Cationic Polypyrrole Composites with Anionic Functional Molecules

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Positively charged pyrroles incorporating the quaternized pyridine moiety, [1-methyl-3-(pyrrol-1-ylmethyl)pyridinium chloride, MPP] and [1-(5-pyrrol-3-ylpentyl)pyridinium bromide, PPP], have been synthesized. The polymer of MPP (PMPP), cationic polypyrrole obtained by chemical polymerization and electropolymerization of MPP, is soluble in various polar solvents and displays anion-exchange ability. The amount of the incorporated anionic species in PMPP is *ca*. five times greater than that in polypyrrole because incorporation is through anodic doping and electrostatic binding with the pyridinium moiety. The PMPP composites with anionic metal complexes and anionic polymers provide films either by the casting method or by the dipping method. These films were also obtained by electropolymerization of MPP in the presence of the anionic functional molecules. The resulting composite-modified electrodes show clear electrochromism (EL) for PMPP/FeBPS and bright electrogenerated chemiluminescence (ECL) for PMPP/RuBPS, respectively. Excellent optical properties are achieved by incorporation of a large amount of the anionic functional molecules and therefore by suppression of undesired background absorption of the PMPP matrix. Another cationic polymer of PPP showed high conductivity $(10^{-2} S cm^{-1})$ as well as high-density incorporation of anionic functional molecules.

Recently, surface modification of electrodes with polymer films containing a variety of functional molecules has attracted considerable attention.¹⁻⁴ Conducting polymers, such as polypyrrole (PPy),^{5,6} polythiophene,⁷ and polyaniline,⁸ are useful materials as matrices for modification of the electrode surface. Unlike conventional insulating polymers,9,10 thick films are available for surface modification because of their high conductivity. We have reported that anionic functional molecules were effectively incorporated into the polypyrrole (PPy) matrix through an anodic doping process during electropolymerization and that the resulting PPy composites with high conductivity showed various functions that reflect the incorporated molecules.¹¹⁻¹⁷ For example, phosphotungstate anion, a typical inorganic electrochromic (EC) material, was incorporated into the PPy matrix by electropolymerization of pyrrole in the presence of sodium phosphotungstate as a supporting electrolyte.17 The composite-modified electrode showed clear and multicoloured electrochromism. However, the PPy matrix has a very broad absorption in the visible region and the amount of anion incorporated in the PPy matrix by the anodic doping process is limited up to the doping ratio $(0.2-0.4)^8$ so that PPy was not so suitable for matrices where a high optical gain (i.e. electrochromic efficiency) of the incorporated functional molecules was desired. High-density incorporation may overcome this shortcoming by polymerizing pyrrole with functional groups.¹⁸⁻²⁰ An alternative method is to utilize a cationic PPy matrix obtained by substituting cationic groups into the conducting polymer matrix. Here, we synthesized cationic polypyrrole derivatives that had the potential for incorporating a large amount of anionic functional molecules through the anodic doping process and electrostatic binding. The composite of the cationic PPy with anionic metal complexes, FeBPS and RuBPS, shows clear electrochromism (EL) and bright electrogenerated chemiluminescence (ECL), respectively.

Experimental

Materials

Scheme 1 shows the synthetic routes to form MPP and PPP.

1-Methyl-3-(pyrrol-1-ylmethyl)pyridinium Chloride (MPP)

2 g $(1.3 \times 10^{-2} \text{ mol})$ of 3-(pyrrol-1-ylmethyl)pyridine (Aldrich) and 2.4 g $(1.3 \times 10^{-2} \text{ mol})$ of methyl toluene-*p*-sulphonate (Nacalai Tesque) were dissolved into 10 cm³ of DMF and heated at 40 °C for 12 h. The solvent was removed *in vacuo*. The residue was dissolved into water and then the counter-ion was exchanged from toluene-*p*-sulphonate to chloride using an anion-exchange resin (IRA-400, Cl⁻ form). The resulting salt was recrystallized from acetone-water solution. ¹H NMR (CD₃SOCD₃) δ (ppm): 9.0 (2H, d), 8.2 (2H, m), 6.93 (2H, t), 6.10 (2H, t), 5.36 (2H, s), 4.38 (3H, s).

