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Template photopolymerization of dimeric aniline by photocatalytic reaction with $Ru(bpy)_3^{2+}$ in the presence of DNA

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A DNA–polyaniline complex has been successfully prepared by the photopolymerization of dimeric aniline *via* photocatalytic reaction with $Ru(bpy)_3^{2+}$ complex in the presence of DNA , a reaction which occurs, even in solution at pH 3.0–6.0, due to the specific local "lower-pH" environment provided by DNA.

Photoinduced electron transfer (PIET) between tris(2,2′-bipyridyl)ruthenium [$Ru(bpy)_3^{2+}$] and electron acceptors, *e.g.* methylviologen (MV^{2+}), has been investigated from the standpoints of photosynthesis, photolysis of water, as a photoenergy conversion system, and so on.[1] Many studies aiming to realize effective vectorial electron transfer in order to increase its efficiency have been reported. Since photoexcited $Ru(bpy)_3^{2+}$ has an oxidation power of about 1.1 V (*vs.* SCE), many electroactive materials can be oxidized by visible illumination of the complex. This process can be utilized to oxidize not only low molecular weight molecules, but also polymers. Therefore, oxidative polymerization by photoillumination is also applicable.

Conducting polymers have been attracting significant interest for potential uses in electronic devices. These polymers are generally prepared by oxidative polymerization. If conducting polymers are prepared by PIET, patterning with conducting polymer is possible at any place and on any geometry. This process would allow the possibility of fabricating molecular electronic and/or optical devices for microprocessing. On the basis of these interests, photopolymerization of pyrrole using $Ru(bpy)_3^{2+}$ has already been performed, resulting in polypyrrole.[2] We have already reported the photopolymerization of aniline derivatives by PIET between $Ru(bpy)_3^{2+}$ and MV^{2+},[3–5] because polyaniline (PAn) is one of the most promising conductive polymers for wider applications due to its high environmental stability in air. We also demonstrated its application for imaging and micropattering.[6,7] However, for the development of electronic devices, the PAn obtained does not seem to be sufficient in its conjugation length since the PAn photopolymerized in homogeneous systems involves branched and/or "compact coil" structures. The use of a polyelectrolyte as a polymerization template has recently been reported for the polymerization of aniline by an enzyme in the presence of hydrogen peroxide in order to minimize the branching.[8] We also carried out the polymerization in the presence of clay minerals[9] and micelles[10] in order to utilize their specific structures as templates and to improve the physicochemical properties of the photopolymerized PAn. Since template polymerization is expected to give a characteristic structure, reflecting that of the template, variation of the template should provide polymers with properties which are advantageous for different applications. In this paper, structurally ordered DNA has been employed as a template to prepare a PAn–DNA complex. The polymerization and the structure of the complex are discussed from the viewpoint of electronic materials because DNA acts as a rigid straightforward template due to its rod-like double helical structure.

$Ru(bpy)_3^{2+}$ was prepared according to the literature procedure and then purified by recrystallization from water. Reagent grade *N*-phenyl-*p*-phenylenediamine (PPD) (Kanto Chemical Co., Ltd.) was used as received. Sodium salts of DNA from Salmon testes were provided by the Nippon Chemical Feed Co., Ltd. An aerated aqueous HCl solution (pH 6.5 or 3.0) containing 6×10^{-5} M $Ru(bpy)_3^{2+}$, 1.0×10^{-3} M PPD, and a given concentration of DNA (concentration of the phosphate groups) was illuminated with a 500 W xenon lamp (Ushio Inc., Tokyo) through a 420–600 nm filter. The light intensity was adjusted to 15 mW cm^{-2} at 450 nm using a Molectron POWER MAX500D Laser power meter. The spectral change was monitored with a Shimadzu UV-1240 spectrophotometer. The emission spectra of $Ru(bpy)_3^{2+}$ were measured with a Hitachi F-4500 fluorescence photospectrometer. Emission decays were measured by the single-photon counting method using a Horiba NAES-1100 time-resolved fluorescence spectrometer. The excitation wavelength was 450 nm. The emission was monitored at 600 nm. Circular dichroism (CD) spectra were recorded on a JASCO J-500 circular dichrograph spectrophotometer. All measurements were carried out at 23–25 °C.

