Effective Photocatalytic System Based on Chelating π-Conjugated Poly(2,2′-bipyridine-5,5′-diyl) and Platinum for Photoevolution of H$_2$ from Aqueous Media and Spectroscopic Analysis of the Catalyst

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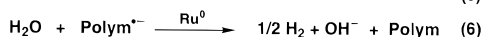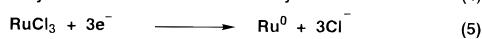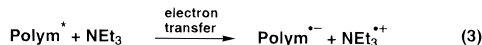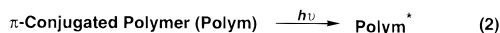*Received: December 4, 1996; In Final Form: March 4, 1997*[⊗]

Effective photocatalytic systems are constructed by using a semiconducting and chelating π-conjugated poly-(2,2′-bipyridine-5,5′-diyl) (PBpy) and Pt compounds. A photoreaction catalyzed by a mixture of PBpy and [Pt(bpy)$_2$](NO$_3$)$_2$ evolves H$_2$ corresponding to a large turnover number (H$_2$/[Pt(bpy)$_2$]$^{2+}$) of 490 in an aqueous solution of NEt$_3$. Colorimetry and X-ray fluorometry (EDX) analysis reveal that added [Pt(bpy)$_2$]$^{2+}$ releases one bpy ligand, and coordinatively unsaturated [Pt(bpy)]$^{2+}$ thus formed is fixed on the surface of particles of PBpy. PBpy bearing the Pt(bpy) complex maintains its catalytic activity in repeated photocatalytic reactions. The PBpy catalyst is also active for photoevolution of H$_2$ from an aqueous solution containing disodium ethylenediaminetetraacetate as the sacrificial reagent. X-ray photoelectron spectroscopy analysis indicates that Pt fixed on PBpy is in an electronic state similar to that of Pt fixed by TiO$_2$.

Introduction

Photoevolution of H$_2$ from water is catalyzed by various inorganic semiconductors such as TiO$_2$ and SrTiO$_3$.[1] Recently, it has been reported[2] that π-conjugated semiconducting polymers[3] such as poly(*p*-phenylene) (PPP) and poly(pyridine-2,5-diyl) (PPy), in combination with RuCl$_3$, also catalyze the photoinduced evolution of H$_2$ from a methanolic aqueous solution containing triethylamine as a sacrificial reagent.


PPP   PPy

$$H_2O + NEt_3 \xrightarrow{\text{semiconducting polymer / Ru}} H_2 \quad (1)$$
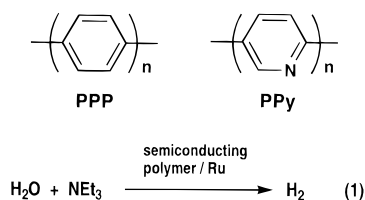
For the catalytic reaction, a mechanism constituted of the following elementary reactions 2−6 has been proposed,[2,4] although the fate[5] of NEt$_3$$^{•+}$ formed by reaction 3 may have some ambiguity. In the mechanism, the colloidal Ru (Ru^0 in eq 5) formed is considered to be absorbed on the surface of the particle of the polymer catalyst and work as "an electron mediator"[2] to transfer the electron from the polymer anion radical (Polym$^{•-}$) to protons (eq 6).

$$\pi\text{-Conjugated Polymer (Polym)} \xrightarrow{h\upsilon} \text{Polym}^* \quad (2)$$

$$\text{Polym}^* + NEt_3 \xrightarrow{\text{electron transfer}} \text{Polym}^{•-} + NEt_3^{•+} \quad (3)$$

$$\text{Polym}^{•-} \longrightarrow \text{Polym} + e^- \quad (4)$$

$$RuCl_3 + 3e^- \longrightarrow Ru^0 + 3Cl^- \quad (5)$$

$$H_2O + \text{Polym}^{•-} \xrightarrow{Ru^0} 1/2\ H_2 + OH^- + \text{Polym} \quad (6)$$