1-(5-Pyrrol-3-ylpentyl)pyridinium Bromide (PPP)

PPP was obtained through the synthetic route in Scheme 1. Since 3-alkylpyrrole is prone to oxidation, the N position of



Scheme 1 The synthetic routes to MPP and PPP

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pyrrole was protected with a triisopropylsilyl group throughout the syntheses and the deprotection was carried out with tetrabutylammonium fluoride just prior to polymerization. Each intermediate product was identified by elemental analysis, ¹H NMR and ¹³C NMR. Here, the identification of the protected form of PPP (4) was shown: Calculated for $C_{23}H_{39}N_2SiBr: C, 61.2\%$; H, 8.7%; N, 6.2%; Br, 17.7%. Found: C, 60.1%; H, 8.8%; N, 6.1%; Br, 18.4%. ¹H NMR (CDCl₃) δ (ppm): 9.44 (2H, dd), 8.50 (1H, t), 8.11 (2H, t), 6.67 (1H, t), 6.49 (1H, br), 6.09 (1H, dd), 5.00 (2H, t), 2.53 (2H, t), 2.08 (2H, m), 1.20 (9H, m), 1.07 (18H, d). ¹³C NMR (CDCl₃) δ (ppm): 145.21, 128.38, 126.05, 125.43, 124.11, 121.16, 110.54, 62.22, 31.79, 30.37, 36.69, 25.72, 17.86, 11.73.

Other Chemicals

Tris(4,7-diphenyl-1,10-phenanthrolinedisulphonic acid) iron complex (FeBPS) was prepared by refluxing $FeCl_2$ (Nacalai Tesque) and three equivalents of sodium 4,7-diphenyl-1,10phenanthrolinedisulphonate (Tokyo Kasei) in DMF and then by recrystallization with acetone-hexane, according to the procedure in ref. 21. Tris(4,7-diphenyl-1,10-phenanthrolinedisulphonic acid) ruthenium complex (RuBPS) was also prepared in the same manner, using RuCl₃ as metal salt. Potassium poly(vinylsulphonate) (PVSK, Nacalai Tesque), sodium perchlorate (NaClO₄, Tokyo Kasei), sodium tetrafluoroborate (NaBF₄, Tokyo Kasei) and TBAF (Wako Chemicals) were used without further purification.

Polymerization of Cationic Pyrrole Derivatives

Chemical polymerization of MPP was carried out with four equivalents of $FeCl_3$ in water or acetonitrile. In the case of PPP the triisopropylsilyl group of 4 was removed with TBAF in water, and without isolation chemical polymerization was carried out with four equivalents of $FeCl_3$. MPP was electropolymerized in aqueous electrolyte solution under potentiostatic or galvanostatic conditions using a glass-coated with indium-tin oxide (ITO, Yoneda Glass) as a working electrode.

Electrochemical and Spectroscopic Measurements

Electrochemical experiments were carried out using an NPGS-301 potentiogalvanostat (Nikko Keisoku) and an NFG-3 function generator (Nikko Keisoku) with a threeelectrode system, consisting of an ITO working and Pt counter-electrodes, and an SCE as a reference. The conductivity was measured according to the standard van der Pauw method. ¹H and ¹³C NMR spectra were recorded on a JEOL EX-100 instrument. IR spectra were recorded using a Nicolet 20DXB FTIR spectrometer. Absorption spectra were measured using an MPS-2000 spectrophotometer (Shimadzu). Luminescence spectra were recorded on an RF-503 fluorescence spectrophotometer (Shimadzu).

Results and Discussion

Polymerization of MPP

Chemical polymerization of MPP with FeCl₃ immediately provided a homogeneous black solution. The residue after removal of the solvent was soluble in various polar solvents ($\varepsilon_r > 25$) such as water, propylene carbonate, DMSO, acetonitrile, DMF, benzonitrile, up to $> 10^{-2}$ mol dm⁻³ per pyrrole unit. The residual chloride ion was easily exchanged

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with others by conventional ion-exchange treatment, so that isolation was carried out by adding perchlorate salt to the residue in water. Elemental analyses showed that the precipitate had 1.49 equivalents of chloride ion per pyrrole unit. The amount of the incorporated perchlorate ion was *ca*. five times larger than the doping ratio of the conventional PPy.⁸

MPP was also electropolymerized under potentiostatic conditions in various kinds of electrolytic solution at *ca.* 0.8 V vs. SCE, 0.2 V higher than that of pyrrole.⁸ No film was obtained on the electrode because the resulting polymer with the anion of the electrolyte used was still soluble in the electrolytic solvents. On the other hand, NaClO₄ and NaBF₄ as supporting electrolytes were effective in obtaining a film. Elemental analysis indicated that the film had 1.45 equivalents of perchlorate ion per pyrrole unit, similar to that of the residue formed by chemical polymerization.

