Bull. Chem. Soc. Jpn., 72, 1153—1162 (1999)

Synthesis of Ru- and Os-Complexes of π-Conjugated Oligomers of 2,2′-Bipyridine and 5,5′-Bipyrimidine. Optical Properties and Catalytic Activity for Photoevolution of H_2 from Aqueous Media

Naoki Hayashida and Takakazu Yamamoto*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503

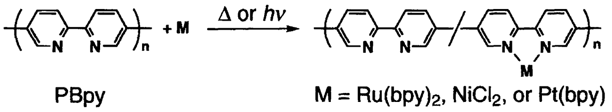
(Received November 27, 1998)

Oligomers of 2,2′-bipyridine (Oligo-bpy) and 5,5′-bipyrimidine (Oligo-bpym) with a linear structure have been prepared by an organometallic C–C coupling reaction. The oligomeric chelating ligands have a molecular weight of about 1500 corresponding to about 10 chelating bpy or bpym units, and form soluble complexes with $[M(bpy)_2]^{2+}$ (M = Ru or Os). The UV-vis absorption spectra of the metal complexes of Oligo-bpy exhibit a π–π^* transition band at 355±6 nm and a peak at 453±18 nm assigned to a MLCT absorption. The UV-vis spectra of the metal complexes of Oligo-bpym also show an absorption peak attributed to the MLCT band. The water-soluble Ru complex of Oligo-bpy catalyzes visible-light-induced H_2 evolution from aqueous media in the presence of Pt cocatalyst and triethylamine.

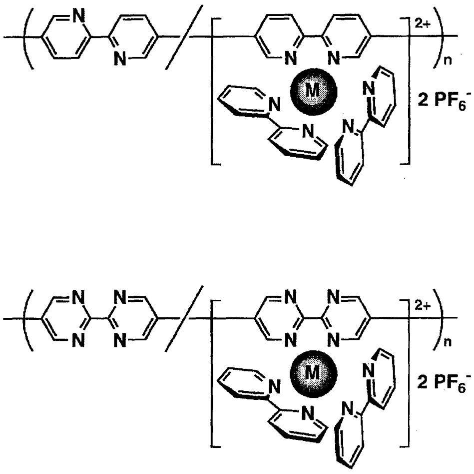
π-Conjugated heteroaromatic polymers such as polythiophenes and polypyridines have attracted the attention of chemists due to their interesting electronical and optical properties.[1] When the polymer has coordinating nitrogen,[2] it forms metal complexes.[2c,2d—4]

For example, poly(2,2′-bipyridine-5,5′-diyl) (PBpy) forms electrically conducting Ru-, Ni-,[2c,2d,4] and Pt-complexes,[5] and the Ru- and Pt-complexes show catalytic activity for photoevolution of H_2 from aqueous media (Scheme 1). However, as for PBpy with a high molecular weight, introduction of the M-unit to the polymeric ligand was not easy. The obtained metal complex did not show good solubility either, and this makes revealing chemical properties of the metal complex difficult. Alkyl derivatives of PBpy show good solubility[2d] and give soluble Cu(I)-complexes,[6a] however, the effective π-conjugation length is shortened because of a steric effect of the alkyl group, and the π–π^* absorption band appears at a rather short wavelength.

In order to reveal basic functions of the π-conjugated polymer ligand to form metal complexes, we have prepared *oligomers* of 2,2′-bipyridine (bpy) and bipyrimidine (bpym) which still possess basic electronic and optical properties of the corresponding π-conjugated polymers with the higher molecular weight (Scheme 2). Herein we report syntheses of the oligomeric π-conjugated ligands and preparation of their water-soluble Ru(II)- and Os(II)-complexes, as well as their catalytic activity for photoevolution of H_2 from an aqueous media. Among the π-conjugated ligands, such a long bipyrimidine ligand was first prepared in this study, and recently Periana, Taube, and their co-workers reported interesting catalytic effect of a Pt complex of 2,2′-bipyrimidine.[6b] A part of this work was reported in a communication form.[7]



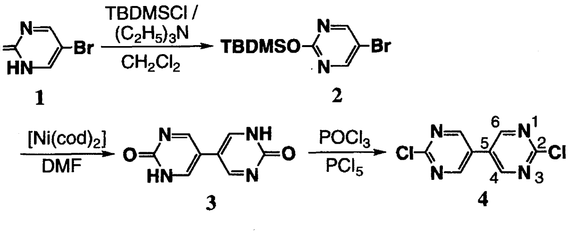
Scheme 1.



Scheme 2.

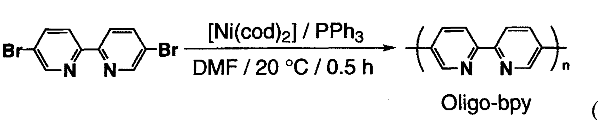
Results and Discussion

Preparation and Characterization of Oligomers of bpy and bpym (Oligo-bpy and Oligo-bpym). The starting material for Oligo-bpy (5,5′-dibromo-2,2′-bipyridine) was prepared by the previously reported method.[8a] 2,2′-Dichloro-5,5′-bipyrimidine, the starting material for Oligo-bpym, was synthesized through the following reaction route (Eq. 1). Lactam-lactim proton of 5-bromopyrimidine-2(1*H*)-one (**1**) was protected with *t*-butyldimethylsilyl (TBDMS) group[8b)] and dimerized with a Ni(0)-complex. The obtained 5,5′-bipyrimidine-2,2′(1*H*,1′*H*)-dione (**3**) was chlorinated by modifying the reported method.[8c)]

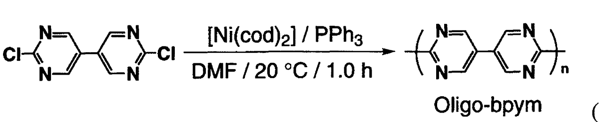


$[Ni(cod)_2]$ = bis(1,5-cyclooctadiene)nickel(0) (1)

Figure 1 shows the molecular structure determined by X-ray crystallography. Previously reported dehalogenation polycondensation using Ni(0)-complexes[2)] was utilized to prepare Oligo-bpy and Oligo-bpym. However, selection of reaction temperature, reaction time, and the supporting ligand was needed to obtain the oligomeric ligands with controlled molecular weights and solubility (Eqs. 2 and 3).



(2)



(3)

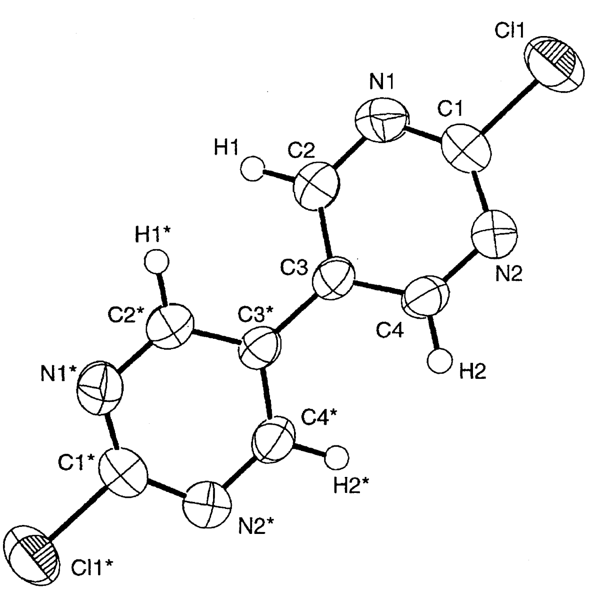


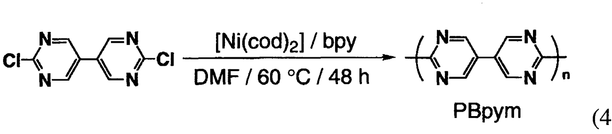
Fig. 1. Molecular structure of **4**: Cl(1)–C(1) 1.732(4), N(1)–C(1) 1.303(5), N(1)–C(2) 1.331(6), N(2)–C(1) 1.334(5), N(2)–C(4) 1.332(5), C(2)–C(3) 1.393(6), C(3)–C(3*) 1.459(8), C(3)–C(4) 1.376(5), C(2)–C(3)–C(3*)–C(2*) 36.7(9), C(4)–C(3)–C(3*)–C(4*) 34.9(9), C(2)–C(3)–C(3*)–C(4*) 144.2(3).