Of the two semiconducting polymers shown above, PPy, with higher electron-accepting ability, shows a higher catalytic activity,[2c,d] presumably due to ease in forming the Polym$^{•-}$ anion radical,[6b] although participation of Polym* in a triplet state in

eq 3 and importance of the stability and reactivity of the triplet state to determine the catalytic activity have recently been suggested.[7]

Recently, poly(2,2′-bipyridine-5,5′-diyl)(PBpy), which is regarded as regiocontrolled PPy and has a much stronger affinity toward metals due to its chelating structure, has been reported.[3,6] Use of this new polymer for the photoevolution of H$_2$ is considered to be intriguing; however, only a limited results have been reported for the photoevolution of H$_2$ by using PBpy in the presence of RuCl$_3$.[6]

PBpy
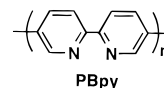
Recently it has been also reported that, among the metal cocatalysts, colloidal platinum and platinum compounds have the highest activity in the photoevolution of H$_2$ catalyzed by the inorganic semiconductors, and this is associated with a lowest overpotential of Pt.[8] For example, TiO$_2$ with dispersed Pt particles exhibits a higher activity than TiO$_2$ itself and TiO$_2$ used with other metals.

On these bases, we have examined photocatalytic activities of catalyst systems consisting of the chelating PBpy and various Pt compounds and here report the results.

The strong ability of PBpy to capture Pt makes detailed analysis of the role of Pt cocatalyst and revealing of the electronic state of Pt absorbed on PBpy possible, and results of these studies will be also reported.

Experimental Section

Apparatus. UV−visible absorption spectra were measured with a Jasco Ubest-35 spectrophotometer. Steady-state photoluminescence spectra were recorded on a Hitachi Model F-4010 spectrofluorometer. The amount of hydrogen was measured with a Shimadzu 3BT gas chromatograph equipped with a thermal conductivity detector and a 5A molecular sieve column (3 m × ϕ 3 mm). Argon was used as a carrier gas. Hydrogen photoproduction was performed with a 500-W Xe lamp (USHIO, UXL500). Light with wavelengths shorter than 320

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Poly(2,2′-bipyridine-5,5′-diyl) and Platinum as Catalyst

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nm was omitted with a cutoff filter. Samples were placed at a constant distance (30 cm) from the lamp, and intensity of light at the sample place was 140 000 lx. EDX analysis was performed with a Philips EDAX PV9900IL. X-ray photoelectron spectra were obtained with a Perkin-Elmer Physical Electronics Model 5600 XPS spectrometer using the Mg Kα radiation as the excitation source.

Materials. π-Conjugated polymers PPP, PPy, and PBpy were synthesized by dehalogenation polycondensation of the corresponding dihaloaromatic compounds with a zero valent nickel complex.[3,6,9] $K_2[PtCl_4]$, $H_2[PtCl_6] \cdot 6H_2O$, and $RuCl_3 \cdot nH_2O$ were used as purchased from Aldrich Chemical Co. Pt colloids were prepared from $H_2[PtCl_6] \cdot 6H_2O$ according to the literature procedure.[8g,h] $[Pt(bpy)_2](NO_3)_2 \cdot H_2O$ (bpy = 2,2′-bipyridyl) was synthesized from $K_2[PtCl_4]$ *via* intermediate $[Pt(bpy)Cl_2]$ according to the published procedure.[8e,10] Data from elemental analysis agreed with calculated values shown in parentheses: C, 36.76 (36.99); H, 2.54 (2.79); N, 13.05 (12.94). IR (KBr pellet): 1384 cm^{-1} $\nu(NO_2)$. Triethylamine (extrapure grade) was obtained from Tokyo Chemical Industry Co. Ltd. and purified by distillation before use. Na_2EDTA (disodium ethylenediaminetetraacetate) was obtained from Kanto Chemical Co. Inc. Methanol was distilled in a usual manner.

