

Photopolymerization of Aniline Dimer by Photocatalytic Reaction of Ruthenium Trisbipyridyl in the Interlayer of Hectorite Clay

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Photoinduced electron transfer (PIET) between ruthenium tris(2,2'-bipyridyl) complex ($\text{Ru}(\text{bpy})_3^{2+}$) and electroactive materials, *i.e.*, electron acceptors and donors, has been studied extensively from the stand point of artificial photosynthesis and photoenergy conversion.¹ Since $\text{Ru}(\text{bpy})_3^{2+}$ can be regenerated in the presence of appropriate sacrificial agents, it acts as a photocatalyst. Polymerization involving oxidation of electroactive material can thus be induced by the photocatalytic reaction of $\text{Ru}(\text{bpy})_3^{2+}$. Photopolymerization of pyrrole using $\text{Ru}(\text{bpy})_3^{2+}$ has been reported.² We reported photopolymerization of aniline and an aniline dimer, *i.e.*, *N*-phenyl-*p*-phenylenediamine (PPD), by illuminating a bilayer film composed of $\text{Ru}(\text{bpy})_3^{2+}$ -incorporated Nafion and methylviologen (MV^{2+})-pendant poly(siloxane)³ or a single layer film composed of $\text{Ru}(\text{bpy})_3^{2+}$ - and MV^{2+} -incorporated Flemion.^{4,5} We concluded that the incorporation of $\text{Ru}(\text{bpy})_3^{2+}$ and protonated aniline derivatives into the anionic domains of the film leads to photoinduced electron transfer and photopolymerization.

Clay minerals have anionically-charged interlayers and intercalate, by cation exchange, positively-charged organic molecules in their interlayer spaces.⁶ Chao *et al.* and Giannelis *et al.* reported chemical oxidizing polymerization of aniline in zirconium phosphate and other clay minerals.^{7,8} In the present study, we intercalated $\text{Ru}(\text{bpy})_3^{2+}$ and protonated PPD in a hectorite clay, *i.e.*, Ionite H (INT), in acidic aqueous solution and examined whether photopolymerization of PPD by $\text{Ru}(\text{bpy})_3^{2+}$ takes place in the two-dimensional interlayer spaces, with anionically-charged clay layers acting as templates and also as counter ions for the acid-doped conducting form of polyaniline (PAN).

EXPERIMENTAL

$\text{Ru}(\text{bpy})_3\text{Cl}_2$ was prepared according to the literature⁹ and purified by recrystallization from water. INT ($\text{Na}_{2/3}\text{-(Mg}_{16/3}\text{Li}_{2/3})[\text{Si}_4]_2\text{O}_{20}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$; cation exchange capacity (CEC): *ca.* 80 meq/100 g) was obtained from Mizusawa Industrial Chemicals, Ltd., Tokyo and was used without further purification. Reagent grade PPD (Kanto Chemical Co., Inc., Tokyo) and HCl were used as re-

ceived.

INT (0.25 g) was stirred magnetically in 200 mL distilled water for one day at room temperature to produce a colloidal solution of 1.25 g dm^{-3} or $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ in terms of cation exchange site concentration. The clay solution was transparent, but showed significant light scattering by colloidal clay particles in the ultraviolet region shorter than 250 nm. To a solution containing INT was added PPD, and pH of the solution was adjusted with aqueous HCl solution. $\text{Ru}(\text{bpy})_3\text{Cl}_2$ was then added. The solution was stirred for a few hours.

The aerated aqueous HCl solution containing $\text{Ru}(\text{bpy})_3^{2+}$ ($6 \times 10^{-5} \text{ mol dm}^{-3}$), PPD ($1 \times 10^{-3} \text{ mol dm}^{-3}$), and INT ($1 \times 10^{-3} \text{ mol dm}^{-3}$) thus prepared was illuminated with a 500-W Xe lamp (Ushio Inc., Tokyo) through a 420–600 nm filter. Light intensity was adjusted to 6.3 mW cm^{-2} using a Topcon UVR-36 radiometer. Spectral change was monitored with a Shimadzu UV-2200 recording spectrophotometer. An aerated HCl solution containing only $\text{Ru}(\text{bpy})_3^{2+}$ and PPD was prepared and illuminated similarly.