Fig. 1 shows the FTIR spectra of the precipitate formed by chemical polymerization and the film produced by electropolymerization. The absorption at 780 cm⁻¹ observed in MPP, assigned to vibration of C—H out-of-plane bending in the pyrrole ring, disappeared in both the precipitate and the film.²² This indicated that both products had a polypyrrole structure. There was also an absorption at 1700 cm⁻¹, which is assigned to the C=O vibration stretching, which suggested α -keto formation due to partial overoxidation. Relatively low conductivity (10⁻⁸ S cm⁻¹) would be responsible for such undesired polymerization including α - β coupling due to a bulky pyridinium moiety at the N position of pyrrole, which will be improved in the last section.

Functionalization of PMPP by Ion-exchange Treatment

When polyanions such as FeBPS or RuBPS were added to aqueous PMPP (Cl⁻ form) solution, PMPP composites with the added functional polyanions were immediately obtained as precipitates. The resulting precipitate was redissolved into concentrated HCl-1,4-dioxane-H₂O mixed solvent (2:3:1 by volume).²³ The PMPP/FeBPS and PMPP/RuBPS composite films were easily obtained on any substrate by casting or spin-coating. The UV-VIS absorption spectra of these films showed absorption bands characteristic of FeBPS and



Fig. 1 FTIR spectra of (a) MPP monomer, (b) PMPP obtained by chemical polymerization, (c) PMPP obtained by electro-polymerization. The counter-ion and the dopant of PMPP were per-chlorate ion

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RuBPS over the broad absorption of the PMPP matrix. These spectra indicated that these metal complexes were effectively incorporated into the PMPP matrix by the ionexchange treatment. The PMPP composite films were also obtained on an electrode by electropolymerization of MPP in the presence of anionic functional molecules such as FeBPS, RuBPS and PVSK as supporting electrolytes. A ratio *ca*. five times larger of the incorporated anion to the pyrrole unit than that of the well known doping process of PPy was interpreted by the sum of anodic doping ratio $(f = 0.2-0.4)^8$ and the number of counter-ions of the pyridinium moiety of the PMPP. This observation led to the conclusion that high-density incorporation of anionic functional molecules occurred for the counter anion of the pyridinium moiety as well as the dopant.

Electrochemical Preparation of PMPP/FeBPS

A PMPP/FeBPS composite film on an ITO electrode was obtained by electropolymerization of 0.05 mol dm⁻³ MPP in aqueous solution in the presence of 0.01 mol dm⁻³ FeBPS as supporting electrolyte under galvanostatic conditions $(3.7 \times 10^{-4} \text{ C cm}^{-2})$. A PPy/FeBPS film as a reference was also prepared as reported previously.^{13,15} Fig. 2 shows the visible absorption spectra of the modified electrodes during electrolysis. While the broad absorption characteristic of PPy or PMPP increased with electrolysis time, another absorption band appeared around 540 nm which is assigned to FeBPS (Fig. 2). Note that the absorption band of FeBPS in the PMPP matrix looked clearer than that in the PPy matrix. Assuming the absorption coefficient of the background absorption of PMPP is comparable with that of PPy,



Fig. 2 Visible absorption spectra of (a) the PMPP/FeBPS-modified ITO electrode and (b) the PPy/FeBPS-modified ITO electrode during electropolymerization of MPP and Py (0.05 mol dm⁻³) with FeBPS (0.01 mol dm⁻³) under galvanostatic conditions $(3.7 \times 10^{-4} \text{ A cm}^{-2})$. Time (in min) is shown on the curves

the absorption of FeBPS, distinguished from the background absorption of polypyrrole matrices, resulted from the incorporation of a larger amount of FeBPS in PMPP than in PPy.

Fig. 3 shows the time course of the substantial absorbance at 540 nm (ΔA_{540}) of the incorporated FeBPS using eqn. (1), and with passed electricity.