Photoreduction of Water. A typical experiment was carried out as follows. NEt_3 (0.5 mL) and an aqueous solution (0.5 mL) of $[Pt(bpy)_2](NO_3)_2 \cdot H_2O$ (8.2×10^{-4} M) were charged in a Schlenk type Pyrex tube (30 mL) fitted with a rubber septum. After addition of powdery PBpy (10 mg), 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 H_2 was determined by GC. Other experiments were carried out analogously. For the reaction in the presence of MeOH, a mixture of MeOH (0.5 mL), NEt_3 (0.5 mL), and H_2O (0.5 mL) was used, instead of the mixture of NEt_3 and H_2O.

Preparation of PBpy Having Fixed Pt(bpy) by Photochemical Reaction of $[Pt(bpy)_2](NO_3)_2$ with PBpy. NEt_3 (0.5 mL) and an aqueous solution (0.5 mL) of $[Pt(bpy)_2](NO_3)_2 \cdot H_2O$ (8.2×10^{-4} M or 4.1×10^{-4} mmol) were added into a Pyrex tube. After addition of powdery PBpy (10 mg, 6.5×10^{-2} mmol bpy unit) to the solution, the mixture was irradiated with light from a 500-W Xe lamp under stirring (for 4 h under argon atmosphere). After filtration, $FeSO_4$ (1.0×10^{-3} mmol) was added to the filtrate, and the amount of free bpy in the solution was analyzed by colorimetry by monitoring the absorbance at $\lambda_{max} = 520$ nm due to $[Fe(bpy)_3]^{2+}$.[11] The amount of free bpy in the solution thus determined was 4.0×10^{-4} mmol. When PPy (10 mg) was used under similar reaction conditions, liberation of 47 mol % of bpy per 1 mol of $[Pt(bpy)_2](NO_3)_2$ was observed. EDX analysis of the PBpy and PPy particles indicated fixation of Pt on the surface of the particles.

To the contrary, similar reaction without irradiation with light did not cause liberation of bpy from $[Pt(bpy)_2](NO_3)_2$ as described below.

In a Pyrex tube were placed NEt_3 (0.5 mL) and an aqueous solution (0.5 mL) of $[Pt(bpy)_2](NO_3)_2 \cdot H_2O$ (1.0×10^{-3} M). After addition of powdery PBpy (10 mg) to the solution, the mixture was stirred for 1 day at room temperature under argon atmosphere under dark. UV−visible analysis of the filtrate of the reaction mixture indicates that almost all $[Pt(bpy)_2](NO_3)_2$ remained unchanged in the solution.

Photoreduction of Water by PBpy Catalyst Having Fixed Pt(bpy). The PBpy catalyst (10 mg) having fixed Pt(bpy), which was prepared by the above shown photochemical reaction, was added to an aqueous NEt_3 solutions [a mixture of H_2O (0.5
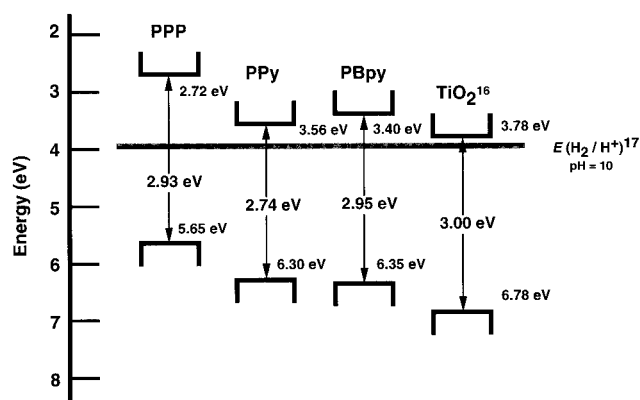
Figure 1. Electronic structures of PPP, PPy, and PBpy, compared with that of TiO_2[16] and the hydrogen evolution potential.[17]

