

In the orientational control experiments, the sample was covered with solvent.

The absorption spectra of TMPyP with *s*- and *p*-polarized light are shown in Figure 3. The absorbance with *s*-polarized light was much larger than that with *p*-polarized one. The polarized absorption experiment with *cis*-DPyP exhibited a similar result. These results clearly indicate that tetracationic and dicationic porphyrins adsorb on the clay surface with orientations that are nearly parallel to the clay surface in water. The tilt angle of the porphyrins against the clay surface was determined to be smaller than 5 degrees by a quantitative analysis of the $p/s$ ratio of the absorbance including a theoretical derivation of the dichroic absorption, the detail of which will be reported elsewhere.

Solvent effects on the porphyrin orientation on the clay surface were examined. Dioxane, which is miscible with water, was used as a typical non-polar additive. The addition of dioxane induced significant spectral changes in the absorption spectra only for *cis*-DPyP, but not for TMPyP. The spectral change for *cis*-DPyP with the addition of dioxane (0–90%) is shown in Figure 4.

The addition of dioxane induced a hypsochromic shift of the Soret band. There are two possibilities for the hypsochromic shift: i) a change of orientational angle of the porphyrin to the clay surface; and ii) desorption of porphyrin from the clay surface. The $\lambda_{\max}$ (430 nm) in water:dioxane (10:90 (v/v)) is apparently different from that (421 nm) in solution without clay. This negates the possibility of porphyrin desorption. To check this further, the centrifugation and filtration of the clay–porphyrin complex were examined. In the supernatant and filtrate, respectively, no porphyrin was detected by absorption spectroscopy. These observations strongly indicate that the porphyrin molecule changes its orientation on the clay surface with the change of solvent polarity. A similar hypsochromic shift was also observed when dimethylformamide (DMF) was added to the samples. The absorption spectra of *cis*-DPyP-clay complex on the quartz waveguide covered with DMF were measured by *s*- and *p*-polarized light with an incident angle of 75 degrees. The spectra obtained are shown in Figure 5. With *s*-polarized light, a weaker absorption at 425 nm was observed. With *p*-polarized light, a stronger absorption at 425 nm and almost no absorption at 455 nm were observed. These results directly indicate that the parallel-adsorbed porphyrin absorbs *s*-polarized light at 455 nm, while the non-parallel-adsorbed porphyrin absorbs *p*-polarized light at 425 nm. The tilt angle of *cis*-DPyP against the clay surface was determined to be 68 degrees by the quantitative analysis.

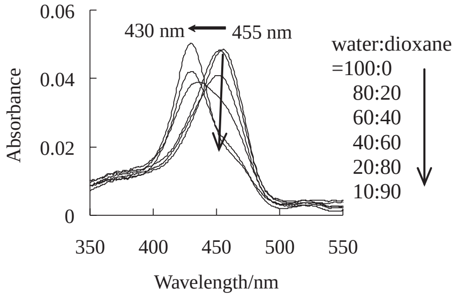


**Figure 4.** Absorption spectra of *cis*-DPyP in water–dioxane (100:0 to 10:90 v/v).

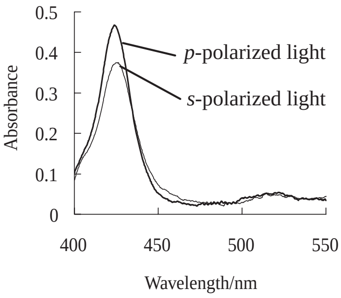


**Figure 5.** Absorption spectra of *cis*-DPyP with *s*- and *p*-polarized light on the quartz waveguide in DMF.

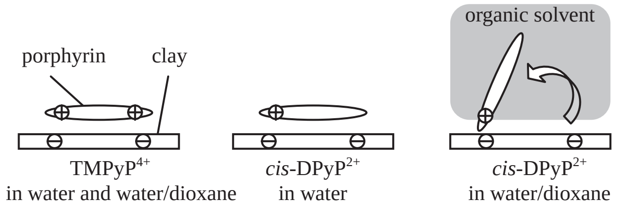


**Figure 6.** Schematic view of the orientation of *cis*-DPyP on the clay surface with change of solvent polarity.

The orientation of *cis*-DPyP on the clay surface in water and water–dioxane or DMF can be illustrated as shown in Figure 6. The change of the orientation angle between the clay sheet and the porphyrin molecule was found to be controlled by the compositional change of solvent. When TMPyP and *cis*-DPyP co-adsorb on the clay surface, it is possible to obtain a complex in which both parallel (TMPyP) and vertically (*cis*-DPyP) adsorbed porphyrin co exist on the same clay surface.

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