



## Switching of energy transfer reaction by the control of orientation factor between porphyrin derivatives on the clay surface



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### ABSTRACT

Photochemical energy transfer was examined on the flat clay surface. By the change of surrounding atmosphere, the molecular adsorption orientation angle of dyes can be modulated. It is turned out that the energy transfer efficiency between dyes can be controlled by the relative orientation change between dyes. The change of orientation factor and spectral overlap factor was the main factor to affect the energy transfer efficiency. This technique would be useful to construct the photo-functional materials such as chromic and light harvesting system.

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### Introduction

We have been investigating unique structure of clay–porphyrin complexes,<sup>1</sup> in which porphyrin molecules do not aggregate on the clay surface even at very high density adsorption conditions. Synthetic saponite (Sumecton SA (SSA)) that provides very flat and negatively charged surface<sup>2–4</sup> has been used as an adsorbent. Cationic porphyrin derivatives such as tetrakis(*N*-methyl-pyridinium-4-yl)porphyrin (TMPyP<sup>4+</sup>), [5,10-phenyl-15,20-bis(*N*-methyl-pyridinium-4-yl)porphyrin (*cis*-DPyP<sup>2+</sup>), and zinc tetrakis(*N,N,N*-trimethyl-anilinium-4-yl)porphyrin (ZnTMAP<sup>4+</sup>) and tetramethyltetrapyrindio [3,4-*b*:3',4'-*g*:3'',4''-*l*:3''',4''''-*q*]porphyrizin (Pc<sup>4+</sup>) whose intermolecular charge distance is almost the same as inter-charge distance on the clay surface (1.20 nm), adsorb on the clay surface up to 100% versus cationic exchange capacity (CEC) of the clay without aggregation.<sup>5,6</sup> We have proposed that the matching of inter-charge distances between in porphyrin molecule and on the clay surface realizes such peculiar adsorption structure without aggregation. We termed this as 'inter-charge distance matching effect' or 'size-matching effect'.<sup>1,5,7</sup> The enough long excited lifetime of porphyrins on the clay surface enable us to examine photochemical reactions such as energy transfer reactions aiming an artificial light harvesting system.<sup>8–10</sup> These dyes adsorb with parallel orientation with respect

to the exfoliated clay surface in water.<sup>11</sup> Recently, we found out that it is possible to control the adsorption orientation angle of dye molecule on the clay surface by changing the surrounding solvent conditions.<sup>12</sup> The molecular orientation change accompanies the change of the direction of transition dipole moment and the large absorption spectral change.<sup>13</sup> It has been turned out that the easiness of orientation change on the clay surface depends on the porphyrin structure. When different porphyrins co-adsorb on the clay surface, it is possible to construct the structure that parallel (p) and non-parallel (np) porphyrins co-exist on the clay surface in appropriate conditions. Here, 'p' means that the orientation of dye is parallel and 'np' means that the dye is standing with respect to the clay surface. Förster type energy transfer rate depends on the parameters such as an orientation parameter and distance between energy donor and acceptor and spectral overlapping between fluorescence of energy donor and absorption of energy acceptor as expressed by Eq. 1.<sup>14–16</sup> The equation indicates that it is possible to control energy transfer efficiency by the relative orientation change of dyes on the clay surface. Although it is not easy to examine this idea by conventional methods, the extremely flat clay surface enables this study.

$$k_{ET} = \frac{9000 \ln 10 \kappa^2 \phi^D}{128 \pi^5 n^4 N_A \tau_D R^6} \int f_d(\tilde{\nu}) \varepsilon_a(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4} \quad (1)$$

where  $\tilde{\nu}$  is the wavenumber,  $\varepsilon_a(\tilde{\nu})$  is the extinction coefficient of the acceptor, and  $f_d(\tilde{\nu})$  is the fraction of the total fluorescence intensity

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of the donor,  $\kappa$  is the orientation parameter ( $\kappa^2 = 5/4$  for randomized orientation in the two dimension system),  $\phi_D$  is the fluorescence quantum yield of the donor, and  $n$  is the refractive index of the bulk medium,  $\tau_D$  is the excited singlet lifetime of donor on the clay surface, and  $R$  is the center-to-center distance between donor and acceptor.  $\int f_d(\bar{\nu})\epsilon_a(\bar{\nu})\frac{d\bar{\nu}}{\bar{\nu}^4}$  is termed as  $J$ . In the present paper, the control of energy transfer efficiency by the adsorption orientation change of porphyrin derivatives (Fig. 1) on the clay surface was examined. The energy transfer behavior in the combination of p, p and p, np was investigated.