The selection of PPh_3[2a,2d)] as the supporting ligand seemed effective to obtain the oligomeric chelating ligands.

Oligo-bpy. Oligo-bpy had an intrinsic viscosity [η] of 0.15 dl g^{-1} (in HCOOH; dl = 100 cm^3) and a weight average molecular weight (M_w) of 1500 (determined by the light scattering method), which corresponded to about 10 recurring bpy units. Oligo-bpy was considered to be H-terminated, since halogen was not detected. Oligo-bpy itself has solubility comparable to that of previously prepared PBpy with a M_w of 3200,[2d)] and it is soluble in acids such as HCOOH, CF_3COOH, and concd H_2SO_4.

Oligo-bpy exhibits a UV-vis peak at 371 nm in HCOOH, which is shifted from those of pyridine and bpy (cf. Table 1 and Fig. 4 shown later) and locates near that (373 nm)[1d)] of PBpy with the higher M_w of 3200 (Table 1). Both cast films of Oligo-bpy and PBpy on a Pt plate show redox potentials at essentially the same position, −2.2 V vs. Ag/Ag^+,[2d)] in their cyclic voltammograms. These results indicate that Oligo-bpy has electric and optical properties similar to those of PBpy, although Oligo-bpy has much higher reactivity toward metal compounds and gives soluble metal complexes in contrast to the case of PBpy.

Oligo-bpym. We have prepared oligomer and polymer of 5,5′-bipyrimidine (Oligo-bpym and PBpym, respectively) under different reaction conditions (Eqs. 3 and 4). The polycondensation using bpy (Eq. 4) as the supporting ligand at higher temperature gave the polymer with M_w of 9.6×10^5 as determined by the light scattering method in concd H_2SO_4.[9a)] On the other hand, the conditions shown in Eq. 3 afforded Oligo-bpym with a M_w of 1800 (n = about 12). Structures of Oligo-bpym and PBpym obtained in Eqs. 3 and 4 are confirmed by elemental analysis, and IR and CP-MAS-^{13}C NMR spectroscopies (Fig. 2). Oligo-bpym and PBpym prepared under different conditions give rise to essentially the same CP-MAS-^{13}C NMR spectrum. Appearance of strong spinning side bands indicates the presence of a strong magnetic anisotropy at the carbon in the oligomer and polymer due to the aromatic planar structure around the carbon.[9b—9d)]



(4)

Oligo-bpym and PBpym themselves have very low solubility in organic solvents. They were only partially soluble in HCOOH, CF_3COOH, and concd HCl. Oligo-bpym obtained in Eq. 3 can be completely dissolved in concd H_2SO_4. PBpym obtained in Eq. 4 is also soluble in concd H_2SO_4, however, its solubility seems lower than that of Oligo-bpym. PBpym is considered to be H-terminated since it does not contain Cl, similar to the case of PBpy.[2d)] Since the polycondensation expressed by Eqs. 3 and 4 proceeds selectively at the C–Cl bond, both Oligo-bpym and PBpym are considered to have a linear structure, similarly to PBpy and Oligo-bpy.[2d)]

Previously we reported preparation of poly(pyrimidine-2, 5-diyl) (PPym),[10)] which is considered to contain the pyrimidine unit both in head-to-tail HT and head-to-head HH se-

Table 1. Optical and Electrochemical Properties of the Oligomers and Polymers of bpy and bpym

No.	Polymer	Absorption	Photoluminescence	E_0/V vs. Ag/Ag$^+$
		λ_{max}/nm	λ_{em}/nm	
1	PBpy[a]	373[b]		−2.21
2	Oligo-bpy	371[b]		−2.16
3	PBpym	342[c]		
4	Oligo-bpym	342[c]	407[d]	−1.93
5		353[e]		
6	PPym[f]	358[e]		−1.72

a) From Ref. 1d. b) In HCOOH. c) In concd H_2SO_4. d) In concd H_2SO_4. Excited at 349 nm. e) In concd HCl (soluble part). f) From Ref. 10.

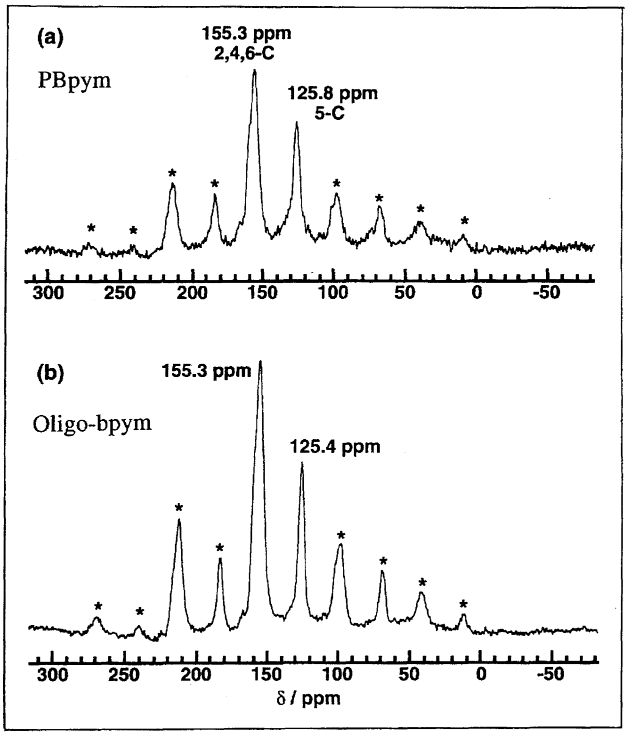


Fig. 2. CP-MAS-^{13}C NMR spectra of (a) PBpym and (b) Oligo-bpym. Peaks with * are assigned to spinning side bands.

quences randomly Chart 1. For PPy and PBpy, the difference in the regioregularity leads to no observable differences in their optical and electrochemical properties, in spite of a large difference in the coordinating ability toward metals.[2c,2d,4]

As shown in Table 1, Oligo-bpym, PBpym, and PPym exhibit UV-vis absorption maxima at 342 nm in concd H_2SO_4 (Nos. 3 and 4) and at 356±3 nm in concd HCl (soluble part; Nos. 5 and 6). These optical properties suggest that Oligo-bpym also bears a π-conjugation system similar to those of PBpym and PPym. However, full assignment of their π–π^* absorption band has not been successful due to their insolubility in usual aqueous or organic solvents and the difficulty to obtain acid-free good film.

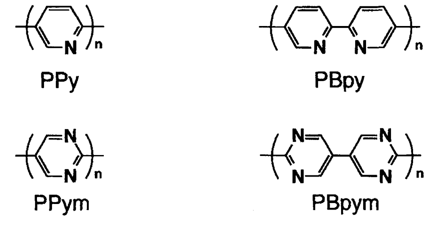
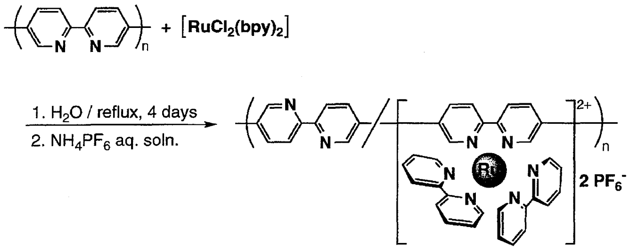


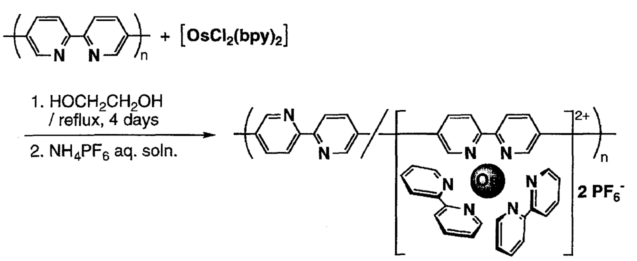
Chart 1. Two categories of polymers with random sequences (left) and HH-controlled sequences (right).

Preparation and Properties of Ru and Os Complexes of Oligo-bpy. 1. Preparation and Characterization. A reaction of a pale yellow powder of Oligo-bpy with $[RuCl_2(bpy)_2]$ (1 mol per 1 mol of the bpy monomer unit) in an aqueous solution gave a homogeneous reddish solution. Addition of NH_4PF_6 led to precipitation of a reddish brown polymer complex, through an anion exchange between Cl$^-$ and PF_6^-.



