High Density Adsorption of Porphyrins onto Clay Layer without Aggregation: Characterization of Smectite-Cationic Porphyrin Complex

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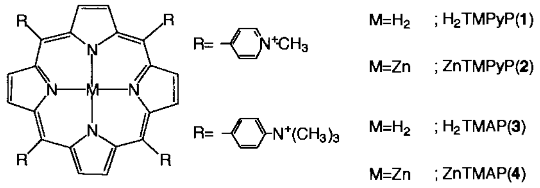
Adsorption of the +4 charged cationic porphyrins onto an artificially synthesized smectite was studied. Porphyrin molecules adsorb on the clay sheet with high density to neutralize all the minus charges of the clay surface without aggregation by a novel method of a size-matching of distances between the charge sites. An efficient energy transfer between different porphyrins was induced on the clay surface, while there was no interaction in the ground state.

Clay minerals are known as multilayered inorganic materials which provide two dimensional wide space for chemical reactions.[1] Recently, synthetic clay minerals have attracted increasing interest, especially for their application to photochemical reactions.[1b,2] Although many kinds of dyes have been used with the chemical reaction field provided by clay minerals, the dye molecules tend to aggregate on the clay surface or in the interlayer space.[3] Because it has been difficult to control the adsorption behavior of dyes on inorganic surfaces, the utilization of clay minerals as photochemical reaction fields has been limited. In this paper, we report a novel method for controlling dye adsorption on a clay surface by size-matching the distances between the charge sites. We chose artificially synthesized smectite as a cation exchangeable clay mineral which does not contain colored or redox active impurities. The +4 charged cationic porphyrins have been well known not only as catalysts but also as sensitizers.[4] In order to control the adsorption behavior of porphyrins on smectite, the separation distances between the adjacent anionic sites in the clay and between the adjacent cationic charges in the porphyrin molecule were made approximately equal. Under these conditions, we found that a high density of porphyrins were absorbed onto the clay layers without aggregation. This observation is important from the point of view as to how to control the intercalation of inorganic and organic dyes onto the clay layers. Here, we further report on the characterization of the structural and photochemical properties of clay-porphyrin complexes. Though several reports of a red shift of the porphyrin Soret band in the clay-porphyrin complex have appeared,[5,6] little is known about the detailed structure, photochemical properties and photochemical reactions of the complex.

Sumecton SA (**SSA**, Kunimine Ind. Co.) was used as an artificially synthesized smectite. The properties of **SSA** are well characterized as follows: the composition: $[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4]^{-0.77}(Na_{0.49}Mg_{0.14})^{+0.77}$, surface area: 750 $m^2\ g^{-1}$, cation exchange capacity (CEC): 0.997 meq g^{-1}. The distance between adjacent anionic sites in the clay was estimated to be approximately 11 Å from the value of surface area and CEC. Tetrakis(1-methyl-4-pyridiniumyl)porphyrin (H_2TMPyP(**1**)), tetrakis(N,N,N-trimethyl-4-aniliniumyl)porphyrin (H_2TMAP(**3**)), and their zinc complex (ZnTMPyP(**2**), ZnTMAP(**4**)) were used as the +4 charged cationic porphyrins. According to PM3 calculations, the distances between adjacent cationic parts in the porphyrin molecules were estimated to be approximately 11 Å for TMPyPs and 13 Å for TMAPs. Three kinds of samples were prepared using the following procedures: i) an aqueous porphyrin solution (1.0×10^{-6} M) was prepared (sample a), ii) a mixture of the aqueous porphyrin(1.0×10^{-6} M) and the **SSA** solution (500 mg L^{-1}) was stirred for a few minutes (sample b), and iii) sample b was put through three freeze-thaw cycles using liquid N_2 (sample c). In the case of samples b and c, 0.8% of the total anionic charges on the clay sheet would be neutralized by the cations of the porphyrin, if all of the porphyrin molecules were to be absorbed on the clay sheet. Absorption spectra of samples a, b and c for each of the porphyrins are shown in Figure 1.



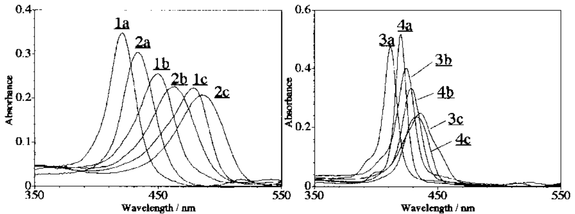


Figure 1. Absorption spectra of sample a, b and c for H_2TMPyP(**1**), ZnTMPyP(**2**)(left), H_2TMAP(**3**) and ZnTMAP(**4**)(right).