## Experimental section

Tetrakis(*N*-methyl-pyridinium-4-yl)porphyrin (*p*-TMPyP<sup>4+</sup>), [5,10-phenyl-15,20-bis(*N*-methyl-pyridinium-4-yl)porphyrin (*cis*-DPyP<sup>2+</sup>), and Zn tetrakis(*N,N,N*-trimethyl-anilinium-4-yl) porphyrin (ZnTMAP<sup>4+</sup>) were purchased from the Frontier Scientific and their purity was checked by TLC. Tetramethyltetrapyrindino[3,4-*b*:3'-4'-*g*:3''-4''-*l*:3''',4'''-*q*]porphyrizin (Pc<sup>4+</sup>) was synthesized by the reaction of 3,4-dicyanopyridine in octan-1-ol to the tetrapyrindino[3,4-*b*:3'-4'-*g*:3''-4''-*l*:3''',4'''-*q*]porphyrizin followed by methylation with dimethylsulfate, according to the literature.<sup>6</sup> Pc was obtained as a mixture of the four possible regioisomers and could not be separated. <sup>1</sup>H NMR: (D<sub>2</sub>O, 500 MHz)  $\sigma$ : 10.9 (m, 4H), 9.9 (m, 4H), 9.6 (m, 4H), 5.0 (s, 12H) ppm. Elemental analysis: calcd for C<sub>32</sub>H<sub>26</sub>Cl<sub>4</sub>N<sub>12</sub>·5H<sub>2</sub>O: C, 47.42; H, 4.48; N, 20.74. Found: C, 47.63; H, 4.43; N, 20.86. The counter ions of porphyrins and Pc<sup>4+</sup> were exchanged for chloride by the use of an ion-exchange column (Organo Amberlite IRA400JCL). Sumecton SA (SSA, a synthetic saponite, (Si<sub>7.20</sub>Al<sub>0.80</sub>)(Mg<sub>5.97</sub>Al<sub>0.03</sub>)O<sub>20</sub>(OH)<sub>4</sub>Na<sub>0.77</sub>) was received from Kunimine Industries Co., Ltd. It was purified by repeated decantation from water and washed with ethanol. The cation exchange capacity (CEC) was 99.7 mequiv/100 g. From the CEC value and the theoretical surface area (750m<sup>2</sup>g<sup>-1</sup>), the average area per anionic site was calculated to be 1.25 nm<sup>2</sup>. Thus, the mean distance between the adjacent anionic sites was estimated to be 1.20 nm, on the basis of a hexagonal array. The particle size was in the range of 20–50 nm, according to the AFM observations. The thickness of the clay sheet is theoretically 0.96 nm. TG-DTA measurements were carried out with a SHIMADZU DTG-60H. AFM measurements were carried out with SPI4000 and SPA300HV systems (Seiko Instruments Inc.). Absorption spectra were obtained on a UV-3150 UV-vis. spectrophotometer (SHIMADZU). Dichroic measurements on a quartz waveguide were performed with a SIS-50 BS surface/interface spectrometer (System Instruments). The thickness of the waveguide was 0.2 mm. The clay-porphyrin complex dispersed in water was prepared by mixing porphyrin aqueous solution and clay aqueous solution with vigorous stirring. The obtained nano-sheets completely exfoliate under the present conditions, and thus the obtained clay-dye aqueous solution is optically transparent. For optical measurement, typical concentrations of SSA and dyes are 2.67 × 10<sup>-6</sup> equiv L<sup>-1</sup> and 1.33 × 10<sup>-7</sup> M, respectively. In energy transfer experiment, [donor dye] = [acceptor dye] = 5.7 × 10<sup>-8</sup> M, [SSA] = 2.29 × 10<sup>-6</sup> equiv L<sup>-1</sup>. Cast films for dichroic measurements

were prepared as follows.<sup>11</sup> The surface of a quartz waveguide was washed with concentrated H<sub>2</sub>SO<sub>4</sub> to enhance the hydrophilicity. An aliquot of aqueous solution (3.5 μL) containing the exfoliated SSA (1.0 × 10<sup>-4</sup> equiv L<sup>-1</sup>) was pipetted onto the hydrophilic quartz waveguide, and the water was allowed to evaporate at room temperature. Subsequently, an aliquot of aqueous porphyrin solution (1.0 × 10<sup>-5</sup> M, 3.5 μL) was pipetted onto the cast film of SSA, and the excess was washed away with deionized water.