$$\Delta A_{540} = A_{540} - (1/2)(A_{380} + A_{620}) \tag{1}$$

where A_{540} , A_{380} and A_{620} are the net absorbances of the composites at 540, 380 and 620 nm, respectively. At 380 and 620 nm FeBPS shows very little absorbance. The surface concentration (Γ) of the incorporated FeBPS was estimated from the equation

$$\Gamma \,(\text{mol cm}^{-2}) = \Delta A_{540} / 10^3 \varepsilon_{540} \tag{2}$$

by using the molar absorption coefficient at 540 nm ($\varepsilon_{540} =$ 7.2×10^3 dm³ mol⁻¹ cm⁻¹, see Appendix). The Γ values increased linearly with electrolysis time, i.e. with the amount of electricity passed, although there was an induction time (ca. 30 s, ca. 0.01 C cm⁻²) which was explained by non-Faradaic current and adhesive efficiency of the initial deposition on an electrode. Since the electropolymerization of MPP and Py proceeds with electrochemical stoichiometry between the polymerization yield and the electricity passed, the linear relationship indicated that FeBPS was incorporated along with the growth of the matrices. The slope, the current efficiency of the incorporation, was 1.6×10^{-6} mol C⁻¹ for PMPP matrix, 4.4 times larger than that for PPy matrix $(3.7 \times 10^{-7} \text{ mol } \text{C}^{-1})$. The ratio of the current efficiencies between PMPP and PPy matrices for incorporation was very similar to that estimated from elemental analysis. The PMPP/FeBPS-modified ITO electrode looked bright red, while the PPy/FeBPS electrode was red-black and not clear enough to be used as an EC material. These electrochromic properties remained for at least several hundred cycles. The response time of the electrochromism, defined as the time necessary for absorption change (10-90%), was estimated to be ca. 100 ms.



Fig. 3 The 540 nm absorbance of the PMPP/FeBPS- (●) and the PPy/FeBPS- (○) modified ITO electrode during electrolytic preparation under the same conditions as in Fig. 2

Electrochromism of PMPP/FeBPS

The PMPP/FeBPS-modified ITO electrode $(3.5 \times 10^{-2} \text{ C})$ cm⁻² of electricity passed during preparation) in 0.1 mol dm⁻³ aqueous KCl solution showed a cyclic voltammogram (CV) with a half-wave potential at 0.85 V, assigned to the Fe^{III/II}BPS redox couple in the PMPP matrix. Reversible absorbance change in the 500-600 nm region was observed with distinct isosbestic points at 415 and 615 nm (Fig. 4) when the potential of the PMPP/FeBPS-modified ITO electrode was varied between 0.5 and 1.3 V in 0.1 mol dm^{-3} aqueous KCl solution. Compared with the PPy/FeBPSmodified ITO electrode, a distinct colour change, bright red (<0.8 V) to almost transparent brown (>1.1 V), was observed on the electrode. The potential at the inflection point of the correlation between the absorbance at 540 nm and the electrode potential was in good agreement with the half-wave potential (0.85 V) estimated from CV of the PMPP/FeBPS-modified ITO electrode. This indicated that the absorbance change was due to the redox reaction of the incorporated FeBPS.

Electrogenerated Chemiluminescence of PMPP/RuBPS

The PMPP/RuBPS-modified ITO electrode was obtained in a similar manner to that described above $(3.5 \times 10^{-2} \text{ C cm}^{-2})$ of electricity passed during preparation). The electrode was clear yellow. In aqueous Na_2SO_4 (0.2 mol dm⁻³), the PMPP/ RuBPS-modified ITO electrode showed a reversible redox wave at 1.1 V, assigned to Ru^{III/II}BPS [Fig. 5(a)]. When potassium oxalate was added as a sacrificial reductant to the electrolyte solution (50 mmol dm⁻³), the anodic current increased and the cathodic current diminished [Fig. 5(b)]. In the region > 1.1 V, orange light, clearly visible to the eye, was emitted from the electrode surface. Fig. 5(c) shows the luminescence intensity at 620 nm of the same electrode during cyclic voltammetry. On a bare ITO electrode, electrolytic oxidation of oxalate occurred in a more anodic region (1.2 V) than the half-wave potential of Ru^{III/II}BPS. This illustrated that the oxalate was catalytically oxidized by Ru^{III}BPS resulting from electrolytic oxidation in the PMPP matrix and that the Ru^{II/III}BPS redox couple played a mediating role in the oxidation of oxalate, which is thus an electrocatalytic process. The decrease of the cathodic current in the CV resulted from in situ re-reduction of Ru^{III}BPS with oxalate, similar to the case of Nafion-coated electrode binding



Fig. 4 Visible absorption spectra of the PMPP/FeBPS-modified ITO electrode at various electrode potentials (V vs. SCE) in 0.1 mol dm⁻³ KCl aqueous solution. The modified electrode used had 3.9×10^{-8} mol cm⁻² of FeBPS. The dotted line shows the spectrum obtained when the electrode was reduced at -0.5 V