(5)

Similarly, an Os complex of Oligo-bpy was obtained as a dark brown powder in ethylene glycol under reflux (Eq. 6).



(6)

In contrast to the poor solubility of the starting oligomeric ligand, both the complexes are readily soluble in polar organic solvents such as acetonitrile, acetone, and DMSO. Their structures have been determined by elemental analysis and IR and UV-vis spectroscopy.

Figure 3 depicts X-ray photoelectron spectra (XPS) of Oligo-bpy and the Ru complex of Oligo-bpy in a region of the 1s electron of nitrogen. As shown in Fig. 3, most of the

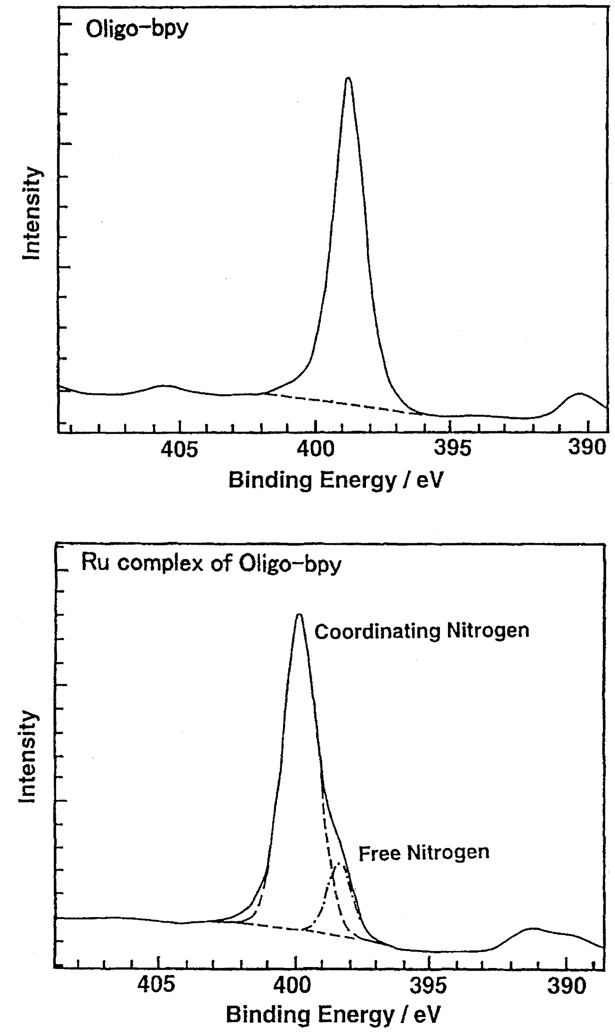


Fig. 3. X-Ray photoelectron spectra (XPS) of Oligo-bpy (top) and the Ru complex of Oligo-bpym (bottom) for N 1s.

nitrogens in Oligo-bpy receives a shift to a higher binding energy by the complex formation. Deconvolution of the peak indicates that most of the nitrogen in Oligo-bpy is bonded to Ru^{2+} (Table 2). These XPS data essentially agree with results of elemental analysis (cf. the Experimental) which indicate a high degree of complexation of the bpy unit of Oligo-bpy with Ru. The attained degree of the complexation of the bpy unit of Oligo-bpy is considerably larger than that (1—15% depending on the preparative conditions) attained with PBpy having the higher M_w value of 3200.[2d] Since nitrogen of bpy coordinated to a cationic transition metal center also gives the XPS peak[5] near the main peak shown in the lower figure of Fig. 3, the main peak is considered to originate from the nitrogen of Oligo-bpy coordinated to $[Ru(bpy)_2]^{2+}$ as well as from bpy in the $[Ru(bpy)_2]^{2+}$ unit. Consequently, obtaining full information about the degree of complexation of Oligo-bpy was not possible, although the peak area ratio of about 6 : 1 (Fig. 3 and Table 2) corresponded to about 67% degree of the complexation of the oligo-bpy ligand to $[Ru(bpy)_2]^{2+}$. Data from elemental analysis indicated a higher degree of the complexation (cf. Experimental).

Table 2. XPS Data of the Ru Complex of Oligo-bpy

Electron	Binding energy/eV (peak area/arb. unit)	
	Oligo-bpy	Ru complex of Oligo-bpy
Ru $3d_{5/2}$		280.8
N 1s	398.8	398.5 (320)[a]
		399.9 (1841)[b]

a) Uncoordinated nitrogen. b) Coordinated nitrogen.

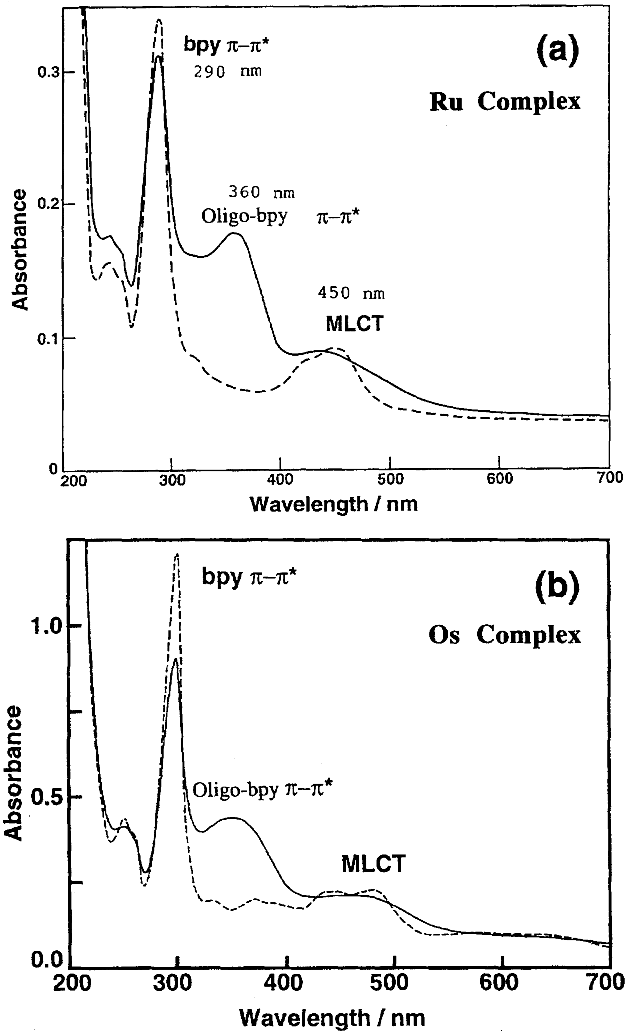


Fig. 4. (a) UV-vis spectra of the Ru complex of Oligo-bpy (solid line) and $[Ru(bpy)_3]^{2+}$ (broken line) in CH_3OH. (b) UV-vis spectra of the Os complex of Oligo-bpy (solid line) and $[Os(bpy)_3]^{2+}$ (broken line) in CH_3CN.

2. Optical Properties. By the complex formation, Oligo-bpy becomes soluble even in organic solvents including methanol. A UV-vis absorption spectrum of its Ru complex in methanol is shown in part (a) of Fig. 4. The UV-vis data of the compounds described in this paper are summarized in Table 3 together with their electrochemical data. The $[Ru(bpy)_2]^{2+}$ complex of Oligo-bpy gives rise to an MLCT absorption band and a π–π* transition band of the bpy ligand at about 450 and 290 nm respectively. In addition to these