Emission spectra of $\text{Ru}(\text{bpy})_3^{2+}$ were measured with a Hitachi F-4500 fluorescence photospectrometer. Emission decay was measured by single-photon counting method using a Horiba NAES-1100 time-resolved fluorescence spectrometer. Excitation wavelength was 450 nm. Emission was monitored at 600 nm.

Infrared spectra were recorded on a Perkin-Elmer 1600 series fourier transform infrared (FT-IR) spectrophotometer. The spectra were measured by the KBr pellet method. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Absorption and emission spectra of dyes such as $\text{Ru}(\text{bpy})_3^{2+}$ in clay solution differ from those in homogenous solution.¹⁰ In the presence of INT, absorption at *ca.* 450 nm attributed to the MLCT (metal-to-ligand charge transfer) band of $\text{Ru}(\text{bpy})_3^{2+}$ shifted, with isosbestic point at 450 nm, to the longer wavelength, compared with that in the absence of INT (Figure 1a). Emission at *ca.* 600 nm from excited $\text{Ru}(\text{bpy})_3^{2+}$ shifted slightly to the longer wavelength with increased intensity as shown in Figure 1b.

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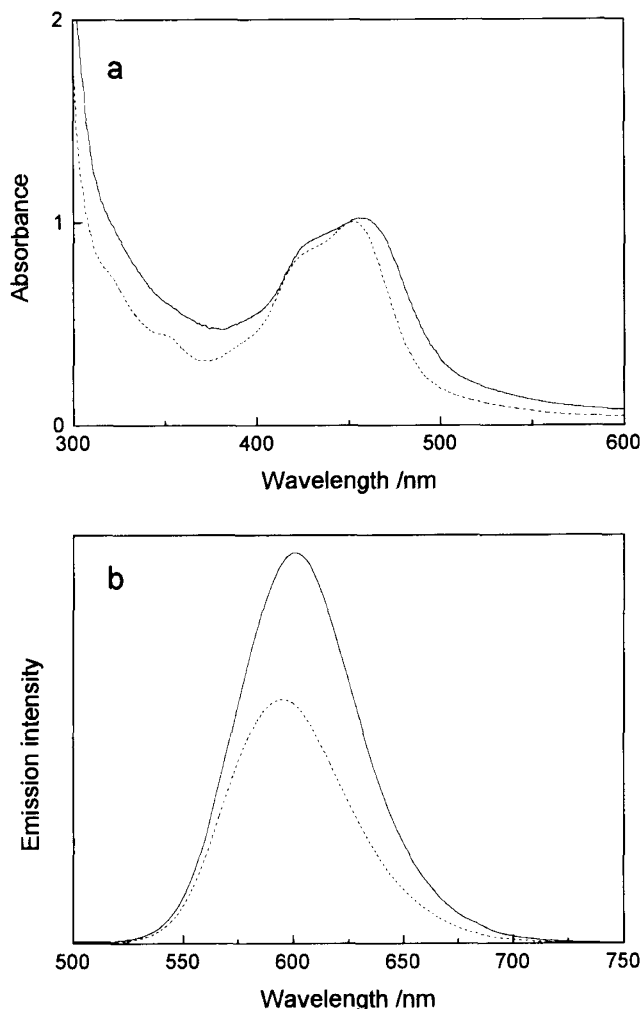


Figure 1. Absorption (a) and emission (b) spectra of $6 \times 10^{-5} \text{ mol dm}^{-3}$ $\text{Ru}(\text{bpy})_3^{2+}$ in aqueous HCl solution (pH 0) in the presence (—) and in the absence (⋯) of $1 \times 10^{-3} \text{ mol dm}^{-3}$ INT, $\lambda_{\text{ex}} = 450 \text{ nm}$.

