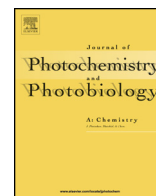




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Color tuning of cationic pyrene derivatives on a clay nanosheet: Retardation of gradual redshift on clay



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ABSTRACT

A novel type of trimethylanilinium-substituted pyrene derivative, 1,6-di(*N,N,N*-trimethylanilinium-4-yl)pyrene 2I[−] (An-Py²⁺), was synthesized. An-Py²⁺ exhibits strong emission with a high-emission quantum yield (approximately 90%) in aqueous solution. An-Py²⁺ was hybridized on a clay (Sumecton SA (SSA)) surface, and the photochemical behavior of An-Py²⁺ on the SSA surface was investigated using absorption and emission spectroscopic analyses, emission quantum yield (Φ_f), and lifetime (τ) measurements. Effective adsorption of An-Py²⁺ on SSA was observed, and adsorption limit was estimated to be 100% relative to the cation-exchange capacity (CEC) of SSA. The previously reported pyridinium-substituted pyrene derivatives cause a gradual redshift of both absorption and emission on the SSA surface. In contrast, An-Py²⁺ effectively suppresses such a redshift on SSA due to anilinium substitution of the pyrene unit.

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1. Introduction

Photoinduced electron or energy transfer reaction efficiency is strongly affected by the distance between the donor and acceptor molecules [1]. Thus, the control over intermolecular distance between photoreactive molecules is essential for achieving efficient photoreactions. Inorganic materials with ordered nanostructures [2–4], such as zeolites [5,6], mesoporous materials [2,3,7–11], layered compounds [12–19], and layered semiconductors [2,3,18–21], are often used as host materials in various photoreactions. Clay nanosheets are attractive materials for this purpose because some clay nanosheets have ordered negative-charge distributions on their surface [17–19,22,23]. Recently, we reported a remarkable emission quenching via energy transfer of tetracationic pyrene derivatives [24] (Py⁴⁺; see Fig. 1a) on a clay surface [25,26]. In this case, the apparent emission-quenching rate constant k_q is $7.4 \times 10^{15} \text{ L mol}^{-1} \text{ s}^{-1}$ due to two different molecules (i.e., the energy-donating Py⁴⁺ and energy-accepting tris(bipyridine)ruthenium(II) (Ru²⁺)) were both fixed on the clay (Sumecton SA (SSA)) surface [26]. Moreover, a remarkable emission

amplification of Ru²⁺ was observed in this system [25]. Therefore, these systems are promising as new types of light energy accumulation systems because Ru²⁺ and its derivatives are frequently used as redox photosensitizers for various photo-reactions [9–11,27–32]. However, the observed energy accumulation property is not that good. Stoichiometric amounts of Ru²⁺ are required for approximately 85% of emission quenching [25]. Emission quenching may occur for a resonance-type energy transfer from Py⁴⁺ to Ru²⁺ on SSA in this system. Thus, we assume that the origin of such low-energy accumulation is the low overlap integral ($J = 0.91 \times 10^{14} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$; Fig. S1 in the supplementary content (SC) section) between the fluorescence of Py⁴⁺ and absorption of Ru²⁺ on SSA. To increase the J -value, the emission spectra of Py⁴⁺ on SSA shift toward a shorter wavelength region. However, the absorption and emission spectra of Py⁴⁺ gradually red-shifted on the SSA surface (Fig. S2) due to the flattening of pyridinium ring with respect to the pyrene ring [24–26,33]. This flattening leads to the enhancement of electron withdrawing and apparent extension of the π -conjugate within the Py⁴⁺ molecule [34–36]. To avoid the redshift of pyrene on the SSA surface, the π -conjugation between the pyridinium ring and the pyrene moiety should be severed. Therefore, we synthesized a novel type of trimethylanilinium-substituted pyrene derivative, 1,6-di(*N,N,N*-trimethylanilinium-4-yl)pyrene 2I[−] (An-Py²⁺), as shown in Fig. 1b.

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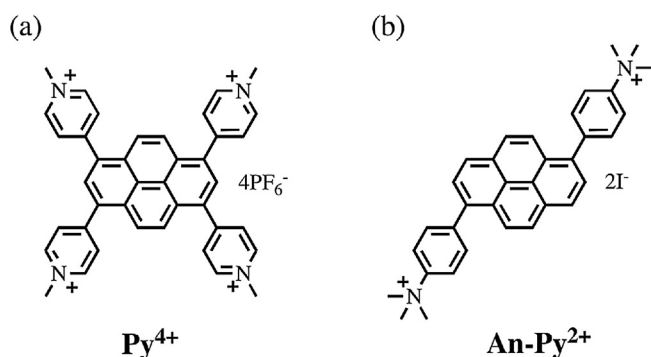


Fig. 1. Molecular formula of Py^{4+} (a) and An-Py^{2+} (b).

In this study, we report the color control (i.e., the retardation of redshift) of cationic pyrene derivatives and their photochemical behaviors on SSA.

2. Experiment

2.1. Materials

Novel type of cationic pyrene derivative, An-Py^{2+} , was synthesized according to the literature method and slightly modified, as shown in Scheme 1 [24,33]. Details of synthesis are summarized in the SC. Cation exchangeable saponite clay (Sumecton SA, SSA) was provided by Kunimine Industrial Co., Ltd., and used as received. Calculated surface area and cation exchange capacity (CEC) of SSA are $750\text{ m}^2\text{ g}^{-1}$ and $0.997\text{ mequiv g}^{-1}$, respectively [36,37]. Water was purified by a Milli-Q water system (Direct-Q[®] 3UV, Millipore, $<18.2\text{ M}\Omega\text{ cm}^{-1}$) and used for all experiments.