Table 3. Optical and Electrochemical Data of the Metal Complexes

No.	Compound	Absorption[a)]	Photoluminescence	Redox potential[b)]			
		λ_{max}/nm	λ_{em}/nm (quantum yield)	E_{ox}/V	$E_{red\ 1}$/V	$E_{red\ 2}$/V	$E_{red\ 3}$/V
1	Ru complex of Oligo-bpy	290, 360*, 435—450[c)]	694[c,d,e)] (2.2×10^{-3} [d)], 1.1×10^{-3} [e)])	0.98	−1.24	−1.85	−2.20
2	$[Ru(bpy)_3]^{2+}$	287, 451[c)]	612[c)] (5.2×10^{-2} [f)])	0.93	−1.71	−1.90	−2.14
3	Os complex of Oligo-bpy	244, 291, 349*, 470		0.54	−1.17	−1.75	−2.13
4	$[Os(bpy)_3]^{2+}$	244, 291, 329, 369, 436, 479		0.51	−1.63	−1.83	−2.13
5	Ru complex of Oligo-bpym	285, 423	No emission[g)]				
6	$[Ru(bpy)_2(bpym)]^{2+}$ [h)]	236, 294, 322(sh), 360, 422, 480(sh)	710[i)]				
7	Os complex of Oligo-bpym	240, 291, ca. 435, ca. 490					
8	$[Os(bpy)_2(bpym)]^{2+}$ [j)]	244, 255(sh), 289, 350(sh), 370, 435, 455, 570(sh), 635(sh)					

a) In acetonitrile unless otherwise noted. Small peaks are omitted. The peak with the * mark is assigned to π–π* transition in the oligomeric ligand. b) Potential vs. Ag/Ag$^+$. For $E_{ox}-E_{red\ 3}$, see part (a) in Fig. 4. c) In methanol. d) Excited at 435 nm (CT band). e) Excited at 361 nm (main chain π–π* band). f) Excited at 453 nm. g) In acetonitrile. h) From Ref. 11c. i) In propylene carbonate. j) From Ref. 13.

peaks characteristic of $[Ru(bpy)_3]^{2+}$, the polymeric complex shows a π–π* transition band originated from the main chain of Oligo-bpy at around 360 nm.

The MLCT band of the polymeric complex is broadened toward the longer wavelength, compared with that of $[Ru(bpy)_3]^{2+}$. The main MLCT band is assignable to Ru → bpy MLCT, whereas the absorption at the longer wavelength seems to contain a contribution from a "Ru → Oligo-bpy" CT band. According to the formation of the π-conjugation system, Oligo-bpy is considered to have a higher energy HOMO and a lower energy LUMO compared with bpy, and this will lead to shifts of the π–π* absorption and MLCT peak to the longer wavelength.

The methanolic solution of the Ru complex of Oligo-bpy shows a photoluminescence peak at 694 nm, which also locates at a longer wavelength compared with that of $[Ru(bpy)_3]^{2+}$ (612 nm, No. 2 in Table 3). Excitation at a π–π* band of Oligo-bpy (361 nm) and at an MLCT band (435 nm) (Table 3, No. 1) give the photoluminescence at the same position, the onset position of the MLCT band at 694 nm, suggesting the occurrence of transfer of energy absorbed by the π-conjugated Oligo-bpy to the Ru complex. The intensity of the photoluminescence, however, is not strong and the quantum yield is less than 1/10 of that of $[Ru(bpy)_3]^{2+}$. Essentially the same data are obtained in other solvents including acetonitrile, DMSO, and pyridine, and these data suggest the π-conjugated Oligo-bpy ligand quenches the photoluminescence.

The Os complex of Oligo-bpy is also soluble in acetonitrile, and it gives a UV-vis spectrum similar to that of the Ru complex of Oligo-bpy, as exhibited in part (b) of Fig. 4.

3. Electrochemical Response. Cyclic voltammetry of the Ru and Os complexes of Oligo-bpy can be carried out in acetonitrile solutions and the CV chart of the Ru complex is shown in Fig. 5. The CV data of the complexes are summarized in Table 3, and compared with those of $[M(bpy)_3]^{2+}$ (M = Ru, Os).[11a)]

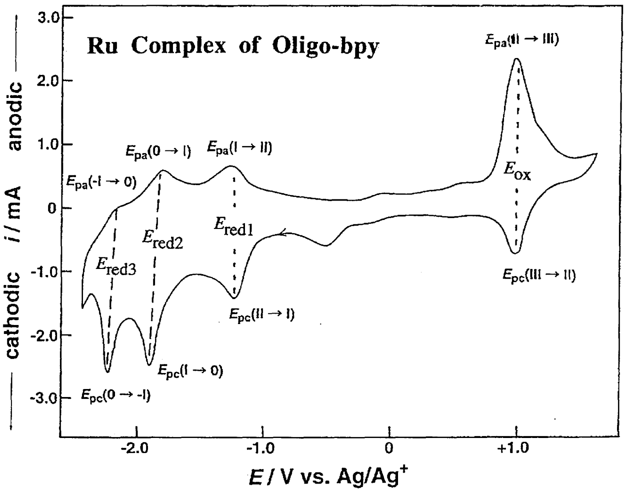
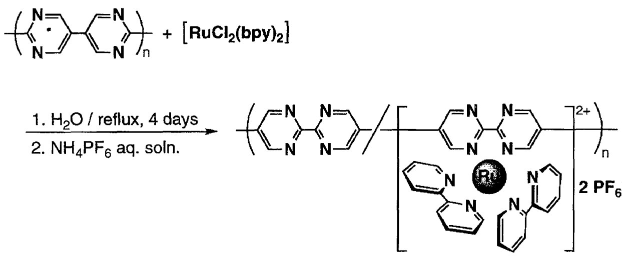


Fig. 5. Cyclic voltammograms of the Ru complex of Oligo-bpy (1.4 mM monomer unit; sweep rate = 60 mV s^{-1}) in a CH_3CN solution containing 0.10 M $[NBu_4]PF_6$ (Bu = butyl).

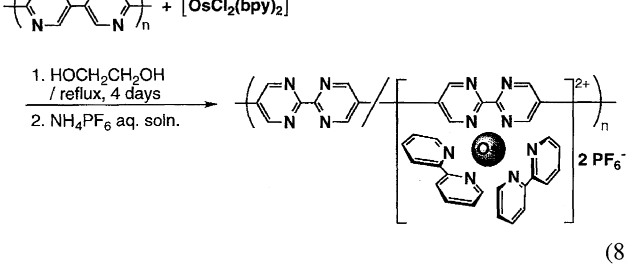
The Ru complex of Oligo-bpy gives a CV chart similar to those of the corresponding monomeric complex. A Ru(II)/Ru(III) couple is observed in a positive potential region, and three couples of peaks appear in a negative potential region (Fig. 5). The first reduction peak E_{pc}(II → I) shifts to a positive direction in both the Ru and Os complexes of Oligo-bpy, compared with the corresponding monomeric complexes $[M(bpy)_3]^{3+}$ (cf. Nos. 1—4 in Table 3; the 3rd last column), indicating that the expansion of the π-conjugation system of the ligand makes the acceptance of electrons easier. The CV chart is somewhat different from that obtained with a film of analogous PBpy–Ru complex,[2d)] which gives highly broadened peaks, possibly due to some intermolecular interaction which occurred in the film. However, the CV peaks of the Ru complex of Oligo-bpy in the solution are still somewhat broadened, compared with those of $[\mathrm{Ru(bpy)_3}]^{2+}$.[11a]

For the Ru complex of Oligo-bpy, the areas of the three reduction peaks (E_{pc} (II → I), E_{pc} (I → 0), and E_{pc} (0 → −1) in Fig. 5 are considerably larger than those of corresponding oxidation peaks (E_{pa} (I → II), E_{pa} (0 → 1), and E_{pc} (−1 → 0)). On the other hand, the E_{pc} (III → II) reduction peak area is much smaller compared with the E_{pa} (II → III) oxidation peak area. These results suggest that the negative charge stored in the Ru complex of Oligo-bpy at the E_{pc} (II → I)−E_{p} (0 →−1) processes is lost only partly at the E_{pa} (I → II)−E_{pa} (−1 → 0) processes, and the remaining negative charge is discharged at the potential agreeing with the E_{pa} (II → III) peak. When the scanning is repeated only within a positive potential region, the E_{pc} (III → II) and E_{pa} (II → III) peak areas become almost same. The Ru complex of Oligo-bpy seems to be able to form highly stable reduced state(s) to lose the stored electron only after the potential is swept to the high oxidation potential near +0.9 V vs. $\mathrm{Ag/Ag^+}$. This may be related to the above discussed photoluminescence results, which indicate the π-conjugation system of Oligo-bpy quenches the photoluminescence. The photoexcited electron in the Ru center may be stabilized (or trapped) by the π-conjugation system of Oligo-bpy; the electrochemically reduced state may also be stabilized due to similar reasons.