Time-resolved emission from excited $\text{Ru}(\text{bpy})_3^{2+}$ was measured by single photon counting using the excitation wavelength of the isosbestic point. $\text{Ru}(\text{bpy})_3^{2+}$ in the absence of INT gave a single exponential luminescence decay with lifetime characteristic of excited $\text{Ru}(\text{bpy})_3^{2+}$ in aerated aqueous solution, *i.e.*, *ca.* 400 ns. In the presence of INT, decay was fitted to a bi-exponential function. Lifetimes were $350(\pm 50) \text{ ns}$ and $950(\pm 40) \text{ ns}$, the former being attributed to $\text{Ru}(\text{bpy})_3^{2+}$ in bulk solution and the latter to that in the interlayer of INT. Relative values of the pre-exponential weights indicate that *ca.* 65% of $\text{Ru}(\text{bpy})_3^{2+}$ exist in the interlayer of INT under the experimental conditions.

Intercalation of PPD into the interlayer of INT was not confirmed by spectral measurements. No significant difference in PPD absorption spectrum was observed in the presence of INT. When a solution containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ PPD and $1 \times 10^{-3} \text{ mol dm}^{-3}$ INT was left standing for several hours, precipitates were formed. The concentration of PPD in the supernatant was determined as *ca.* $1 \times 10^{-4} \text{ mol dm}^{-3}$ by UV absorption, suggesting at least *ca.* 90% of PPD is intercalated in the interlayer of INT under the present experimental conditions. In accordance with this, quenching of excited $\text{Ru}(\text{bpy})_3^{2+}$

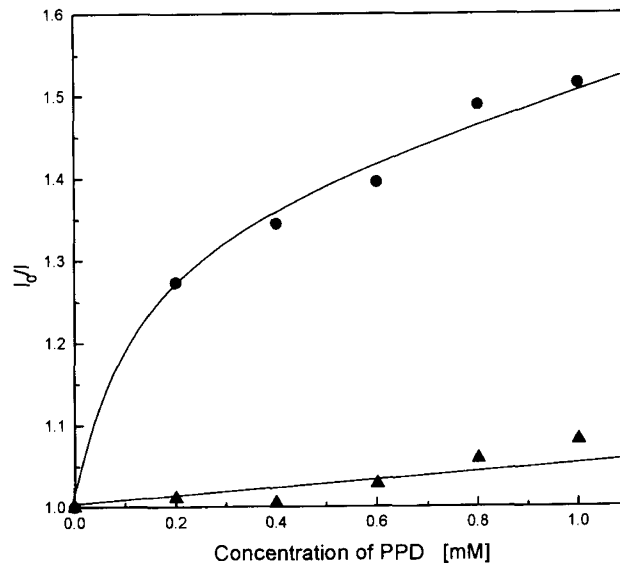


Figure 2. Stern-Volmer plots for quenching of $\text{Ru}(\text{bpy})_3^{2+}$ emission by PPD in aqueous HCl solution (pH 0) in the presence (●) and in the absence (▲) of $1 \times 10^{-3} \text{ mol dm}^{-3}$ INT, $\lambda_{\text{ex}} = 450 \text{ nm}$.

by PPD in the presence of INT was markedly different from that in the absence of INT (Figure 2). The much steeper slope of the Stern-Volmer plot in the presence of INT indicates PIET between $\text{Ru}(\text{bpy})_3^{2+}$ and PPD proceeds much more efficiently in the presence of INT. The Stern-Volmer plot levels off at higher PPD concentrations, which is consistent with the partial presence of unquenchable $\text{Ru}(\text{bpy})_3^{2+}$ in bulk solution.

