

Ruthenium and Nickel Complexes of a π -Conjugated Electrically Conducting Polymer Chelate Ligand, Poly(2,2'-bipyridine-5,5'-diyl), and their Chemical and Catalytic Reactivity

Takakazu Yamamoto*, Yutaka Yoneda and Tsukasa Maruyama

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Poly(2,2'-bipyridine-5,5'-diyl) (PBpy), a π -conjugated electrically conducting chelate polymer, forms electrochemically active complexes with Ru and Ni; a cyclic voltammogram of the Ru-complex shows redox peaks which are accounted for by assuming electron exchange between the Ru species through the polymer backbone, and a RuCl₃-PBpy system serves as an excellent catalyst for photoevolution of hydrogen in an aqueous medium.

π -Conjugated electrically conducting polymers are the subject of recent interest.¹ Also, many investigations have been carried out on the preparation, catalytic activity and electrochemical properties of metal complexes coordinated to polymer ligands.^{2,3} However, metal complexes coordinated

with π -conjugated electrically conducting polymer ligands have attracted much less attention.⁴ Previously we reported the preparation of electrically conducting poly(2,2'-bipyridine-5,5'-diyl): PBpy,^{4,5} which consists of a typical chelating ligand unit, bpy, we now report the electrochemical properties

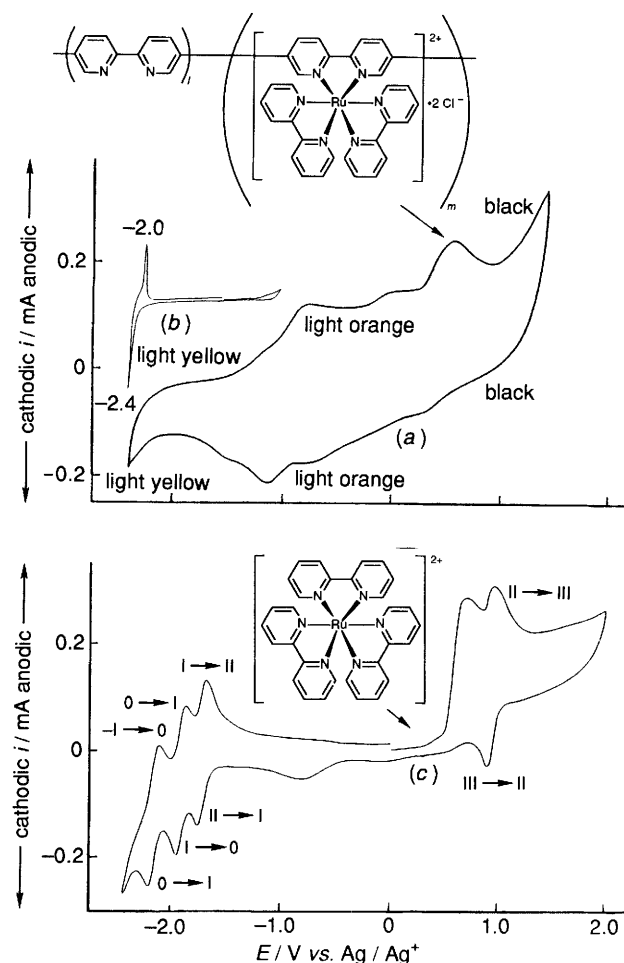


Fig. 1 CV of (a) the PBpy-Ru film prepared by the reaction of PBpy with $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$, (b) PBpy film, and (c) $[\text{Ru}(\text{bpy})_3]^{3+}$ (from ref. 7); in MeCN containing $0.1 \text{ mol dm}^{-3} [\text{NBu}_4^+\text{X}]$ [(a) and (c): $\text{X} = \text{ClO}_4^-$; (b): $\text{X} = \text{BF}_4^-$]. Scan rate for (a) and (b) 100 mV s^{-1} ; for (c) 20 mV s^{-1} .

and the chemical and catalytic activity of Ru and Ni complexes of PBpy.

