

Supporting information

The Elucidation of the Adsorption Distribution of Cationic Porphyrin on the Inorganic Surface by Energy Transfer as a Molecular Ruler

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SI 1. Purification of clay nano sheet

In an Erlenmeyer flask, clay nano sheet (Sumecton SA; SSA) was dispersed in 300 mL of distilled water. The dispersion was left for a few days. The supernatant liquid was pour into centrifugation tubes (50 mL) and centrifuged. At first time, the condition was 6000 rpm for 3h. Then the supernatant liquid was pour into new centrifugation tubes and centrifuged at 7000 rpm for 5 h. The second precipitate was dried in vacuum for a day.

SI 2. Synthesis of pyrene modified clay nanosheet

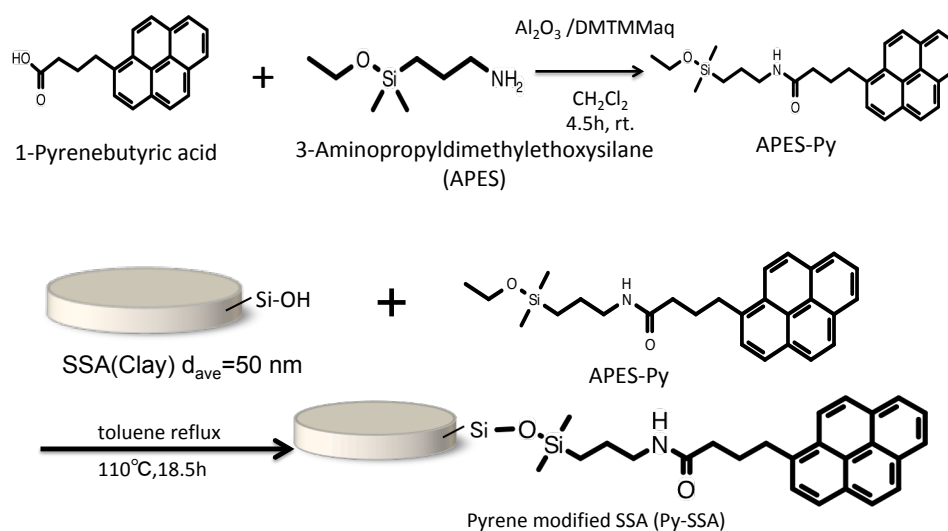


Figure S1. Synthesis of pyrene modified clay nanosheet (Py-SSA).