When aqueous HCl solution (pH 0) of $\text{Ru}(\text{bpy})_3^{2+}$ and PPD was illuminated with a xenon lamp through a 420–600 nm filter, absorption peaks emerged at *ca.* 400 and 800 nm, attributed to polaron and bipolaron bands of PAN (Figure 3a).¹¹ The spectrum was similar to that reported by Okamoto and Kotaka for protonated short-chain PAN polymerized electrochemically at high pH (pH 3.7),¹² indicating only PAN of a limited chain length is produced in the absence of INT. The mechanism for photocatalytic polymerization has already been discussed.⁴ PPD, protonated at the primary amino group at pH 0 ($\text{p}K_{\text{a}1} = -0.1$, $\text{p}K_{\text{a}2} = 5.72$), is oxidized by excited $\text{Ru}(\text{bpy})_3^{2+}$, and $\text{Ru}(\text{bpy})_3^{2+}$ formed is oxidized back to $\text{Ru}(\text{bpy})_3^{2+}$ by oxygen in aerated solution. Apparently, polymerization proceeds with the protonated doubly-oxidized quinoid form of PPD reacting with unoxidized PPD, followed by further oxidation at the chain end. (Considering redox potentials of PPD in acidic solution reported in the literature ($E_{1/2} = \text{ca. } 0.45$ and *ca.* 0.55 V vs. SCE at pH 0.02),¹³ the second oxidation of PPD also appears to be effected by PIET with excited $\text{Ru}(\text{bpy})_3^{2+}$.)

Figure 3b shows change in the absorption spectrum induced by illuminating an aqueous HCl solution (pH 0) containing $\text{Ru}(\text{bpy})_3^{2+}$, PPD, and INT. A bipolaron absorption, similar to that in the absence of INT, emerged. Absorption λ_{max} , however, shifted significantly to the longer wavelength, *i.e.*, by *ca.* 100 nm. The longer-wavelength shift indicates the formation of PAN of a longer conjugation.¹² FT-IR spectra of PAN/INT composite and PAN, obtained in the presence and absence of INT and recovered by precipitation after standing for several

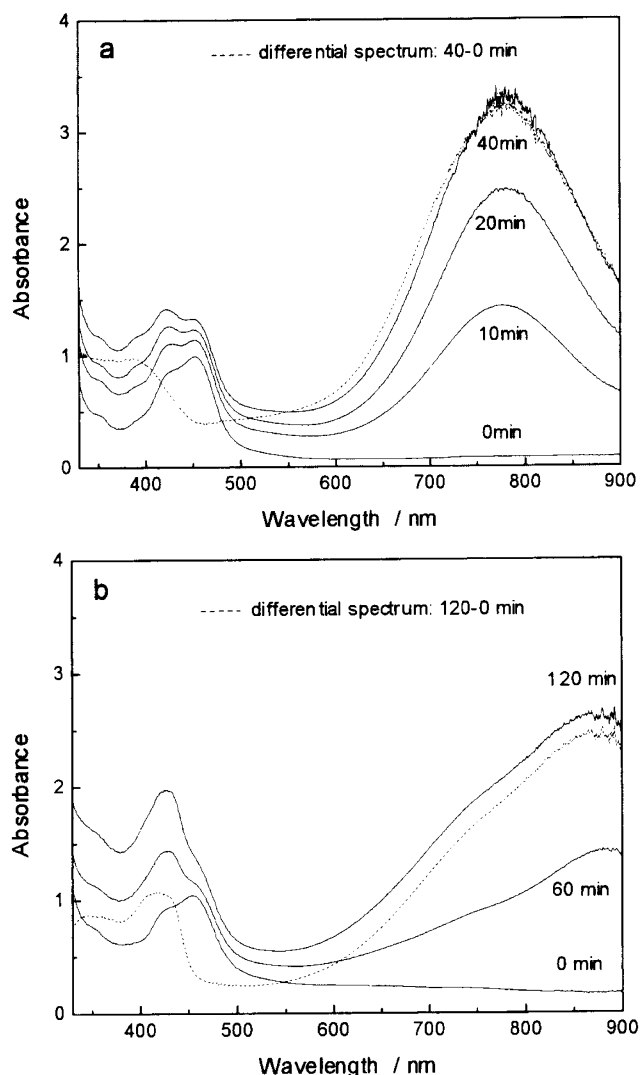


Figure 3. Change in absorption spectra induced by visible light illumination (420–600 nm) of aqueous HCl solution (pH 0) containing $6 \times 10^{-5} \text{ mol dm}^{-3}$ $\text{Ru}(\text{bpy})_3^{2+}$ and $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ PPD in the absence (a) and in the presence (b) of $1 \times 10^{-3} \text{ mol dm}^{-3}$ INT. Differential spectra (a: 40 min–0 min; b: 120 min–0 min) are also shown.

