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Unique photochemical behavior of novel tetracationic pyrene derivative on the clay surface

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ABSTRACT

Novel tetracationic pyrene derivative $(1,3,6,8-tetrakis(N-methylpyridinium-4-yl)pyrene, Py^{4+})$ was synthesized. Photochemical properties such as fluorescence quantum yield and fluorescence lifetime were observed for Py^{4+} and Py^{4+} /clay complexes. Judging from Lambert-Beer plot analysis, Py^{4+} molecules adsorb on the clay surface without aggregation up to 69% versus cation exchange capacity of the clay. Py⁴⁺ molecule emits strong fluorescence from an excited state of monomer, while the emission from excimer was not detected, in spite of high density adsorption condition on the solid surface. It is supposed that strong interaction between host and guest by the 'Size-Matching Effect' inhibits the formation of excimer on the clay surface.

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Clay minerals are inorganic materials that provide negatively charged flat surface. Artificially synthesized clay aqueous solution is colorless and transparent in the visible region. Several papers reported the photochemical behavior of organic dyes/inorganic clay complexes.^{1,2} We have successfully prepared the unique complexes in which the porphyrin molecules adsorb on the clay surfaces without aggregation. By using such an adsorption structure, an efficient energy transfer reaction was achieved in porphyrin/ clay complexes toward the establishment of artificial lightharvesting system.³ The crucial factor for high density adsorption of porphyrin with controlled intermolecular gap distance is matching of the distance between negatively charged sites on the clay sheet and that between positively charged sites in the porphyrin molecules ('Size-Matching Rule').⁴⁻⁷ In the present Letter, we aim to develop the artificial light-harvesting system by the addition of pyrene as a dye, which can absorb shorter wavelength light in the visible region. The absorption of porphyrin/clay complexes is around 426–465 nm.⁴ It is expected that pyrene/clay complexes absorb the light below 426 nm. Several researches reported a synthesis of pyrene derivative and their photochemical behavior.^{8,9} However, as far as we know, 1,3,6,8-tetrakis(N-methylpyridinium-4-yl)pyrene (Py⁴⁺) has not been synthesized. In this work, we synthesized Py⁴⁺ and observed its photochemical properties with and without clay in aqueous solution.

Pv⁴⁺ was synthesized as a tetracationic pyrene derivative as shown in Scheme 1.

3.5 mL of tetrahydrofuran, 0.5 mL of toluene, and 3.0 mL of 2 M aqueous potassium carbonate were added to a solid mixture of 1,3,6,8-tetrabromopyrene and 4-pyridinyl boronic acid (375.8 mg, 3.0 mmol) under N₂ atmosphere. Finally, tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) (3.25 mg, 0.0028 mmol) was added to the mixture. The mixture was refluxed under nitrogen for 4 days.¹⁰ The crude product poured into 10 mL of methanol was filtered with the PTFE membrane filter ($\Phi = 0.1 \,\mu\text{m}$) and washed by water. The yellow powder was obtained (150.6 mg, 59%). Identity



Scheme 1. The synthetic routes of Py4+.





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of the product was confirmed using ¹H NMR. Synthesized 1,3,6,8tetrakis(pyridine-4-yl)-pyrene (150.6 mg, 0.29 mmol) was added to a solution of 3.6 mL of iodomethane and 90 mL of acetonitrile. The mixture was refluxed under nitrogen for 6 days. After the reaction mixture was evaporated and dried, 76 mL of water was added and the formed precipitates were removed by filtration. Ammonium hexafluorophosphate (219.4 mg) was added to the filtrate under vigorous stirring. The precipitated yellow solid was collected by filtration with the PTFE membrane filter ($\Phi = 0.1 \,\mu\text{m}$) (75.9 mg, 48%). ¹H NMR(CD₃CN, 500 MHz) δ (ppm): 8.85 (d, J = 9.2 Hz, 8H), 8.32 (d, J = 6.8 Hz, 4H), 8.31 (4H, s), 8.30 (s, 2H), 7.60 (s, 12H). Elemental analysis: Found: C, 41.31; H, 2.76; N, 4.92; Calcd for $C_{40}H_{34}F_{24}N_4P_4{\cdot}0.4H_2O{:}$ C, 41.49; H, 3.03; N, 4.84. Sumecton SA (SSA, Kunimine Ind, Co.) was used as clav minerals. Cation exchange capacity (CEC) of SSA is 0.997 meq g^{-1} . According to the PM3 calculation, estimated inter-cationic distances in Pv⁴⁺ are 0.95 nm and 1.1 nm as indicated in Scheme 1, while inter-anionic distance on the clay surface is 1.2 nm.⁴ This indicates that the structure of Py⁴⁺ fulfills almost the 'Size-Matching Rule'.