TABLE 1: Spectroscopic and Electrochemical Data of PBpy, PPy, and PPP

	solid state[a]					cyclic voltammogram[b] E^0/V	
polymer	λ_{max}[c]/ nm	λ_{em}[d]/ nm	IP[e]/ eV	Eg[f]/ eV	EA[g]/ eV	E_{red}[h]	E_{ox}[i]
PBpy	363	540	6.35	2.95	3.40	−2.21	
PPy	390	535	6.30	2.74	3.56	−2.21	
PPP	354[j]	483[k]	5.65	2.93[l]	2.72	−2.60[m]	+1.18[n]

[a] Film casting from a formic acid solution on a quartz plate. [b] From ref 3. E^0 *vs* Ag/Ag$^+$. [c] Absorption maximum wavelength. [d] Emission maximum wavelength. [e] Ionization potential; from ref 12. [f] Estimated from the edge of the absorption spectra. [g] Electron affinity; EA = IP-Eg. [h] n-Doping potential. [i] p-Doping potential. [j] From ref 13. [k] Measured in powder. [l] From ref 14. [m] From ref 15a. [n] From ref 15b.

mL) and NEt_3 (0.5 mL)] or an aqueous solution (0.5 mL) of 0.1 M Na_2EDTA. The photocatalytic reaction was carried out under magnetic stirring at room temperature.

Results and Discussion

Energy Diagram. Figure 1 depicts energy diagrams of PPP, PPy, and PBpy estimated from their spectroscopic[12−14] and electrochemical data.[6b,15] Positions of band edge potentials of the polymers are shown in Figure 1. For a comparison, the energy diagram of TiO_2[16] as well as the energy of an electron required to reduce H$^+$ [17] at a pH value of about 10 (pH of the 1:1 mixture of H_2O and NEt_3) is also exhibited in Figure 1.

Table 1 summarizes basic spectroscopic and electrochemical data of the polymers, from which the energy diagram shown in Figure 1 is obtained. The large ionization potentials (IP) and electron affinities (EA) of PPy and PBpy suggest that they serve as n-type organic semiconductors and easily form the Polym$^{•-}$ anion radical shown in eq 3. Actually these polymers are active for electrochemical n-type doping.[3,6b]

As shown in Figure 1, PBpy and PPy have an edge of the conduction band near that of TiO_2, and excited electrons in the conduction band of PBpy and PPy can reduce H$^+$ to H_2. Excited electrons in PPP also have sufficient energy to reduce H$^+$. However, PPP has only low activity for the H_2 evolution,[2b−d] presumably due to the high energy required to put the electron into its conduction band, its hydrophobic properties,[18] and/or its weak ability to fix transition metal. The electron in the conduction band of PBpy and PPy has only a small excess energy to reduce H$^+$, and in such a case, metal cocatalyst is considered to play an important role for efficient H_2 evolution. The metal cocatalyst will decrease overpotential for H_2 evolution and make effective charge separation possible.