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Fig. 5 The cyclic voltammograms of the PMPP/RuBPS-modified ITO electrode in 0.2 mol dm⁻³ Na₂SO₄ aqueous solution in the absence (a) and the presence (b) of 50 mmol dm⁻³ K₂C₂O₄. (c) The ECL intensity of the PMPP/RuBPS-modified ITO electrode during cyclic voltammetry under the same solutions as (b)

 $Ru(bpy)_3^{3^+}$.²⁴ The ECL spectrum was obtained by applying a rectangular potential sweep (2 Hz) between 0 and 1.5 V, sufficient to oxidize $Ru^{II}BPS$ (Fig. 6). The ECL spectrum obtained was in good agreement with the emission spectrum of PMPP/RuBPS-coated electrode under excitation at 450 nm. The ECL resulted from the MLCT excited state of RuBPS, which was generated through the highly exothermic electron-transfer reaction between the Ru^{III}BPS generated and the strong reductant, CO_2^{--} , of electrocatalytical oxidation of oxalate.

Improvement of Conductivity of Cationic Polypyrrole

The low conductivity of the PMPP matrix could result from its low molecular weight because of the steric hindrance of the bulky pyridinium moiety at the N position of pyrrole. In order to overcome this shortcoming another monomer (PPP)



Fig. 6 (a) The ECL spectrum of the PMPP/RuBPS-modified ITO electrode by applying rectangular potential sweep (2 Hz) between 0 and 1.5 V in 0.2 mol dm⁻³ aqueous Na₂SO₄ solution containing 50 mmol dm⁻³ K₂C₂O₄. (b) The luminescence spectra of the electrode under photoexcitation at 450 nm

was synthesized with a quaternized pyridine group distinct from the pyrrole ring. Poly-PPP (PPPP) had similar properties to PMPP in terms of solubility, the processibility, and the incorporation of anionic functional molecules. The PPPP disk with tetrafluoroborate ion showed relatively high conductivity $(10^{-2} \text{ S cm}^{-1})$.

Conclusion

The present cationic polypyrrole matrices were available for modification of the electrode surface with various kinds of anionic functional molecules, with respect to easy processibility and their excellent optical functions such as EC and ECL. Further study on the optical properties of the PPPP composites with EC or ECL molecules is in progress.

Appendix

The ε_{540} value used here was 7.2×10^3 dm³ mol⁻¹ cm⁻¹, one-third smaller than that in aqueous solution (=2.2 × 10⁴ dm³ mol⁻¹ cm⁻¹).²⁵ Itaya *et al.* reported²³ $\varepsilon_{540} = 1.5 \times 10^4$ dm³ mol⁻¹ cm⁻¹ of FeBPS bound to poly(*N*-methylethyleneimine) and explained that the smaller value resulted from the difference of the environment. The ε_{540} value was checked by comparing the ε_{540} values of PPy/FeBPS and PMPP/FeBPS, which were estimated assuming the following: (1) the doping ratio [f(PPY) = 0.30, f(PMPP) = 0.45] calculated from elemental analysis, (2) the net charge (*n*) of FeBPS is -4, and (3) the electrochemical stoichiometry [(2 + f) electron per pyrrole unit] of polymerization and anodic doping processes:

$$\Gamma(PPy) = (Q/F)(1/4) \{ f(PPy) / [2 + f(PPy)] \}$$
(i)

$$\Gamma(PMPP) = (Q/F)(1/4)\{[f(PMPP) + 1]/[2 + f(PMPP)]\}$$
(ii)

Next, the ε_{540} value of the FeBPS incorporated was obtained from eqn. (2) in the text and the ΔA_{540} value obtained from Fig. 2. The ε_{540} value for PPy and PMPP matrices were 7.2×10^3 and 6.8×10^3 dm³ mol⁻¹ cm⁻¹, respectively, which allowed us to consider that they had almost the same values. The electrode potential during galvanostatic conditions on preparing the PMPP/FeBPS was *ca*. 0.8 V. In Fig. 3 the 540 nm absorbance at 0.8 V was *ca*. 7% smaller than that for E < 0.5 V, where the FeBPS incorporated could be a reduced state (Fe^{II}BPS). Therefore, the partial oxidation of the incorporated Fe^{II}BPS to Fe^{III}BPS was not necessarily significant. This small ε_{540} value was considered to be due to an environmental effect. The authors thank Dr. Akira Ohtani, Central Research Laboratory, Nitto Denko Co. Ltd., for his valuable discussion. Part of this work was supported by Grant-in-Aid from the Ministry of Education of Japan.

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