Ru and Os Complexes of Oligo-bpym. Oligo-bpym also forms Ru- and Os-complexes (Eqs. 7 and 8). Both the complexes are soluble in polar organic solvents.



(7)



(8)

Figure 6 depicts a UV-vis spectrum of the Ru complex of Oligo-bpym in acetonitrile. Table 3 includes optical and electrochemical data of the complexes. For comparison, positions of MLCT transition bands of corresponding low molecular complexes, $[\mathrm{Ru(bpy)_2(bpym)}]^{2+}$ and $[\{\mathrm{Ru(bpy)_2}\}_2(\mu\text{-bpym})]^{4+}$ (bpym = 2,2′-bipyrimidine), are shown in the lower part of Fig. 6.[11b,11c] The MLCT band of the Ru complex of Oligo-bpym appears near that of $[\mathrm{Ru(bpy)_2(bpym)}]^{2+}$, indicating that Oligo-bpym forms a similar 1 : 1 adduct of $[\mathrm{Ru(bpy)_2}]^{2+}$ as the major species. However, the MLCT band of the Ru complex of Oligo-bpym at 435 nm seems to have a tailing part toward longer wavelengths, suggesting that the complex contains a 1 : 2 adduct like $[\mathrm{(bpy)_2Ru(\mu\text{-}bpym)Ru(bpy)_2}]^{4+}$. Data from elemental analysis also suggests formation of such species (cf. Experimental Section).

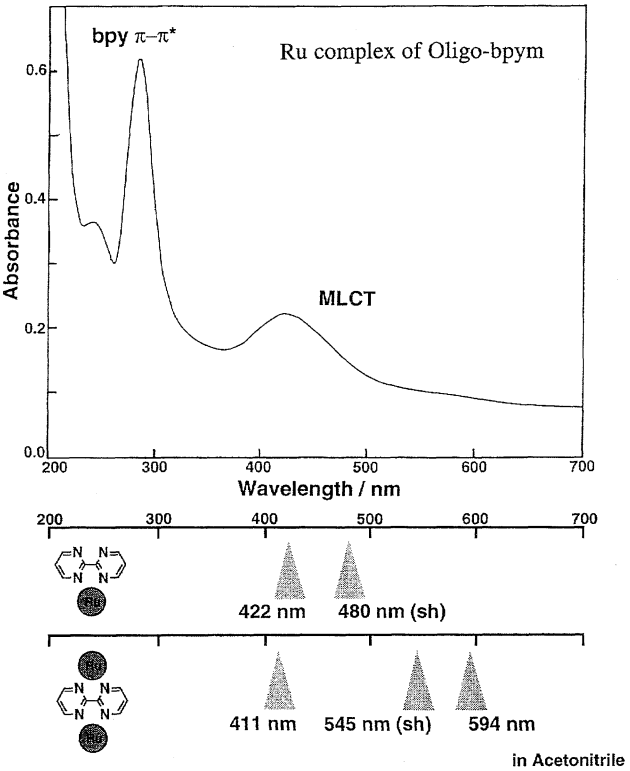


Fig. 6. UV-vis spectra of the Ru complex of Oligo-bpym in $\mathrm{CH_3CN}$.

The Ru complex of Oligo-bpym is not photoluminescent (surveyed for a range of 300—800 nm), which is related to the reported fact that monomeric $[\mathrm{Ru(bpy)_2(bpym)}]^{2+}$ has an extremely short life time of excited state (< 1/10 of $[\mathrm{Ru(bpy)_3}]^{2+}$).[11b,12] The UV-vis spectrum of the Os complex of Oligo-bpym is similar to that of the Ru complex, and shows an MLCT band near that of $[\mathrm{Os(bpy)_2(bpym)}]^{2+}$ (No. 7, Table 3).[13]

Ru Complex of Oligo-bpy as Catalysis for Photoevolution of $\mathrm{H_2}$ from Aqueous Media. Recently it has been reported that π-conjugated polymers such as poly(*p*-phenylene), PPy, and PBpy catalyze the photoinduced evolution of $\mathrm{H_2}$ from aqueous media.[5,14] Photoevolution of $\mathrm{H_2}$ from aqueous media using non-π-conjugated polymer complexes has also been reported.[15]

We have examined such photocatalytic activity of the Ru complex of Oligo-bpy by using visible light as a light source. Photoevolution of $\mathrm{H_2}$ from homogeneous aqueous media using *soluble* metal complexes of π-conjugated long ligands as the catalysts has no precedent to our knowledge.

The catalytic activity was tested in the same aqueous medium previously used for the photoevolution of $\mathrm{H_2}$ catalyzed by mixtures of PBpy and metal or metal compounds.[5] Namely a methanolic aqueous solutions containing Pt colloid or $[Pt(bpy)_2]^{2+}$ as a cocatalyst and triethylamine (NEt_3) as a sacrificial electron donor were adopted as the aqueous media. The UV light from a Xe lamp was omitted and only visible light ($\lambda > 400$ nm) was irradiated (cf. Experimental Section), and time-course of the photoevolution of H_2 is shown by curves (a) and (b) in Fig. 7. For comparison, the catalytic effect of Oligo-bpy was also measured, and it was found that Oligo-bpy had catalytic activity given by the curve (c) in Fig. 7, which is comparable to that of PBpy previously reported.[5]

As exhibited in Fig. 7, the Ru complex of Oligo-bpy shows a better catalytic activity in the presence of the Pt colloid cocatalyst than in the presence of $[Pt(bpy)_2]^{2+}$. The turn-over number (based on the Ru in the Ru complex of Oligo-bpy) after 6 h is about 6 (or about 100 based on Pt). Addition of methyl viologen chloride as an electron mediator often enhances the photoevolution of H_2, however, such effect was not observed with the present system. As described previously, a $Ru(bpy)_2^{2+}$ complex of PBpy has certain electrical conductivity,[2d] and the present Ru complex of Oligo-bpy also shows analogous electrical conductivity. By irradiation of a film of the present Ru complex of Oligo-bpy with Xe-lamp light (> 320 nm, about 10^5 lx), the electric conductivity is enhanced by a factor of about 4. This phenomenon suggests the evolution of carrier species by the photoactivation and may be related to the photocatalysis.

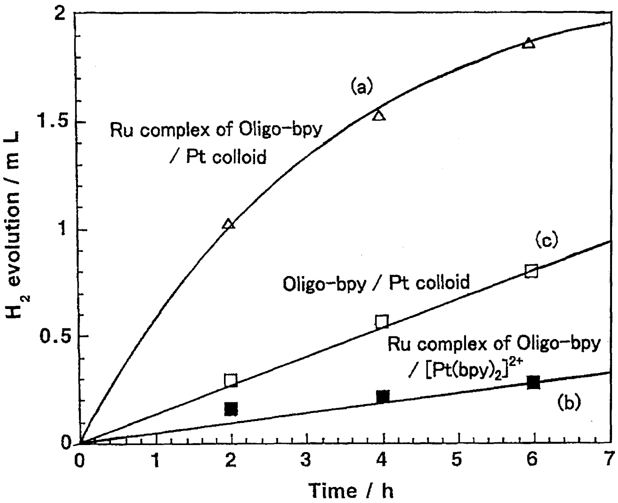


Fig. 7. Photoevolution of H_2 from the aqueous solution (a mixture of 0.5 cm^3 of H_2O, 0.5 cm^3 of CH_3OH, and 0.5 cm^3 of NEt_3) catalyzed by the Ru complex of Oligo-bpy in the presence of Pt cocatalysts. Catalyst: △: Ru complex of Oligo-bpy (10 mg)+Pt colloid (5.9×10^{-4} M or 0.89 μmol of Pt) (curve (a)); ■: Ru complex of Oligo-bpy (10 mg)+$[Pt(bpy)_2](NO_3)_2$ (2.4×10^{-4} M or 0.36 μmol) (line (b)). For comparison, data obtained by using Oligo-bpy (10 mg) and Pt colloid (5.9×10^{-4} M or 0.89 μmol of Pt) are shown by the line (c). At about 25 °C.