The emission behavior of $Ru(bpy)_3^{2+}$ in a polyanionic environment is different from that in homogeneous solution. The emission intensity and lifetime at about 600 nm of excited $Ru(bpy)_3^{2+}$ increased with the concentration of DNA. However, an increase in the degradation temperature of DNA and a hypochromic effect on the absorption of $Ru(bpy)_3^{2+}$ were not observed with increasing concentrations of $Ru(bpy)_3^{2+}$ and DNA, respectively. These observations indicate that $Ru(bpy)_3^{2+}$ is not intercalated in the DNA.[11] Rather, they suggest that $Ru(bpy)_3^{2+}$ is bound to the outside of the main chain of DNA by electrostatic interactions.

The absorption of PPD at *ca.* 280 nm in aqueous HCl

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solution (pH 3) containing DNA underwent a slight red shift and exhibited a 25% decrease of hypochromicity on increasing the concentration of DNA from 7.5×10^{-5} to 1.25×10^{-4} M. However, the absorption of PPD at pH 6.5 did not show hypochromicity. These results suggest that PPD, protonated at the primary amino group at pH 3.0 ($pK_{a1}=-0.1$, $pK_{a2}=5.72$), is associated with duplex DNA by intercalation and/or electrostatic interaction.

When an aqueous solution (pH 6.5) containing 6×10^{-5} M $Ru(bpy)_3^{2+}$, 1.0×10^{-3} M PPD and 1.0×10^{-3} M DNA was illuminated with a xenon lamp through a 420–600 nm filter, absorption peaks at *ca.* 400 and 800 nm emerged (Fig. 1), which are assignable to the polaron band of PAn.[12] The mechanism of photocatalytic polymerization has already been discussed:[4] protonated PPD is oxidized by excited $Ru(bpy)_3^{2+}$, and the $Ru(bpy)_3^{+}$ formed is oxidized back to $Ru(bpy)_3^{2+}$ by the acceptor, in this case, in an aerated solution, oxygen. The polymerization proceeds through the reaction of the protonated form of doubly-oxidized PPD with unoxidized PPD, followed by successive reaction at the chain end *via* PIET. When the polymerization was carried out at pH 6.5 in the absence of DNA, absorption peaks were observed at *ca.* 300 and 600 nm, which are assignable to π–π* transitions of the benzenoid ring and exciton absorption of the quinoid ring of PAn, respectively.[13,14] This strongly suggests that the photopolymerized PAn is acid-doped, *i.e.* protonated, by DNA, and that the phosphate groups of DNA provide a local lower-pH environment.

Fig. 2 shows the change in the absorption spectrum of an aqueous HCl solution containing 6×10^{-5} M $Ru(bpy)_3^{2+}$, 1.0×10^{-3} M PPD and 1.0×10^{-3} M DNA at pH 3.0 upon visible light illumination. The polaron absorption also emerged at 600–800 nm at pH 3.0 in the absence of DNA. Its absorption maximum (λ_{max}), however, is significantly shifted to longer wavelength by *ca.* 200 nm in the presence of DNA. This change indicates the formation of PAn with a longer π-electron conjugation. MacDiarmid and Epstein have reported that such a shift is attributable to the delocalization of electrons in the polaron band of PAn due to a conformational change of the polymer from the "compact coil" to the "expanded coil" structure.[15] The shift, therefore, is also explained by the

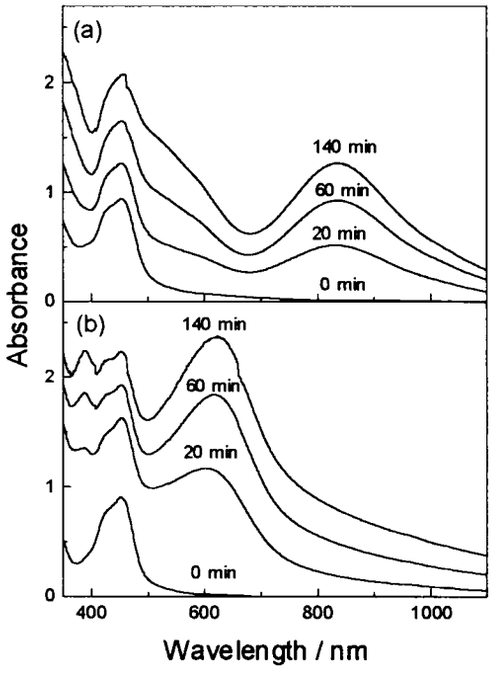

Fig. 1 Change in the absorption spectra of aqueous solutions (pH 6.5) containing 6×10^{-5} M $Ru(bpy)_3^{2+}$ and 1.0×10^{-3} M PPD (a) with 1.0×10^{-3} M DNA and (b) in the absence of DNA, upon visible light illumination (420–600 nm).