Catalytic Activity. *1. Effect of Medium and Metal Cocatalyst. 1.1. Mixture of H_2O, NEt_3, and MeOH.* Figure 2 shows
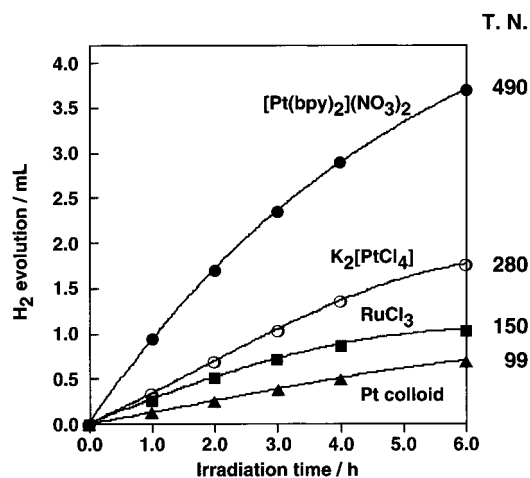
Figure 2. Photoreductive H_2 evolution catalyzed by PBpy in an aqueous NEt_3/MeOH solution ($H_2O = 0.5$ mL; $NEt_3 = 0.5$ mL; MeOH = 0.5 mL) in the presence of $[Pt(bpy)_2](NO_3)_2$ (2.3×10^{-4} M, 0.35 mmol), $K_2[PtCl_4]$ (1.9×10^{-4} M, 0.29 mmol), $RuCl_3$ (1.9×10^{-4} M, 0.29 mmol), and prepared Pt colloids (0.32 mmol). T. N. = turnover number per Pt atom or Ru atom.
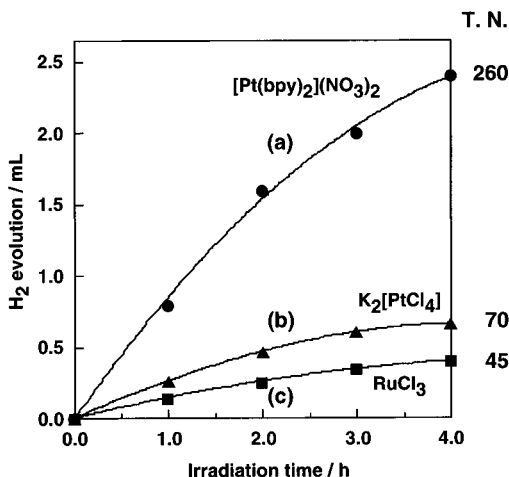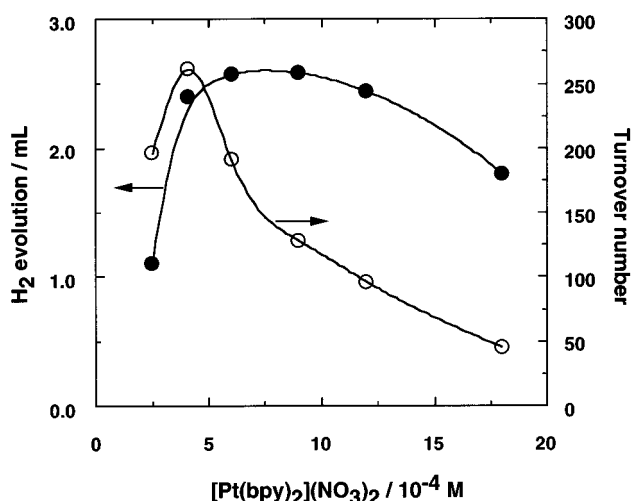

Figure 3. Photoreductive H_2 evolution catalyzed by PBpy in a 1:1 mixture of H_2O and NEt_3 ($H_2O = 0.5$ mL; $NEt_3 = 0.5$ mL) in the presence of $[Pt(bpy)_2](NO_3)_2$ (4.1×10^{-4} M, 0.41 mmol), $K_2[PtCl_4]$ (4.1×10^{-4} M, 0.41 mmol), and $RuCl_3$ (3.9×10^{-4} M, 0.39 mmol). T. N. = turnover number per Pt atom or Ru atom.

the photocatalytic activity of PBpy for the H_2 evolution in the presence of various transition metal cocatalysts. In these cases, a mixture of H_2O, NEt_3, and methanol is used for the reaction medium. As described in the Experimental Section, light from a Xe lamp and having wavelengths longer than 320 nm is used for the photocatalysis.

As shown in Figure 2, the PBpy$-[Pt(bpy)_2](NO_3)_2$ system exhibits about 3.3 times larger activity than that of the previously reported PBpy$-RuCl_3$ system.[6b] After 6 h, evolution of H_2 corresponding to turnover numbers ($H_2/[Pt(bpy)_2](NO_3)_2$) of 490 is observed. No H_2 evolution was observed in the absence of any of light, NEt_3, and PBpy. $K_2[PtCl_4]$ has about half the activity of $[Pt(bpy)_2](NO_3)_2$.

1.2. Mixture of H_2O and NEt_3. In the absence of MeOH (use of a 1:1 mixture of H_2O and NEt_3), the catalytic activity of the catalysts decreases, as shown in Figure 3. However, the PBpy$-[Pt(bpy)_2](NO_3)_2$ catalyst still serves as the most effective catalyst in this medium (activity ratio against $RuCl_3$ = 5.8).