Adsorption of the porphyrins onto the clay sheet showed significant metachromatic effects. The λ_{max} of the Soret band of sample b shifted to a longer wavelength compared to sample a. Sample c exhibited a further red shift compared to sample b in all porphyrins. These observations clearly indicate that sample c is a different complex from sample b. The spectral shape of sample c was almost the same as that of the film (sample d) obtained by filtration of sample b through a membrane filter (pore size = 0.5 µm) and drying at room temperature. A similar bathochromic shift of the Soret band has been reported in the case of **1** with laponite.[6] That study suggested that an enhanced π conjugation, due to a flattening of TMPyP on the clay, induced the spectral change. By a flattening one means that the four cationic tetramethylpyridyl moieties become parallel to the porphyrin ring. The bathochromic shifts are understood to depend on the degree of flattening. Our study showed smaller bathochromic shifts in TMAPs compared to TMPyPs. In the case of TMAPs, the bulky trimethyl ammonium groups probably prevent the complete flattening of TMAPs on the clay. According to XRD analysis of sample d(loading level=96% vs CEC), the clearance space were 4.6 Å for **1**, 4.8 Å for **2**, 5.6 Å for **3**, and 5.9 Å for **4**, compared to 4.0 Å without porphyrin. These observations indicate that an intercalation of porphyrin molecules induces an expansion of the interlayer distance and the porphyrin plane in the interlayer space is almost parallel to the clay layer. The similar expansion was observed in other clay-porphyrin complexes.[5] Judging from the above results, sample b could be assigned to a complex in which the porphyrin molecules are adsorbed on the outer surfaces of the clay, and sample c, which has the same absorption spectra as sample d, could be assigned to a complex in which the porphyrin molecules are intercalated with the stacked clay layers. The larger spectral shifts in sample c compared to sample b suggest a more enhanced flattening of the porphyrin molecule by the intercalation. Although aggregation of the dye is generally enhanced in a clay-dye complex,[3] our observations strongly suggest the presence of a monomeric dye in the clay-dye complex, without aggregation, judging from the spectral shapes in samples b and c. Because an aggregation drastically reduces the lifetime of the excited states and suppresses photochemical reactions, control of the aggregation process is an important problem in the field of photochemistry. In order to obtain more detailed information on the aggregation phenomena, the concentration effect of porphyrin was studied. Absorption spectra of sample b with various concentrations of **3** (loading level; 0–96% vs CEC) were observed. Surprisingly, the absorption spectra of **3** consistently kept the same shape and the linearity of Beer's low was retained for every loading levels. It was thus concluded that aggregation was completely inhibited and that **3** existed as a monomer for every loading levels in the **SSA-3** complex. Because these results indicate that porphyrin molecules can adsorb onto the clay surface, even at a nearly 100% loading level, the **SSA** must exist as a single sheet in water and the porphyrin molecules are therefore adsorbed on the clay sheet at a high density in order to neutralize all of the minus charges of the clay surface, without aggregation (Figure 2). Our observations also demonstrate the swelling model hypothesis of layered silicates by Norrish.[7]

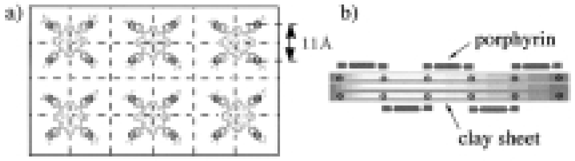


Figure 2. Possible structure for **SSA**-porphyrin complex; a)top view, b)side view.

In general, a fluorescence of dye in clay minerals exhibits a multi-component decay owing to a dye aggregation. Fluorescence decays were observed for samples **3a** and the **SSA- 3** complex (**3b** and **3c** with loading level of 6.7% vs CEC). All of the decay curves were well analyzed using single exponential fitting. Excited singlet lifetimes were estimated to be 9.3 ns for **3a**, 4.1 ns for **3b** and 3.2 ns for **3c**. These also indicate that the porphyrin molecules do not aggregate on the clay sheet.

The possibility of energy transfer between the different porphyrins on the clay sheet was further investigated as one of the typical photochemical reactions. The **SSA-1b-4b** complex was prepared at various loading levels of the porphyrins (1.6, 24, 48, 72 and 96% vs CEC), where each porphyrin was set to be in equal amounts ([**1b**]=[**4b**], [**1b**]+[**4b**] =loading level). The absorption spectra retained the same shape as that of the sum of the two porphyrin's spectra at every loading level of the porphyrins. This indicates that each of the two different kinds of porphyrins adsorbed randomly onto the clay sheet without aggregation. The excitation wavelength was set at 428 nm, which was the λ_{max} of **4b**. Because the λ_{max} of **1b** was 450 nm, 79% of the excitation light was absorbed by **4b** in this experiment. At a low loading level, the fluorescence was mostly emitted from **4b** (λ_{max} = 625 nm). When the loading level of the porphyrin was increased, the fluorescence spectral shape continually became similar to that of **1b** (λ_{max} = 691 nm), in spite of the selective excitation of **4b** (Figure 3). Obviously, an efficient energy transfer from the excited **4b** to **1b** was induced on the clay surface, while there was no interaction in the ground state. The energy transfer was also checked by fluorescence excitation experiment. The findings of this energy transfer experiment could offer an important clue to construct artificial light harvesting systems. The relationship between the distance between adjacent anionic charges on the clay and that between the adjacent cationic charges in porphyrin molecule should be one of the key points in this study. The size-matching method adopted here was demonstrated as a novel method for controlling the dye adsorption onto the clay. It turned out that it is possible to construct the clay-dye complex with very attractive characteristics from the view point of photochemistry, such as high density adsorption of the dye without aggregation.

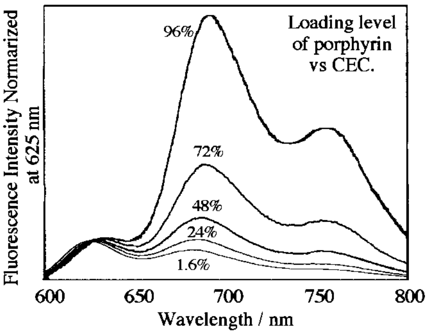


Figure 3. Fluorescence spectra of **SSA-1b-4b** complex normalized at 625 nm. Loading level of porphyrin were 1.6, 24, 48, 72 and 96% vs CEC from bottom; [**1b**]=[**4b**], [**1b**]+[**4b**]=loading level.

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