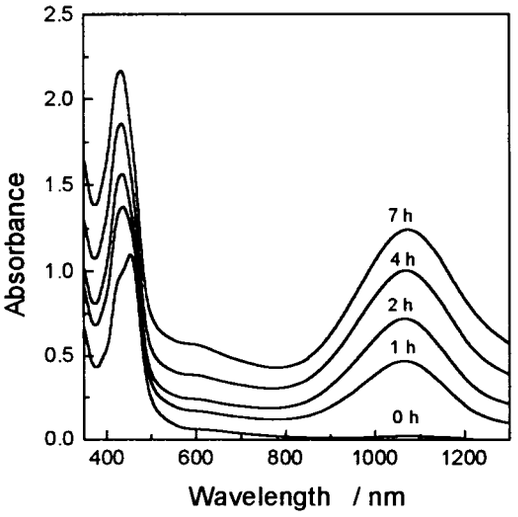

Fig. 2 Change in the absorption spectrum of an aqueous solution (pH 3.0) containing 6×10^{-5} M $Ru(bpy)_3^{2+}$, 1.0×10^{-3} M PPD in the presence of 1.0×10^{-3} M DNA upon visible light illumination (420–600 nm).

"expanded coil" formation of PAn photopolymerized at pH 3.0 in the presence of DNA. When polymerization was carried out at pH 3.0 in the presence of DNA, a larger amount of PPD could be electrostatically interacted with DNA than at pH 6.5 due to protonation of PPD. In other words, while DNA at pH 6.5 provides a local lower-pH environment required for the photopolymerization, the template effect of DNA on polymerization was not sufficient. Differential CD spectra of the solution containing DNA and PPD and that containing only DNA at pH 3.0 showed a negative CD band at 280 nm assignable to a π–π* transition of PPD. However, this band was not found at pH 6.5. These results indicate that PPD in the DNA solution at pH 3.0 is aligned along the main chain of the DNA through intercalation and/or electrostatic interaction, leading to the formation of the "expanded-coil" PAn structure in the PAn–DNA complex.

Notes and references

1 A. Moradpour and E. Amouyal, *J. Photochem.*, 1979, **10**, 13.
2 J. M. Kern and J. P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1989, 657.
3 K. Teshima, K. Yamada, N. Kobayashi and R. Hirohashi, *Chem. Commun.*, 1996, 829.
4 K. Teshima, S. Uemura, N. Kobayashi and R. Hirohashi, *Macromolecules*, 1998, **31**, 6783.
5 S. Uemura, K. Teshima, S. Tokuda, N. Kobayashi and R. Hirohashi, *Synth. Met.*, 1999, **101**, 701.
6 Y. Kim, N. Kobayashi, K. Teshima and R. Hirohashi, *Synth. Met.*, 1999, **101**, 699.
7 Y. Kim, K. Teshima and N. Kobayashi, *Electrochim. Acta*, 2000, **45**, 1549.
8 W. Liu, A. L. Cholli, R. Nagarajan, J. Kumar, S. Tripathy and F. F. Samuelson, *J. Am. Chem. Soc.*, 1999, **121**, 11345.
9 S. Uemura, M. Yoshie, N. Kobayashi and T. Nakahira, *Polym. J.*, 2000, **32**, 987.
10 S. Uemura, S. Tokuda, T. Nakahira and N. Kobayashi, *Synth. Met.*, in press.
11 A. Sitlani, E. Long, A. M. Pyle and J. K. Barton, *J. Am. Chem. Soc.*, 1992, **114**, 2303.
12 Y. Furukawa, F. Ueda, Y. Hyodo, I. Harada, T. Nakajima and T. Kawagoe, *Macromolecules*, 1988, **21**, 1297.
13 F. L. Lu, F. Wudl, M. Nowak and A. J. Heeger, *J. Am. Chem. Soc.*, 1986, **108**, 8311.
14 S. Stafstrom, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang and A. G. MacDiarmid, *Phys. Rev. Lett.*, 1987, **59**, 1464.
15 A. G. MacDiarmid and A. J. Epstein, *Synth. Met.*, 1995, **69**, 85.