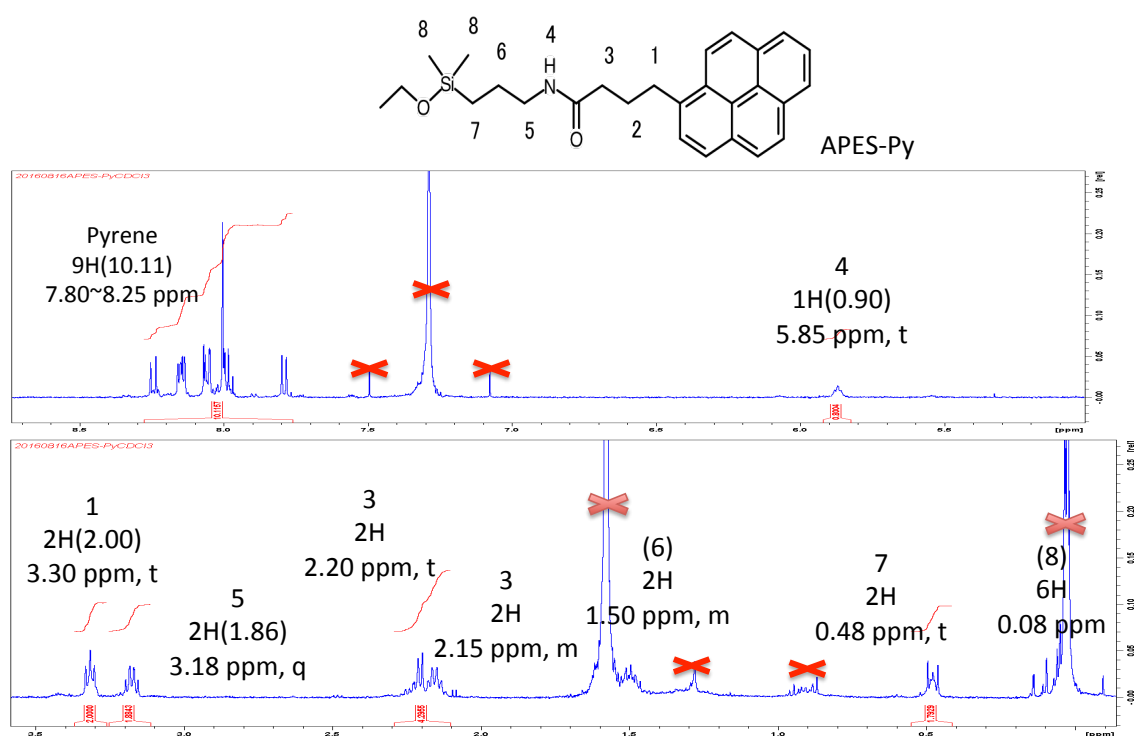


Figure S2. ¹H-NMR of APES-Py (Solvent: CDCl₃)

The ¹H-NMR of APES-Py is shown in Figure. S2. According to this result, the ethoxy group was not confirmed in CDCl₃, but it seemed the hydrolysis was occurred at the observation.

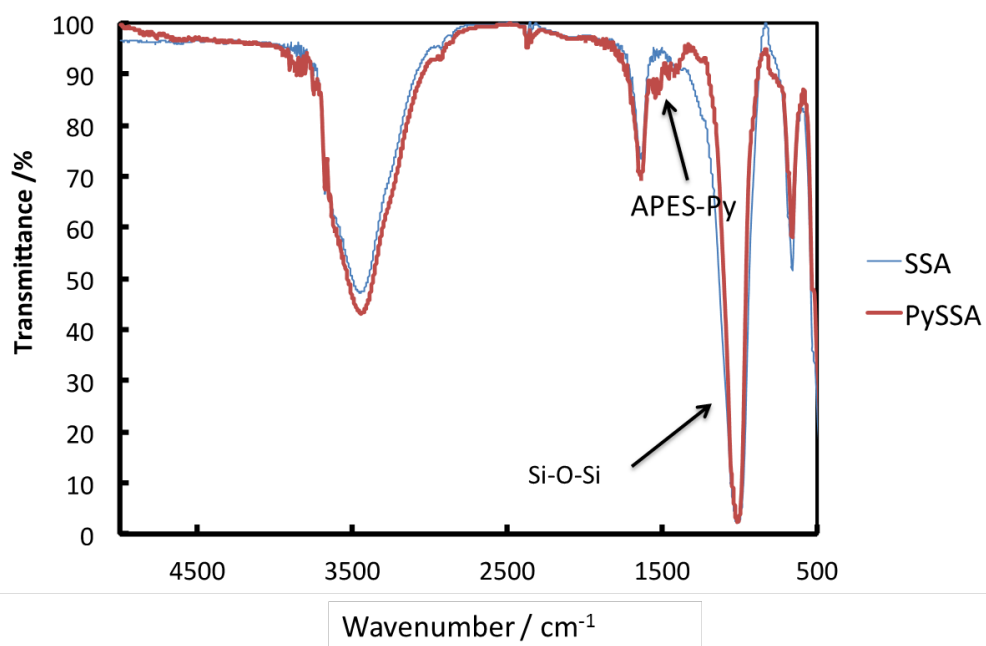


Figure S3. FT-IR spectra of SSA and PySSA (KBr)

The FT-IR spectra of SSA and pyrene modified SSA is shown in Figure.S3. Compared PySSA with SSA, the peak of N-H vibration and pyrene were observed around 1500 cm^{-1} , thus the presence of APES-Py was confirmed.