Although, of the two reaction media described above, the former gives the higher activity, the photocatalytic activity of the catalyst was mostly examined in the latter simpler medium

Figure 4. Effect of $[Pt(bpy)_2](NO_3)_2$ concentration on the H_2 evolution in a 1:1 mixture of H_2O and NEt_3 ($H_2O = 0.5$ mL; $NEt_3 = 0.5$ mL). (Amount of PBpy = 10 mg; irradiation time = 4 h.)
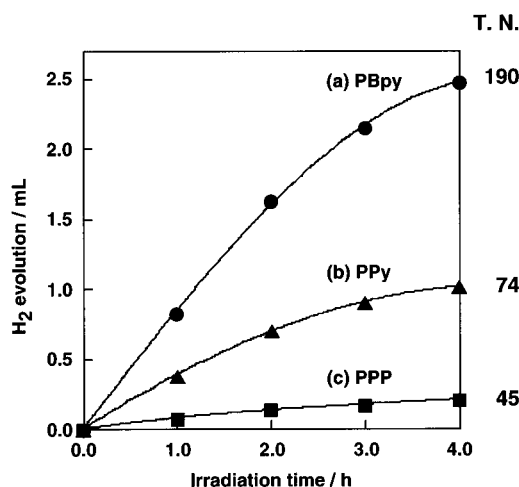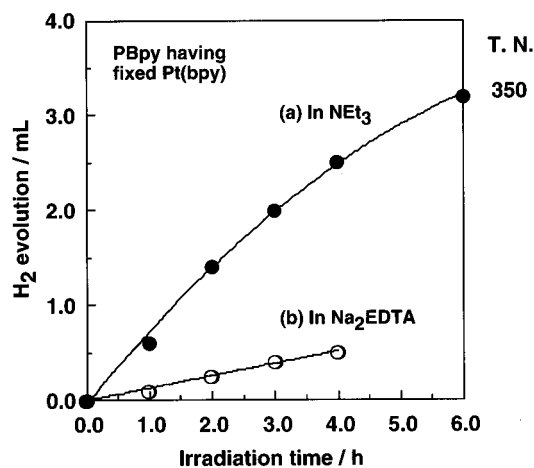

Figure 5. Photoreductive H_2 evolution catalyzed by PPP, PPy, and PBpy (polymer = 10 mg) in a 1:1 mixture of H_2O and NEt_3 ($H_2O = 0.5$ mL; $NEt_3 = 0.5$ mL) in the presence of $[Pt(bpy)_2](NO_3)_2$ (6.0×10^{-4} M, 0.60 mmol). T. N. = turnover number per Pt atom.

to avoid the complexing factor of CH_3OH, and details of the results are described below.

2. Effect of Concentration of $[Pt(bpy)_2](NO_3)_2$ and Comparison with Other Polymers. Figure 4 shows the dependence of the H_2 photoproduction on the concentration of $[Pt(bpy)_2]$-$(NO_3)_2$. At $[Pt(bpy)_2](NO_3)_2 = 4.1 \times 10^{-4}$ M, the turnover number reaches the maximum. Addition of excess $[Pt(bpy)_2]$-$(NO_3)_2$ rather decreases the catalytic activity, and this may be attributed to covering the surface of the PBpy particle by photodeposited Pt species, which will prevent the light from reaching to the PBpy particles.
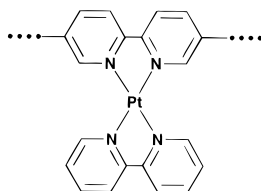
Figure 5 compares the photocatalytic activity of PBpy with those of PPy and PPP in the 1:1 mixture of H_2O and NEt_3 containing $[Pt(bpy)_2](NO_3)_2$. As shown in Figure 5, PBpy with the chelating structure has double the catalytic activity of PPy with regioirregular structure.