Conclusion and Scope

Oligomeric chelating ligand of bpy and bpym can be obtained by Ni(0)-promoted dehalogenation polycondensation under selected reaction conditions. Oligo-bpy and Oligo-bpym give essentially the same optical and electrochemical properties as PBpy and PBpym with higher molecular weights, respectively. However, these oligomeric chelating ligands easily form soluble Ru- and Os-complexes, in contrast to low reactivity of PBpy[2d] and PBpym with the higher molecular weights. Elemental and XPS analyses indicate high degrees of the complexation of the bpy and bpym units in the oligomer. The soluble Ru complex of Oligo-bpy serves as photocatalyst for H_2 evolution from the aqueous media. The obtained results are expected to contribute to better understanding of chemical properties of metal complexes of long π-conjugated ligands and their catalysis.

Experimental

Materials. 2-Hydroxypyrimidine hydrochloride and $[RuCl_2(bpy)_2]$ were used as purchased. 5,5′-Dibromo-2,2′-bipyridine,[2c] $[OsCl_2(bpy)_2]$,[16] $[Ru(bpy)_3](PF_6)_2$,[17] and $[Os(bpy)_3](PF_6)_2$[18] were prepared according to the literature. Triphenylphosphine (PPh_3) and 2,2′-bipyridiyl (bpy) were used as purchased. $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) was prepared as reported in the literature.[19] $[Pt(bpy)_2](NO_3)_2$[20] and Pt colloid[21] were prepared according to the literature as previously reported.[5] Solvents were dried, distilled, and stored under N_2.

Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer with KBr pellets. ^1H and CP-MAS-^{13}C NMR spectra were taken using a JEOL JNM-EX-90 spectrometer and a JEOL GSX-270 spectrometer, respectively. The weight average molecular weights of Oligo-bpy was determined with Otsuka electronics DLS-700 dynamic light scattering spectrophotometer. UV-vis absorption and photoluminescence spectra were measured with a Shimadzu UV-2100PC spectrometer and a Hitachi F-4010 spectrometer, respectively. X-Ray photoelectron spectra (XPS) were obtained with a Shimadzu ESCA3200 XPS spectrometer using the Mg *Kα* radiation as the excitation source. Cyclic voltammetry was carried out in acetonitrile solutions containing 0.1 M $[(C_4H_9)_4N]PF_6$ (1 M = 1 mol dm^{-3}) with a Hokuto Denko HABF-501 galvanostat/potentiostat. For Oligo-bpy and Oligo-bpym, their films were prepared by casting from HCOOH or CF_3COOH solutions on a Pt electrode (1 cm×1 cm); with these electrodes cyclic voltammograms were obtained. In cases of their metal complexes, their acetonitrile solutions containing 0.1 M $[(C_4H_9)_4N]PF_6$ were used. The photocurrent was measured with an Advantest R8340A ultra high resistance meter. For the photocurrent measurement and the photoreduction, 500 W Xe lamp (Ushio, UXL500) was used as a light source. Light with wavelength shorter than 320 nm (for the photocurrent measurement) or 400 nm (for the photoevolution of H_2) was omitted with a cutoff filter. The photoevolution of H_2 was performed as follows. Samples were placed at a constant distance (30 cm) from the lamp, and intensity of light at the sample place was about 140000 lx. The amount of hydrogen was determined with a Shimadzu 3BT gas chromatograph equipped with a thermal conductivity detector and a 5A molecular sieve column (3 m×ϕ3 mm). Argon was used as a carrier gas.

Preparation of 2,2′-Dichloro-5,5′-bipyrimidine. 5-Bromo-2-(*t*-butyldimethylsiloxy)pyrimidine (**2**) was prepared from 2-hydroxypyrimidine hydrochloride according to the literature.[8b,22] **2** was coupled with [Ni(cod)$_2$]. [Ni(cod)$_2$] (2.5 g, 9.1 mmol) and a small amount of 1,5-cyclooctadiene were added to 47 cm^3 of DMF in a Schlenk tube under nitrogen. To this mixture was added **2** (4.21 g, 14.5 mmol). After the reaction mixture was stirred at 40 °C for 1 h, this mixture was poured into concd aqueous ammonia and stirred overnight. This solution was carefully neutralized with hydrochloric acid under cooling with an ice bath to yield a white precipitate. The precipitate was collected by filtration, washed with water, and dried in vacuo to obtain a white powder of 5,5′-bipyrimidine-2,2′(1*H*,1′*H*)-dione (**3**) (1.19 g, yield 86%). ^{1}H NMR (CF_3COOD) $\delta = 9.32$ (s, 4-H and 6-H). IR 3412, 2828, 1631, 1553, 1480, 1387, 1329, 987, 911, 792, 586 cm^{-1}. Anal. Found: C, 47.9; H, 3.6; N, 28.0%. Calcd for $C_8H_6N_4O_2{\cdot}0.6H_2O$: C, 47.8; H, 3.6; N, 27.9%.

3 was chlorinated with $POCl_3$.[8c] To a mixture of $POCl_3$ (5.0 cm^3) and PCl_5 (5.10 g, 24.5 mmol) was added **3** (717 mg, 3.77 mmol). This mixture was stirred and vigorously refluxed for 20 h under nitrogen. After cooling to room temperature, this mixture was carefully dropped into an ice bath. The solution was neutralized with NaOH to afford a brown precipitate. This precipitate was collected and dried under vacuum. The dark brown solid was added into $CHCl_3$ (300 cm^3) and the mixture was stirred. An insoluble part was removed by filtration and the filtrate was concentrated. The crude product was purified by column chromatography (silica gel, $CHCl_3$), recrystallized from $CHCl_3$/toluene, and dried in vacuo. 2,2′-Dichloro-5,5′-bipyrimidine (**4**) was obtained as pale yellow crystals (258 mg, yield 30.2%). Mp 257—260 °C. ^{1}H NMR ($CDCl_3$) $\delta = 8.83$ (s, arom.). IR (KBr) 3034, 1571, 1528, 1389, 1344, 1259, 1171, 993, 930, 768, 750, 648, 442 cm^{-1}. Anal. Found: C, 42.3; H, 1.7; N, 24.7; Cl, 30.8%. Calcd for $C_8H_4Cl_2N_4$: C, 42.3; H, 1.8; N, 24.7; Cl, 31.2%.

Polymerization. Oligo-bpy. [Ni(cod)$_2$] (3.25 g, 11.8 mmol), a small amount of 1,5-cyclooctadiene, and PPh_3 (6.19 g, 23.6 mmol) were dissolved in 130 cm^3 of DMF in a Schlenk tube under nitrogen, and stirred for ca. 10 min at 20 °C. To the solution was added 5,5′-dibromo-2,2′-bipyridine (2.24 g, 7.14 mmol). After stirring at 20 °C for 30 min, the mixture was poured into aqueous ammonia. The product was collected by filtration, and washed with methanol, toluene, methanol, a hot aqueous solution of ethylenediaminetetraacetic acid, distilled water, and methanol in this order. The product was dried in vacuo to obtain a pale yellow powder of Oligo-bpy (668 mg, yield 60.7%). Anal. Found: C, 77.1; H, 4.4; N, 17.7; Br, 0%. Calcd for $(C_{10}H_6N_2{\cdot}0.1H_2O)_n$: C, 77.0; H, 4.0; N, 18.0%. $M_w = 1500$ (determined by the light scattering method).

PBpym (with Higher Molecular Weight). In a Schlenk tube under nitrogen, [Ni(cod)$_2$] (730 mg, 2.65 mmol), a small amount of 1,5-cyclooctadiene, and bpy (424 mg, 2.71 mmol) were dissolved in 15 cm^3 of DMF, and the mixture was stirred for about 10 min at room temperature To the solution was added 2,2′-dichloro-5,5′-bipyrimidine **4** (262 g, 1.15 mmol), and the mixture was stirred at 60 °C for 48 h. The mixture was poured into aqueous ammonia, and the precipitated product was washed in a manner analogous to that used for the preparation of oligomeric PBpy, and dried in vacuo to obtain an orange powder of PBpym (184 mg, yield 92.7% (based on carbon recovered)). IR 1576, 1522, 1409, 1142, 992, 935, 768, 658 cm^{-1}. Anal. Found: C, 55.8; H, 3.9; N, 30.7; Cl, 0%. Calcd for $(C_8H_4N_4{\cdot}1.0H_2O)_n$: C, 55.2; H, 3.5; N, 32.2%.