The reaction of PBpy with $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$ (1 mol per mol of the bpy unit of PBpy) in water under reflux followed by thorough washing with water and methanol gives the PBpy-Ru complex. Microanalysis of Ru and Cl indicates 1.3 and 1.4 mol% of Ru per bpy unit of PBpy after 10 and 40 h, respectively, and the molar ratio between Ru and Cl is 1:2. It is reported that labile $[\text{Ru}(\text{bpy})_2\text{Cl}_2]^{3+}$ forms complexes with polymer ligands like poly(4-vinylpyridine)^{3,6a} under similar conditions. PBpy, which has low electrical conductivity ($\sigma = 10^{-12} \text{ S cm}^{-1}$), is converted into a semiconducting material ($\sigma = 10^{-5} \text{ S cm}^{-1}$) by the complex formation, implying generation of carrier(s) in the polymer chain.

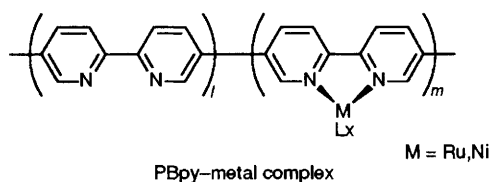
When the complex formation was carried out with a thin PBpy film laid on Pt or ITO (indium tin oxide) glass plate,† the film takes about 5 mol% of Ru per bpy unit as estimated by X-ray photoelectron spectroscopy. The PBpy film laid on Pt and containing the complex shows peaks due to redox reactions of the PBpy-Ru complex in cyclic voltammetry (CV) [curve (a) in Fig. 1]. The CV cycle was repeated without any

† The PBpy film (amount of PBpy: $6.5 \times 10^{-8} \text{ mol}$ of the bpy monomer unit per 1 cm^2 of the Pt plate, corresponding to thickness of about 100 nm) was laid on the Pt plate by painting the Pt plate with an HCO_2H solution of PBpy and removing HCO_2H by evaporation. The film was dipped in an aqueous solution of $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$, and the complex formation was carried out under reflux for 10 h. Similar film of PBpy laid on ITO glass plate was prepared analogously.

Table 1 Photoreduction of H_2O ^a

Entry	Catalyst ^b	Amount of H_2 evolved (μmol)	
		In the presence of NEt_3 ^c	Without NEt_3 ^d
1	Ppy-RuCl ₃	39	
2	PBpy	1	0
3	PBpy-RuCl ₃	137	0
4	Complex obtained from the [PBpy-Ru(bpy) ₂ Cl ₂] system [eqn (1)]	4	Trace

^a Reaction time 6 h; 500 W Xe lamp ($>300 \text{ nm}$) was used. In all cases light was irradiated from the same distance. ^b Amount of polymer or the complex in entry 4 = 20 mg. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O} = 3.6 \text{ mg}$; 0.05 mol per mol of monomer unit of Ppy (entry 1) and 0.1 mol per mol of monomer unit of PBpy (entry 3), respectively. In the case of entry 4, the complex prepared after 10 h reflux (see text) was used. ^c In a mixture of H_2O (1 cm^3), methanol (1 cm^3) and triethylamine (1 cm^3). ^d In a mixture of H_2O (1.5 cm^3) and methanol (1.5 cm^3).



observable change for more than 10 times. The redox peaks of PBpy alone [curve (b) in Fig. 1]⁴ are weakened or not observable in PBpy-Ru, indicating a profound change in the electronic state of PBpy, whereas the CV of PBpy-Ru shows several new peaks, which are considered to arise from the presence of coordinated $\text{Ru}(\text{bpy})_2$ centres.