SI 3. Control experiment of energy transfer reaction (between free pyrene to SSA-*p*-TMPyP complex)

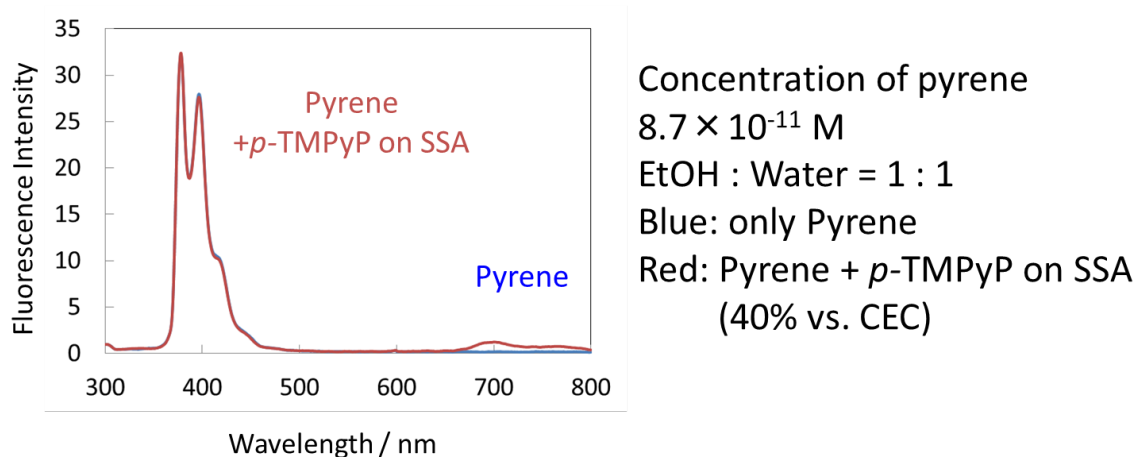


Figure S4. The fluorescence spectra of pyrenebutyric acid solution and pyrenebutyric acid added SSA-*p*-TMPyP complex solution (Solvent : Ethanol / Water = 1 / 1 (v/v)).

As seen from Figure. S4, the energy transfer reaction was not confirmed from pyrenebutyric acid which was not bonded at edge of SSA to *p*-TMPyP on SSA.

SI 4.Details for theoretical calculation of energy transfer efficiencies (η_{ET})

To discuss the adsorption distribution of *p*-TMPyP, distinctive three models were assumed. Three adsorption models are i) random adsorption, ii) from edge to center and iii) from center to edge. The theoretical energy transfer efficiencies (η_{ET}) were calculated for three adsorption models. Here, ii) from edge to center and iii) from center to edge were described as below.

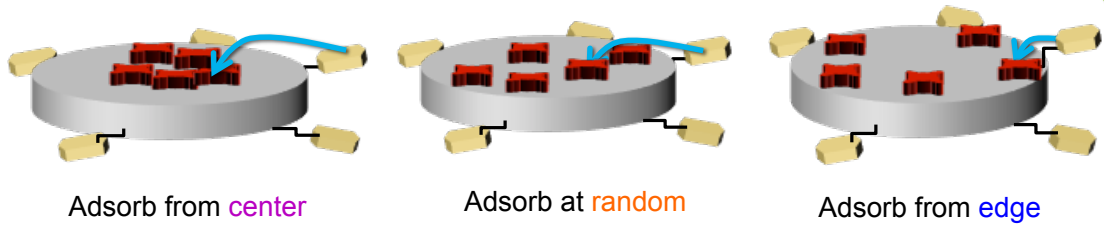


Figure S5. Three adsorption types of *p*-TMPyP on the clay surface.

The energy transfer efficiency (η_{ET}) when n porphyrins adsorb on one side of clay nanosheet were calculated in consideration of specific arrangements. The arrangement pattern of porphyrins on both sides of clay nanosheet is defined as i . The energy transfer efficiency $\eta_{ET}(2n)$ when $2n$ porphyrins adsorb on clay nanosheet was evaluated by eq. 1. Because porphyrins adsorb both side of clay, the number of porphyrins is described $2n$.

$$\eta_{ET}(2n) = \sum_{i=1}^{N_D} \eta_{ET(i)} p_{(i)} \quad (1)$$

, where $\eta_{ET(i)}$ is the energy transfer efficiency for the arrangement i , $p_{(i)}$ is the appearance probability for the arrangement i and N_D is the number of all arrangement i including both sides of clay nanosheet. $\eta_{ET(i)}$ was calculated according to eq. 2.,

$$\eta_{ET(i)} = \frac{k_{ET(i)}}{1/\tau_D + k_{ET(i)}} \quad (2)$$

, where the energy transfer rate constant of arrangement i ($k_{ET(i)}$) was represented the sum of energy transfer rate constants between porphyrin adsorbed on S_m and the edge modified pyrene.