2.2. Sample preparation

A hybrid of An-Py^{2+} adsorbed onto SSA ($\text{An-Py}^{2+}/\text{SSA}$) was prepared by mixing an aqueous SSA dispersion and aqueous An-Py^{2+} solution for 2 h at room temperature in the dark condition [26]. The loading amounts of the An-Py^{2+} are expressed as the percentage of cationic charge on the An-Py^{2+} relative to the CEC of the SSA (hereafter denoted % CEC).

2.3. Analysis

UV–vis absorption spectra were obtained in transmittance mode and recorded on a V-670 (JASCO) spectrometer. Emission spectra were recorded by a steady state emission spectrometer (PF-6300 (JASCO)). Emission quantum yields were measured by an absolute emission quantum yield measurement systems equipped with calibrated integrating sphere (QW-2100NU; Otsuka Electronics Co., Ltd) [9–11,38]. Emission lifetimes were measured by using Fluoro Cube spectrofluorometer (Horiba) equipped with

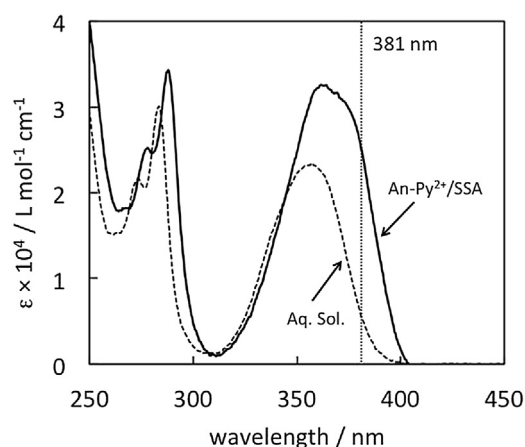


Fig. 2. Absorption spectra of An-Py^{2+} (dashed) and $\text{An-Py}^{2+}/\text{SSA}$ (solid) in the aqueous solution; $[\text{An-Py}^{2+}] = 4\text{ }\mu\text{mol L}^{-1}$ (0.1% CEC), $[\text{SSA}] = 8\text{ g L}^{-1}$.

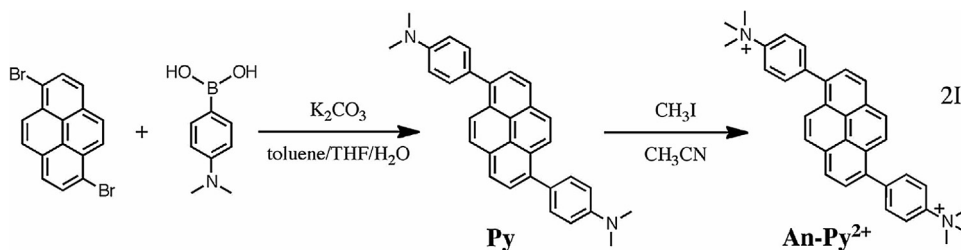
diode pulse laser (DD-375L: excitation wavelength = 376 nm, 0.4 ns fwhm) [25,26]. In order to remove oxygen molecules from the solution, Ar gas was bubbled through all of the samples for 30 min [25,26].

3. Results and discussion

3.1. Adsorption of An-Py^{2+} onto the SSA surface

The typical absorption and emission spectra for considerably low loading amounts of An-Py^{2+} (0.1% cation-exchange capacity (CEC)) are illustrated in Figs. 2 and 3, respectively, and their maxima with and without SSA are summarized in Table 1. The absorption spectral shapes were identical at $[\text{An-Py}^{2+}] = 0.008\text{--}6\text{ }\mu\text{mol L}^{-1}$ (0.1%–75% CEC), as described below. Both the absorption and emission spectra of $\text{An-Py}^{2+}/\text{SSA}$ were slightly red-shifted relative to An-Py^{2+} in an aqueous solution. The previously reported Py^{4+} system exhibits a gradual redshift on the SSA surface (Fig. S2). The difference between the absorption maxima of Py^{4+} at a longer wavelength region (400–500 nm) in an aqueous solution and the one adsorbed on the SSA surface ($\Delta\lambda_{\text{A,max}}$) is 25 nm. Additionally, the absorption spectral shapes of Py^{4+} are identical when the amount of adsorption of Py^{4+} is less than 69% CEC. Based on the photochemical characterization, this gradual redshift is caused by adsorption and Py^{4+} may exist as a monomer on the SSA surface. In contrast, the anilinium-substituted An-Py^{2+} molecule effectively suppresses the redshift of the absorption band at approximately 360 nm even when the An-Py^{2+} is adsorbed on the SSA surface ($\Delta\lambda_{\text{A,max}} = 7\text{ nm}$). Such retardation of gradual redshift on clay surface may cause by the little electronic interaction between the pyrene moiety and anilinium group of An-Py^{2+} on SSA surface, as described in the introduction part.

Absorption spectra and the corresponding Lambert–Beer (LB) plot at 381 nm of $\text{An-Py}^{2+}/\text{SSA}$ with various loading amounts of



Scheme 1. The synthetic routes of An-Py^{2+} .

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