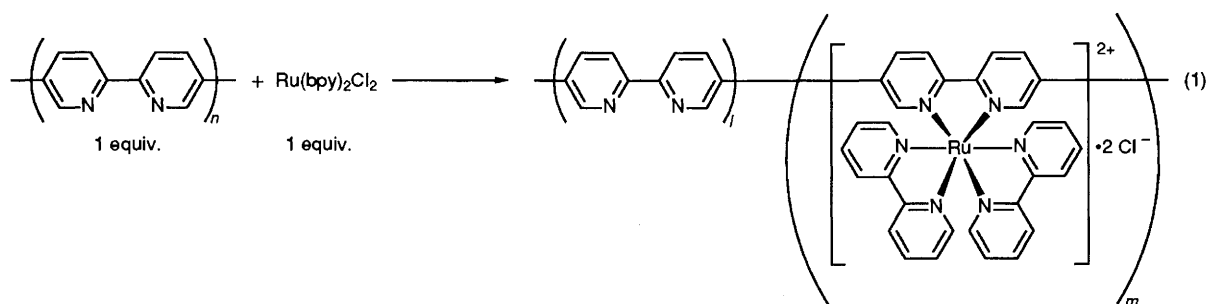
Fig. 1(c) shows the CV curve of the corresponding low molecular mass complex, $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$.⁷ It is seen from Fig. 1 that (i) the redox peaks of $[\text{Ru}(\text{bpy})_3]^{3+}$ related to ligand-based radical anions are shifted to higher potentials, in the PBpy-Ru complexes whereas the $\text{Ru}^{\text{II}} \rightleftharpoons \text{Ru}^{\text{III}}$ redox peaks are shifted to lower potentials, and (ii) all the redox peaks are broadened. These results suggest the presence of electronic interactions between the Ru species through the electrically conducting polymer matrix. These CV results are in sharp contrast to those obtained with a $\text{Ru}(\text{bpy})_2\text{L}_2$ -type complex attached to a non-conjugated polymer ligand (e.g. poly-4-vinylpyridine),^{6d} the CV curves of the attached complex groups showing the redox peaks at almost the same positions as in the corresponding monomer complex.

Thus, the PBpy-Ru complex presents a unique redox behaviour, which is considered to be characteristic of the metal complexes of electrically conducting π -conjugated polymer ligands. Similar behaviour was reported for an $\text{Fe}^{\text{II}} \rightleftharpoons \text{Fe}^{\text{III}}$ redox reaction in poly(ferrocene-1,1'-diyl).⁸

Recently Yanagida and his coworkers reported high catalytic activity of a mixture of poly(pyridine-2,5'-diyl) (Ppy) and RuCl_3 for photoevolution of hydrogen from water.⁹ Since Ppy has only a low coordinating ability toward transition metals compared with PBpy,⁴ the use of the PBpy-RuCl₃ system is expected to have a strong effect due to the complex formation on the photoevolution of hydrogen from water.

Table 1 summarizes the results. The Ppy-RuCl₃ system (entry 1) showed catalytic activity essentially the same as that reported by Yanagida and his coworkers.

On the other hand, the PBpy-RuCl₃ system (entry 3) shows activity about 3.5 times higher than the Ppy-RuCl₃ system, indicating the important role of the coordination of Ru to PBpy. On the contrary, the PBpy-Ru complex obtained by eqn. (1) (entry 4 in Table 1) showed lower catalytic activity.



The difference in the catalytic activity between the PBpy–RuCl₃ system and the PBpy–[Ru(bpy)₂]²⁺ complex may be due to the difference in the density of Ru species in the surface region of the PBpy polymer particles or to the difference in the catalytic activity between the Ru species formed. Photogeneration of H₂ from water by heterogeneous systems containing Ru–bpy complexes has been reported.¹⁰