The appearance probability $p_{(i)}$ of arrangement i depends on the adsorption distribution models.

For calculation of ii) from edge to center and iii) from center to edge, the clay surface was approximately divided by concentric rings of width 2.1 nm shown in Figure. S3. This width 2.1 nm was the radial component of the distance between the centers of the sites (2.4 nm). Those rings were named as A_1 , A_2 and A_3 in order from the outermost layer, and the number of adsorption sites in the regions A_1 , A_2 and A_3 were defined as N_1 , N_2 and N_3 , respectively. When one side of clay (the diameter was 50 nm) was considered, N_1 , N_2 and N_3 were calculated to be 62, 56 and 51, respectively. Then, the total number of adsorption site was 392.

The number of adsorption site per one side of clay nanosheet was defined as N_S . The number

of arrangements when n porphyrins adsorbed on one side of clay nanosheet is $N_S C_n$. Therefore, the number of all arrangements i including both sides of clay nanosheet N_D is $(N_S C_n)^2$. In the case of ii) from edge to center and iii) from center to edge, N_S is depend on the number of adsorbed porphyrins n .

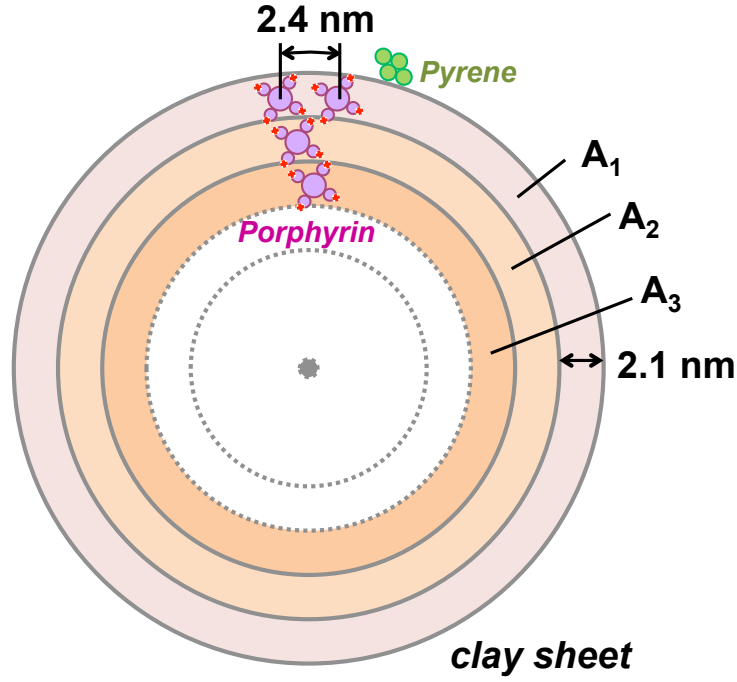


Figure. S6. Structural model of clay nanosheet / pyrene /porphyrin ternary complex for calculation of ii) from edge to center and iii) from center to edge.

The case of ii) from edge to center

It was assumed that porphyrins adsorb from outermost area A_n in ascending order. Thus the $p_{(i)}$ was changed as the loading level of porphyrins.

$$0 < n \leq 62 : p_{(i)} = 1 / ({}_{62}C_n)^2$$

$$63 \leq n \leq 118 : p_{(i)} = 1 / ({}_{56}C_{n-62})^2$$

$$119 \leq n \leq 169 : p_{(i)} = 1 / ({}_{51}C_{n-118})^2$$

$$170 \leq n : p_{(i)} = 1 / ({}_{223}C_{n-169})^2$$

The case of iii) from center to edge

The calculation method was the reverse of the case of ii) from edge to center.

$$1 \leq n \leq 223 : p_{(i)} = 1 / ({}_{223}C_n)^2$$

$$224 \leq n \leq 274 : p_{(i)} = 1 / ({}_{51}C_{n-223})^2$$

$$275 \leq n \leq 331 : p_{(i)} = 1 / ({}_{56}C_{n-274})^2$$

$$332 \leq n : p_{(i)} = 1 / ({}_{62}C_{n-331})^2$$