## Results and discussions

The complex formation behavior of dyes with clay was examined by absorption spectra and dichroic spectra using evanescent light. The absorption spectra of dyes without and with clay in aqueous solution are shown in Figure S1. In all cases, the  $\lambda_{\max}$  was shifted to longer wavelength by the complex formation with clay. The  $\lambda_{\max}$  of *p*-TMPyP<sup>4+</sup>, Pc<sup>4+</sup>, *cis*-DPyP<sup>2+</sup>, and ZnTMAP<sup>4+</sup> was shifted from 421 to 451 nm, from 690 to 696 nm, from 419 to 455 nm and from 422 to 430 nm, respectively (Table 1). It is well known that a co-planarization of adsorbed molecule on the clay surface induces the absorption spectral shift to longer wavelength.<sup>13</sup> This indicates that all dyes would adsorb on the clay surface with parallel way. It is reported that parallel adsorption is favored in aqueous solution because of hydrophobic interaction between the porphyrin ring and clay surface, in the case of *cis*-DPyP<sup>2+</sup>.<sup>12</sup> The reason for small  $\lambda_{\max}$  shift for Pc<sup>4+</sup> is that the planarity of Pc<sup>4+</sup> is originally rather high and the co-planarization effect of the clay surface is not so large.

To confirm the molecular orientation angle of dyes, dichroic absorption spectra of porphyrin on the clay nano-sheet by using evanescent light on the waveguide glass<sup>11,12</sup> were measured. Here, the orientation angle is defined as the angle between the clay surface and the transition dipole moment of the dye. The sample setup for the dichroic measurement is shown in Figure S2. The dichroic spectra for dyes are shown in Figure 2. As can be seen, the absorption due to *s*-polarized light was much stronger than that due to *p*-polarized light for all dyes. These results indicate that all dyes adsorb on the clay surface with parallel orientation with respect to the clay surface in aqueous solution. According to the literature,<sup>11,12</sup> the orientation angle of *p*-TMPyP is <5 degree, judging from the dichroic ratio.

The adsorption orientation change behavior of *p*-TMPyP<sup>4+</sup>, Pc<sup>4+</sup>, *cis*-DPyP<sup>2+</sup>, and ZnTMAP<sup>4+</sup> on the clay surface was examined by changing the surrounding solvent conditions. As mentioned above, the orientation behavior can be examined by the observation of absorption spectra and dichroic observations. The absorption spectral changes of each dye in acetone-water mixture are shown in Figure 3. The content of acetone was changed from 0% to 90% (v/v). In the case of *p*-TMPyP<sup>4+</sup> and Pc<sup>4+</sup>-clay complexes, the increase of acetone content induced the small absorption shift to longer wavelength. This seems to be a typical solvent effect. On the other hand, prominent blue shifts were observed for *cis*-DPyP<sup>2+</sup> and ZnTMAP<sup>4+</sup>-clay complexes by the increase of acetone content. Judging from these observations, it is suggested that *p*-TMPyP<sup>4+</sup> and Pc<sup>4+</sup> adsorb on the clay surface with parallel orientation in

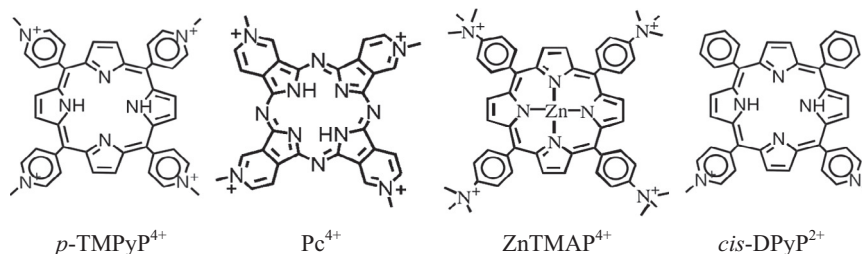


Figure 1. The structure of tetra- and di-cationic porphyrin derivatives.

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