Oligo-bpym. [Ni(cod)$_2$] (2.34 g, 8.51 mmol), a small amount of 1,5-cyclooctadiene, and PPh_3 (4.46 g, 17.0 mmol) were dissolved in 95 cm^3 of DMF in a Schlenk tube under nitrogen, and the mixture was stirred for about 10 min at 20 °C. To the solution was added **4** (1.00 g, 4.40 mmol), and the mixture was stirred at 20 °C for 1.0 h. After the reaction, the mixture was poured into aqueous ammonia, and the precipitated product was washed similarly to the case of the preparation of Oligo-bpy, and dried in vacuo to obtain an orange powder of Oligo-bpym (314 mg, yield 45.6%). Anal. Found: C, 58.3; H, 3.2; N, 33.8%. Calcd for $(C_8H_4N_4{\cdot}0.5H_2O)_n$: C, 58.2; H, 3.1; N, 33.9%.

Preparation of Ru Complexes of Oligo-bpy and Oligo-bpym. Preparation of the Ru complex of oligo-bpy was carried out as follows. Air in distilled water (18 cm^3) was removed by bubbling with argon for 30—60 min in a Schlenk tube, and Oligo-bpy (80.5 mg, 0.52 mmol unit) and [RuCl$_2$(bpy)$_2$] (271 mg, 0.52 mmol) were added. This reaction mixture was heated under reflux and stirred for 4 d under nitrogen atmosphere. After an insoluble part was removed by centrifugation, the solution was condensed to about 5 cm^3 by evaporation. To this solution was added an aqueous solution of NH_4PF_6 (small excess) to precipitate the Ru complex of Oligo-bpy as the PF_6 salt. The product was washed with a small amount of distilled water repeatedly to remove unreacted [RuCl$_2$(bpy)$_2$] and other ionic products until the absorption for [RuCl$_2$(bpy)$_2$] disappeared almost completely in the UV-vis spectra of the supernatants, and dried in vacuo. The crude was washed with chloroform to remove [RuCl$_2$(bpy)$_2$] completely and dried under vacuum to obtain a reddish brown powder of the Ru complex of Oligo-bpy (340 mg). IR 1603, 1559, 1544, 842, 762, 729, 557 cm^{-1}. Anal. Found: C, 41.8; H, 3.0; N, 9.7%. Calcd for a 1 : 1 complex between Ru(bpy)$_2$ and the bpy unit of Oligo-bpy $(C_{30}H_{22}F_{12}N_6P_2Ru)_n$: C, 42.0; H, 2.6; N, 9.8%. Calcd for a 0.8 : 1 complex $(C_{26}H_{18.8}F_{9.6}N_{5.2}P_{1.6}Ru_{0.8}{\cdot}2H_2O)_n$: C, 41.5; H, 3.1; N, 9.7%.

The Ru complex of Oligo-bpym was prepared analogously from Oligo-bpym (79.7 mg, 0.51 mmol unit) and [RuCl$_2$(bpy)$_2$] (266 mg, 0.51 mmol). The Ru complex of Oligo-bpym was obtained as a dark green powder (353 mg). IR 1604, 1557, 1527, 841, 762, 728, 557 cm^{-1}. Anal. Found: C, 37.3; H, 2.5; N, 11.2%. Calcd for a 1 : 1 complex between Ru(bpy)$_2$ and the bpym unit of Oligo-bpy, $(C_{28}H_{20}F_{12}N_8P_2Ru{\cdot}2H_2O)_n$: C, 37.6; H, 2.7; N, 12.5%. Calcd for a 1.3 : 1 complex $(C_{34}H_{24.8}F_{15.6}N_{9.2}P_{2.6}Ru_{1.3}{\cdot}2H_2O)_n$: C, 36.9; H, 2.6; N, 11.6%. In contrast to the high reactivity of Oligo-bpym with [RuCl$_2$(bpy)$_2$], PBpym with the higher molecular weight had very low reactivity toward [RuCl$_2$(bpy)$_2$]. An analogous reaction of PBpym with [RuCl$_2$(bpy)$_2$] gave only a solid product, whose IR spectrum agreed with that of PBpym and showed no obvious sign of the complex formation of PBpym with Ru.

Os Complexes. The Os complex of Oligo-bpy was prepared analogously from Oligo-bpy (40.0 mg, 0.26 mmol unit) and [OsCl$_2$(bpy)$_2$] (156 mg, 0.26 mmol) by the reaction in 5.5 cm^3 of ethylene glycol in a Schlenk tube (under nitrogen, 4 d under reflux). A dark brown powder of the Os complex of Oligo-bpy (210 mg) was obtained. IR 1458, 1423, 840, 760, 725, 557 cm^{-1}. Anal. Found: C, 36.7; H, 2.6; N, 8.7%. Calcd for a 1 : 1 complex between Os(bpy)$_2$ and the bpy unit of Oligo-bpy $(C_{30}H_{22}F_{12}N_6OsP_2{\cdot}2H_2O)_n$: C, 36.7; H, 2.7; N, 8.6%.

The Os complex of Oligo-bpym was prepared similarly using Oligo-bpym (40.7 mg, 0.26 mmol unit) and [OsCl$_2$(bpy)$_2$] (154 mg, 0.26 mmol). A black powder of the Os complex of Oligo-bpym (164 mg) was obtained. IR 1602, 1557, 1520, 1254, 1060, 842, 760, 724, 658, 556 cm^{-1}. Anal. Found: C, 35.4; H, 2.7; N, 10.0%. Calcd for a 1 : 1 complex between Os(bpy)$_2$ and the bpym unit of PBpym $(C_{28}H_{20}F_{12}N_8OsP_2)_n$: C, 35.5; H, 2.1; N, 11.8%. Calcd for a 1.1 : 1 complex $(C_{30}H_{21.6}F_{13.2}N_{8.4}Os_{1.1}P_{2.2}{\cdot}3H_2O)_n$: C, 33.3; H, 2.6; N, 10.9%.

Photocurrent of the Ru Complex of Oligo-bpy. Photocurrent was measured with paired micro Pt-electrodes purchased from B.A.S. Co. Ltd. An acetonitrile solution of the Ru complex of Oligo-bpy was cast on the Pt-electrodes, and dried in vacuo (about 4 μm in thickness). The paired electrodes were set in a Schlenk type tube and connected to an amperometer. After filling the tube with pure argon, the polymer film was irradiated with a Xe lamp (about 170000 lx), and the photocurrent was measured.

Photoreduction of Aqueous Media with the Ru Complex of Oligo-bpy. A typical experiment was carried out as follows. NEt_3 (0.5 cm^3), and 1.0 mL of an Pt colloidal solution[21)] of aqueous methanol (8.8×10^{-4} M, $CH_3OH : H_2O = 1 : 1$) were charged in a Schlenk type Pyrex tube (25 cm^3) fitted with a rubber septum. After addition of 10 mg of the Ru complex of Oligo-bpy, the tube was degassed and then filled with pure argon. The photocatalytic reaction was carried out under magnetic stirring at room temperature. The amount of evolved H_2 was determined by GC. Other experiments were carried out analogously. For the reaction using $[Pt(bpy)_2]^{2+}$ as a cocatalyst, a mixture of NEt_3 (0.5 cm^3), methanol (0.5 cm^3), and an aqueous solution of $[Pt(bpy)_2]^{2+}$ (7.3×10^{-4} M, 0.5 cm^3) were used.

X-Ray Diffraction Analysis of 4. Crystal data: $C_8H_4N_4Cl_2$, $M_r = 227.05$, tetragonal, $P4_12_1$ (No. 92), $a = 7.055(1)$, $c = 18.922(4)$ Å, $V = 931.9(3)$ Å^3, $Z = 4$, $\mu = 6.5$ cm^{-1}, $F(000) = 456$, $D_{calcd} = 1.601$ Mg m^{-3}, 2θ range = 5.0—54.8°, hkl ranges: $0 \leq h \leq 9$; $0 \leq k \leq 6$; $0 \leq l \leq 24$, no. of unique reflections = 713, no. of used reflections ($I > 3\sigma(I)$) = 531, no. of variables = 64. The final $R(F_o)$ and $R_w(F_o)$ values were 0.045 and 0.040, respectively; $R = \sum||F_o|| - |F_c|/\sum|F_o|$; $R_w = \sum w|F_o - F_c|^2/\sum w|F_o|^2]^{1/2}$; weighting scheme $w = [\{\sigma(F_o)\}^2]^{-1}$. The unit cell parameters were obtained by least-squares refinement of 2θ value of 25 reflections with $25° \leq 2\theta \leq 35°$.