Photochemical properties such as absorption, fluorescence and its lifetime were observed for Py^{4+} itself and $Py^{4+}/clay$ complexes in water. $Py^{4+}/clay$ complex in water was prepared as follows. Aqueous Py^{4+} solution was mixed with aqueous clay solution under vigorous stirring. Absorption spectra were measured by SHIMADZU UV-3150 ([SSA] = 4.0×10^{-6} equiv L⁻¹, [Py⁴⁺] = 1.1×10^{-6} 10^{-7} –2.2 × 10^{-6} M). Fluorescence spectra were measured by Jasco FP-6600 ([SSA] = $6.7 \times 10^{-7} - 8.0 \times 10^{-4}$ equiv L⁻¹, [Py⁴⁺] = 1.1×10^{-4} 10^{-7} M). Fluorescence quantum yield ($\Phi_{\rm f}$) and fluorescence lifetime (τ) were measured for Py⁴⁺ itself and Py⁴⁺/clay complexes in water where the loading level is 0.06% versus CEC of the clay ([SSA] = 8.0×10^{-4} equiv L⁻¹, [Py⁴⁺] = 1.1×10^{-7} M). Timeresolved fluorescence signals were measured by Hamamatsu Photonics C4780 system based on a streak detector. A laser diode (Hamamatsu Photonics C4725, 406 nm, FWHM 71 ps, 1 kHz) and an Nd³⁺ YAG laser with an OPG (EKSPLA PL2210JE + PG-432, 410 nm, FWHM 25 ps. 1 kHz) were used for excitation.

Absorption and fluorescence spectra are shown in Figure 1. λ_{max} of Py⁴⁺ in aqueous solution and on the clay surface were 422 nm and 450 nm, respectively. The shift of λ_{max} by the complex formation with clay was 28 nm ($\Delta E = 1.5 \times 10^3 \text{ cm}^{-1}$). In the case of porphyrin/clay complexes where porphyrin molecule adsorbs on the clay surface with a parallel orientation, λ_{max} was shifted to longer wavelength due to the flattening of the *meso*-substituents with respect to the porphyrin ring.^{5,11} In the case of porphyrin molecule with a standing orientation respect to the clay surface, such a large shift of λ_{max} was not observed. Thus, the λ_{max} shift of Py⁴⁺ indicates that Py⁴⁺ molecule adsorbs on the clay surface with a parallel orientation as expected. It is due to the flattening of the 1,3,6,8-substituents with respect to the pyrene ring.

Absorption spectra of Py⁴⁺/clay complex were measured at various loading levels of Py⁴⁺. Judging from the normalized spectra,



Figure 2. Absorption spectra and Lambert–Beer plot of Py⁴⁺/clay complexes in water. [SSA] = 4.0×10^{-6} equiv L⁻¹, [Py⁴⁺] = 1.1×10^{-7} – 2.2×10^{-6} M.

all spectra were identical up to 66% versus CEC of the clay. As can be seen in Figure 2 inset, Lambert–Beer plot was straight up to 69% versus CEC of the clay. Absorption spectra of Py⁴⁺ in aqueous solution were superimposed above 69% versus CEC of the clay. These indicate that Py⁴⁺ molecules adsorb on the clay surface up to 69% versus CEC without aggregation. It should be noted that 69% is extremely high value. In the case of methylene blue, that is a typical dye, the aggregation was observed on the clay surface even below 5% versus CEC of the clay.¹² In the case of Py⁴⁺/clay complexes, coulombic interaction between Py⁴⁺ molecule (guest) and clay (host) is strong due to four points and effective interaction between clay and dye due to 'Size-Matching Effect'. Thus, the interaction between Py⁴⁺ molecules (guest–guest) that induces the aggregation was suppressed.

Fluorescence λ_{max} of Py⁴⁺ in aqueous solution and on the clay surface were 485 nm and 498 nm, respectively (Fig. 1b). The shift of fluorescence λ_{max} by the complex formation with clay was 13 nm ($\Delta E = 5.4 \times 10^2 \text{ cm}^{-1}$). The shapes of both fluorescence spectra were relatively sharp compared to excimer emission of non-substituted pyrene (Py) as shown in Table 1.

Full width half maximum (FWHM) of monomer emission of Py and that of excimer emission were 2774 cm^{-1} and 5137 cm^{-1} , respectively. Full width half maximum of Py⁴⁺ on the clay surface was 2319 cm^{-1} . These indicate that Py⁴⁺ exists as monomer without excimer formation on the clay surface, although Py forms excimer easily on the clay surface.¹⁶ It should be noted that such monomer adsorption on the solid surface is highly unique. In fact, when Py⁴⁺ aqueous solution (700 µL of 1.45×10^{-5} M) was casted on the quartz glass substrate, only excimer emission was observed at 552 nm. It is supposed that Py⁴⁺ molecules can retain the long



Figure 1. Absorption (a) and fluorescence (b) spectra of Py⁴⁺ itself in water (dashed line) and Py⁴⁺/clay complexes in water (solid line). (a) [SSA] = 4.0×10^{-6} equiv L⁻¹, [Py⁴⁺] = 3.3×10^{-7} M. (b) [SSA] = 8.0×10^{-4} equiv L⁻¹, [Py⁴⁺] = 1.1×10^{-7} M.