PBpy also forms a complex with NiCl₂; the PBpy–Ni complex film laid on a Pt plate shows a CV with a redox cycle at about –1.5 V (vs. Ag/Ag⁺), which is considered to arise from nickel complex(es) of PBpy.‡ It is reported that CV of poly(pyridine-2,5-diyl) film which is prepared by electroreduction of a bromopyridylnickel(II) complex and considered to contain Ni species shows a redox cycle at about –1.35 V (vs. Ag/Ag⁺) associated with the contained Ni species.¹¹ One of the interesting electrochemical properties of the PBpy–Ni complex is that reduction of the PBpy–Ni complex in a CO₂ atmosphere causes an irreversible flow of reducing electric current. This is characteristic of the electrochemical reduction of the complex in the CO₂ atmosphere and presumably related to electrochemical reduction of CO₂ by the PBpy–Ni complex. Recently many papers have been published on electrochemical reduction of CO₂ with Ni complexes.¹²

Received, 30th June 1992; Com. 2/03463H

‡ CV of NiBr₂(bpy) in an acetonitrile solution of [NET₄]ClO₄ shows cathode peak potentials at –1.12, –1.40 and –1.60 V (vs. Ag/Ag⁺) and corresponding anode peaks.

References

- 1 *Handbook of Conductive Polymers, Vols. I and II*, ed. T. A. Skotheim, Marcel Dekker, New York, 1986; A. G. MacDiarmid and A. J. Heeger, *Rep., Proc. Mol. Electron Devices Workshop*, NRL Memo., 1981, AD-A, 105816, 208; *Science and Application of Conductive Polymers*, ed. W. R. Salaneck, D. T. Clark and E. J. Samuelsen, Adams Hilger, New York, 1990; J.-M. Andre, J. Delhalle and J.-L. Breads, *Quantum Chemistry Aided Design of Organic Polymers*, World Scientific, London, 1991.
- 2 R. W. Murray, in *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1984, vol. 13, p. 191; H. D. Abruna, in *Electroresponsive Molecular and Polymer System*, ed. T. A. Skotheim, Marcel Dekker, New York, 1988, vol. 1, p. 97.
- 3 R. Ramaraj and P. Natarajan, *J. Polym. Sci., A*, 1991, **29**, 1339.
- 4 T. Yamamoto, Z.-H. Zhou, T. Maruyama and T. Kanbara, *Chem. Lett.*, 1990, 223.
- 5 T. Yamamoto, T. Maruyama, T. Ikeda and M. Sisido, *J. Chem. Soc., Chem. Commun.*, 1990, 1306.
- 6 (a) M. A. Hayes, C. Mekel, E. Schtz and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1992, 703; (b) J. M. Calvert and T. J. Meyer, *Inorg. Chem.*, 1982, **21**, 3089; (c) B. Durham, J. L. Walsh, C. L. Carter and T. J. Meyer, *Inorg. Chem.*, 1980, **19**, 860; (d) G. J. Samuels, and T. J. Meyer, *J. Am. Chem. Soc.*, 1981, **103**, 307.
- 7 N. E. Tokei-Takvoryam, R. E. Hemingway and A. J. Bard, *J. Am. Chem. Soc.*, 1973, **95**, 6582. This paper shows a CV of [Ru(bpy)₃](ClO₄)₂ and describes the dichloride salt, which shows irreversible oxidation at about 1.16 V (vs. SCE) in accord with Fig. 1(c).
- 8 N. Oyama, Y. Takimura, H. Matsuda, T. Yamamoto, and K. Sanechika, *Denki Kagaku*, 1988, **56**, 781.
- 9 S. Masuoka, T. Kohzuki, A. Nakamura, C. Pac and S. Yanagida, *J. Chem. Soc., Chem. Commun.*, 1991, 580.
- 10 E. G. M. C. Cooke, J. Homer, A. W. P. Jarvie and J. D. Miller, *J. Chem. Soc., Chem. Commun.*, 1984, 1202.
- 11 N. W. Alcock, P. N. Bartlett, V. M. Eastwick-Field, G. A. Pike and P. G. Prigle, *J. Mater. Chem.*, 1991, **1**, 569.
- 12 E. g. S. Dérien, E. Duñach and J. Périchon, *J. Am. Chem. Soc.*, 1991, **113**, 8447.