Intensities were collected on a Rigaku AFC-5R automated four-cycle diffractometer by using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) and the ω–2θ method. Empirical absorption correction (ψ-scan method) of the collected data was applied. Calculations were carried out by using the program package teXsan on a VAX-II computer. Atomic scattering factors were taken from the literature.[23)] A full-matrix least squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming ideal positions and were included in the structure calculation without further refinement of the parameters.

We are grateful to Professors Y. Inoue and K. Domen, Dr. N. Asakawa, Dr. T. Maruyama, and Ms. S. Ai for helpful discussion and experimental support. Thanks are due to Prof. K. Kubota of Gunma University for determination of M_w of Oligo-bpym and PBpym. We wish to thank Dr. T. Koizumi of our laboratory for determination of the molecular structure of **4**.

References

1) a) "Handbook of Organic Conductive Molecules and Polymers," ed by H. S. Nalwa, John Wiley, Chichester (1997), Vol. 2; b) "Handbook of Conducting Polymers," 2nd ed, ed by T. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, Dekker, New York (1997); c) "Science and Application of Conductive Polymers," ed by W. R. Salaneck, D. T. Clark, and E. J. Samuelsen, Adam Hilger, Bristol (1991); d) T. Yamamoto, *Progr. Polym. Sci.*, **17**, 1153 (1992).

2) a) T. Yamamoto, T. Ito, and K. Kubota, *Chem. Lett.*, **1988**, 153; b) T. Yamamoto, T. Ito, K. Sanechika, K. Kubota, and H. Hishimura, *Chem. Ind. (London)*, **1988**, 337; c) T. Yamamoto, Z. -H. Zhou, T. Kanbara, and T. Maruyama, *Chem. Lett.*, **1991**, 223; d) T. Yamamoto, T. Maruyama, Z. -H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, and K. Kubota, *J. Am. Chem. Soc.*, **116**, 4832 (1994).

3) a) Z. Peng, A. R. Gharavi, and L. Yu, *J. Am. Chem. Soc.*, **119**, 4622 (1997); b) E. C. Constable, F. Heirtzler, M. Neuburger, and M. Zehnder, *J. Am. Chem. Soc.*, **119**, 5606 (1997); c) K. D. Ley, C. E. Whittle, M. D. Barberger, and K. S. Schange, *J. Am. Chem. Soc.*, **119**, 3423 (1997); d) B. Wang and M. R. Wasielewski, *J. Am. Chem. Soc.*, **119**, 12 (1997); e) P. L. Vidal, M. Billon, B. Divisia-Blohorn, G. Bidan, J. M. Kern, and J. P. Sauvage, *Chem. Commun.*, **1998**, 629; f) M. O. Woff and M. S. Wrighton, *Chem. Mater.*, **6**, 1526 (1994); g) T. Yamamoto, H. Suganuma, T. Murayama, T. Inoue, Y. Muramatsu, M. Arai, D. Komarudin, N. Ooba, S. Tomaru, S. Sasaki, and K. Kubota, *Chem. Mater.*, **9**, 1217 (1997).

4) a) T. Yamamoto, Y. Yoneda, and T. Maruyama, *J. Chem. Soc., Chem. Commun.*, **1992**, 1552; b) T. Yamamoto, Y. Yoneda, and K. Kizu, *Macromol. Rapid Commun.*, **16**, 549 (1995).

5) T. Maruyama and T. Yamamoto, *J. Phys. Chem. B*, **101**, 3806 (1997). The concentration of metal or the metal complex shown in the captions of Figs. 2, 3, and 5 in this paper is correct. However, the amount of metal or the metal complex should be multiplied by 10^{-3} (correction of mmol to μmol).

6) a) T. Maruyama and T. Yamamoto, *Inorg. Chim. Acta*, **238**, 9 (1995); b) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, and H. Fujii, *Science*, **280**, 560 (1998).

7) T. Yamamoto, N. Hayashida, T. Maruyama, and K. Kubota, *Chem. Lett.*, **1998**, 1125.

8) a) S. Oae, T. Kawai, and N. Furukawa, *Phosphorus Sulfur*, **34**, 123 (1987); b) J. Arukwe, G. Keilen, and K. Undheim, *Acta Chem. Scand.*, **B42**, 530 (1988); c) R. Pater, *J. Heterocycl. Chem.*, **8**, 743 (1971).

9) a) The very large M_w may be due to partial aggregation of the polymer in concd H_2SO_4; b) H. Saito and I. Ando, *Ann. Rep. NMR Spectrosc.*, **21**, 299 (1989); c) E. O. Stejskal, J. Schaefer, and J. S. Waugh, *Magn. Res.*, **28**, 105 (1977); d) J. Herzfield and A. Berger, *J. Chem. Phy.*, **73**, 6021 (1980).

10) T. Kanbara, T. Kushida, N. Saito, I. Kuwajima, K. Kubota, and T. Yamamoto, *Chem. Lett.*, **1992**, 583.

11) a) N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, *J. Am. Chem. Soc.*, **95**, 6582 (1973); b) S. D. Ernst and W. Kaim, *Inorg. Chem.*, **28**, 1520 (1989); c) D. P. Rillema, G. Allen, T. J. Meyer, and D. Conrad, *Inorg. Chem.*, **22**, 1617 (1983).

12) H. Sun, M. Z. Hoffman, and Q. G. Mulazzani, *Res. Chem. Intermed.*, **20**, 735 (1994).

13) K. A. Goldsby and T. J. Meyer, *Inorg. Chem.*, **23**, 3002 (1984).

14) a) S. Yanagida, A. Kabumoto, K. Mizumoto, C. Pac, and K. Yoshino, *J. Chem. Soc., Chem. Commun.*, **1985**, 474; b) T. Shibata, A. Kabumoto, T. Shiragami, O. Ishitani, C. Pac, and S. Yanagida, *J. Phys. Chem.*, **94**, 2068 (1990); c) S. Matsuoka, T. Kohzuki, Y. Kuwana, A. Nakamura, C. Pac, and S. Yanagida, *J. Chem. Soc., Chem. Commun.*, **1991**, 580; d) S. Matsuoka, T. Kohzuki, Y. Kuwana, A. Nakamura, and S. Yanagida, *J. Chem. Soc., Parkin Trans. 2*, **1992**, 679; e) K. Maruo, Y. Wada, and S. Yanagida, *Bull. Chem. Soc. Jpn.*, **65**, 3439 (1992); f) K. Maruo, K. Yamada, Y. Wada, and S. Yanagida, *Bull. Chem. Soc. Jpn.*, **66**, 1053 (1993); g) K. Maruo, N. Yasuda, Y. Wada, and S. Yanagida, *Chem. Lett.*, **1992**, 1951.

15) a) M. Kaneko, H. Araki, and A. Yamada, *Sci. Papers Inst.*

Chem. Res., **73**, 67 (1979); b) M. Suzuki, S. Kobayashi, M. Kimura, K. Hanabusa, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1997**, 227.

16) E. M. Kober, J. V. Caspar, B. P. Sullivan, and T. J. Meyer, *Inorg. Chem.*, **27**, 4587 (1988).

17) J. A. Broomhead and C. G. Young, *Inorg. Synth.*, **21**, 127 (1982).

18) a) F. H. Burstall, F. P. Dwyer, and E. C. Gyarfas, *J. Chem. Soc.*, **1950**, 953; b) I. Fujita and H. Kobayashi, *Z. Phys. Chem. N. F.*, **79**, 309 (1972).

19) B. Bogdanovic, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966).

20) R. Palmans and A. J. Frank, *J. Phys. Chem.*, **95**, 9438 (1991).

21) a) N. Toshima, M. Kuriyama, Y. Yamada, and H. Hirai, *Chem. Lett.*, **1981**, 793; b) N. Toshima and T. Yonezawa, *Makromol. Chem., Makromol. Symp.*, **59**, 281 (1992).

22) D. G. Crosby and R. V. Berthold, *J. Org. Chem.*, **25**, 1916 (1960).

23) "International Tables for X-Ray Crystallography," Kynoch, Birmingham, U.K. (1974), Vol. IV.