Table 1	
Photochemical properties of Py and	Py^{4+}

	FWHM (cm ⁻¹)	$\Phi_{ m f}$	τ (ns)	$k_{\rm f}^{\rm c}({\rm s}^{-1})$	$\frac{k_{\rm isc} + k_{\rm nr} + k_q [O_2]}{(s^{-1})}^{\rm c}$
Py Monomer Excimer	2774 ^a 5137 ^a	0.04 ^b	11.7 ^b	$\textbf{3.42}\times 10^6$	$\textbf{8.21}\times 10^7$
Py ⁴⁺ Without clay With clay	2709 ^d 2319 ^e	0.70 ^{d,f} 0.42 ^{e,f}	3.4 ^d 3.2 ^e	$\begin{array}{c} 2.06\times10^8\\ 1.31\times10^8\end{array}$	$\begin{array}{l} 8.81\times 10^7 \\ 1.82\times 10^8 \end{array}$

^a Estimated from fluorescence spectra in Ref. 13.

^b Pyrene in aerated chloroform solution at concentration 10^{-5} M.¹⁴

^c Calculated using the equations, $\Phi_f = k_f \tau$ and $\tau = 1/(k_f + k_{isc} + k_{nr} + k_q[O_2])$. ^d In aerated water ([Py⁴⁺] = 1.1×10^{-7} M).

^e In aerated water where the loading level is 0.06% of Py⁴⁺ versus CEC of the clay $([SSA] = 8.0 \times 10^{-4} \text{ equiv } L^{-1}, [Py^{4+}] = 1.1 \times 10^{-7} \text{ M}).$

 $\Phi_{\rm f}$ values were determined using rhodamine 6G ($\Phi_{\rm f}$ = 0.95) as a standard in aerated condition.15

intermolecular distance and the formation of excimer was suppressed due to the 'Size-Matching Effect'^{4–7} that fixes the position of dyes on the clay surface. When the adsorbed amount of Py⁴⁺ on the clay surface increased, the shape of fluorescence spectra was retained, although the fluorescence intensity decreased gradually. This also supports that excimer does not form in the clay complex.

 $\Phi_{\rm f}$ of Py and Py⁴⁺ itself were 0.04 in aerated chloroform solution and 0.70 in aerated aqueous solution, respectively. $\Phi_{\rm f}$ of Py⁴⁺ is much higher than that of Py. $\Phi_{\rm f}$ of Py were 0.52 in de-aerated solution.¹⁴ Thus, fluorescence of Py is quenched by oxygen in aerated condition.¹⁷ It is unique that high $\Phi_{\rm f}$ of Py⁴⁺ was observed in spite of the presence of oxygen. $\Phi_{\rm f}$ of Py⁴⁺ in de-aerated aqueous solution was almost identical with that of Py⁴⁺ in aerated aqueous solution, thus, the effect of oxygen was negligible for Py^{4+} . τ_{Py}^{4+} was 3.4 ns in aerated aqueous solution. On the other hand, τ_{Pv} was 150.1 ns in de-aerated chloroform solution.¹⁴ In the case of Py⁴⁺, it is supposed that the collision between Py4+ molecules and oxygen molecules is not effective in excited states, since τ_{Py}^{4+} was short. Generally, τ of substituted pyrene is shorter than that of Pv.^{8,18}

 $\Phi_{\rm f}$ and τ were measured for Py⁴⁺ itself in water and Py⁴⁺/clay complexes in water at 0.06% loading level versus CEC. At such loading level, fluorescence self-quenching does not occur. $\Phi_{\rm f}$ of Py⁴⁺ itself and Py⁴⁺/clay complexes were 0.70 and 0.42, respectively. The structural change of Py⁴⁺ on the clay surface would affect the nonradiactive deactivation rate constant, and, thus, induce the change of $\Phi_{\rm f}$.

This Letter firstly reported the synthesis of 1,3,6,8-tetrakis(Nmethylpyridinium-4-yl)pyrene and its photochemical properties. As a result, we found out that Py⁴⁺ adsorbs on the clay surface without aggregation at high density condition. It is turned out that Py⁴⁺ is a suitable dye for energy transfer reaction, especially as an energy donor. In addition, interestingly, Py4+ molecules emit fluorescence from its excited monomer state. These unique behaviors were realized by the 'Size-Matching Effect'.

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