days, showed characteristic absorption of PAN, *i.e.*, bands at *ca.* 1600 and *ca.* 1500 cm^{-1} due to the benzene ring deformation, at *ca.* 1315 cm^{-1} due to the C–N stretching vibration of a secondary aromatic amine and at *ca.* 800 cm^{-1} due to the C–H out-of-plane bending of *para*-substituted benzene (Figure 4).^{12,14} In the absence of INT, bands at *ca.* 750 and *ca.* 695 cm^{-1} due to the C–H out-of-plane bending of mono-substituted and/or *meta*-substituted benzene were noted.¹⁵ These bands were not observed with PAN/INT composite obtained in the presence of INT. IR results are consistent with the formation of PAN of a longer chain length in the presence of INT. The use of a polyelectrolyte as a polymerization template has recently been reported for polymerization of aniline by an enzyme in the presence of hydrogen peroxide.¹⁶ A similar, but more precise template effect must work in the present case as INT provides a rigid two-dimensional environment for PPD molecules. PAN with longer chain length formed would interact with the polyanionic layers of the clay, stabilizing the acid-doped (pro-

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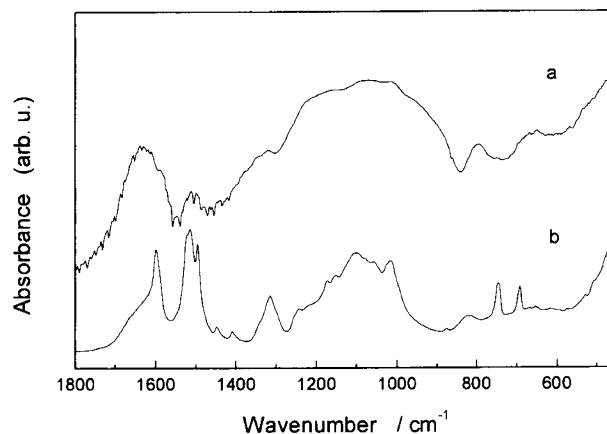
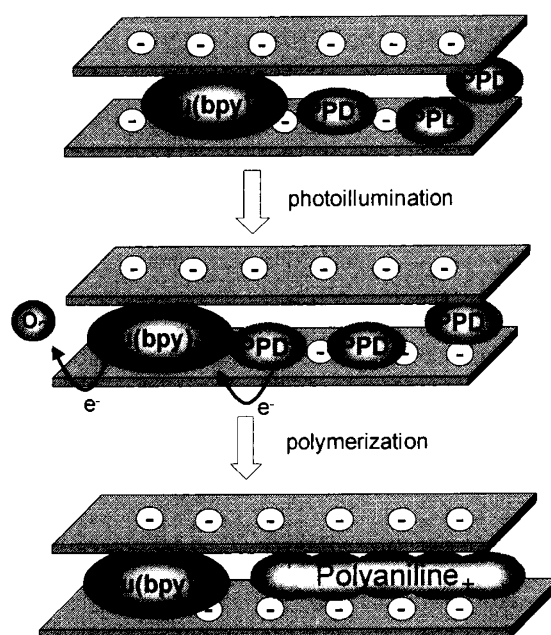


Figure 4. FT-IR spectra of PAN polymerized in the presence (a) and in the absence (b) of INT.



Scheme 1. Schematic representation of photopolymerization of PPD in the clay interlayer.

tonated) emeraldine structure of PAN (Scheme 1). Apparently, polymerization in the interlayer of INT is slower, *i.e.*, less efficient, than in bulk solution due to slower diffusion of PPD in the clay interlayer.

Formation of PAN of a longer chain length, together with stabilization of its protonated emeraldine form by the anionically-charged clay layers, should be reflected by the redox property of PAN. This point is now being investigated and will be reported in a future publication.

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