3. Fixation of $[Pt(bpy)_2](NO_3)_2$ on PBpy. In order to clarify the reason for the high activity of the PBpy$-[Pt(bpy)_2](NO_3)_2$ system, reactions between PBpy and $[Pt(bpy)_2](NO_3)_2$ have been investigated. An aqueous NEt_3 solution containing powdery PBpy and $[Pt(bpy)_2](NO_3)_2$ not irradiated by light is stable after 1 day and the UV$-$visible spectrum of the solution is identical to that of $[Pt(bpy)_2](NO_3)_2$.

Figure 6. Photoreductive H_2 evolution catalyzed by PBpy having fixed Pt(bpy) (10 mg) in (a) a 1:1 mixture of H_2O and NEt_3 ($H_2O = 0.5$ mL; $NEt_3 = 0.5$ mL) and (b) aqueous 0.1 M Na_2EDTA solution (0.5 mL). In the absence of added $[Pt(bpy)_2](NO_3)_2$ in the solution.

CHART 1

Figure 7. (a) Pt 4f XPS spectrum of PBpy having fixed Pt(bpy). (b) Positions of Pt 4f (Pt $4f_{5/2}$ and Pt $4f_{7/2}$) signals of $TiO_2-Pt(bpy)$ catalyst (i),[8e] TiO_2-Pt catalyst (ii),[19] and the related Pt complexes (iii and iv).[8e]

However, irradiation of the reaction system with light causes a great change in the UV−visible spectrum, and a strong absorption peak of free bpy (281 nm) appears. Colorimetry (cf. Experimental Section) indicates liberation of 1 mol of bpy from 1 mol of $[Pt(bpy)_2](NO_3)_2$. When PPy was used instead of PBpy, about half of the bpy is liberated after irradiation with light. To the contrary, no liberation of bpy is observed after irradiation of the 1:1 mixture of H_2O and NEt_3 containing the mixture of PPP and $[Pt(bpy)_2](NO_3)_2$.
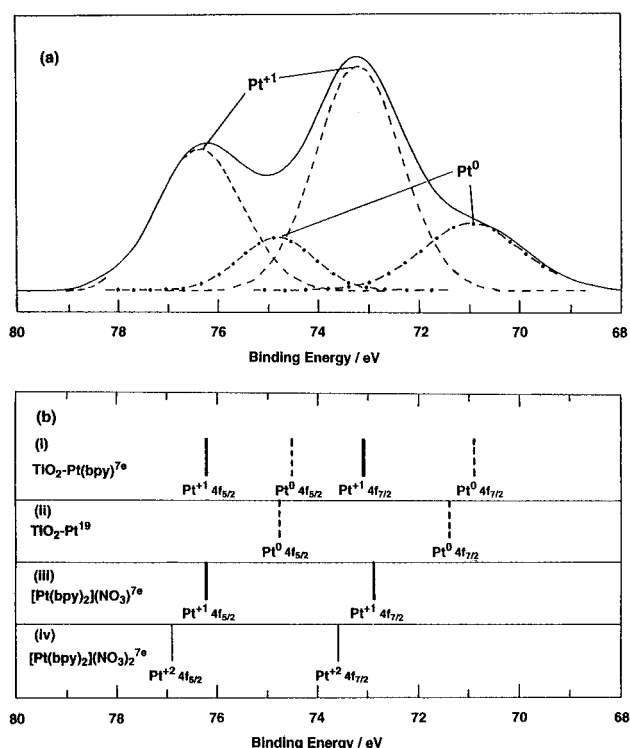
These results are apparently related to the coordinating ability of the π-conjugated polymers. Namely, photoactivated [Pt-$(bpy)_2](NO_3)_2$ will first release bpy, and $[Pt(bpy)]^{2+}$ thus formed seems to be trapped by PBpy particles through the coordination with the bpy-like unit on the surface (Chart 1). The coordination of Pt(bpy) on the surface of the PBpy catalyst is accompanied by a color change of the PBpy powder from yellow to brownish yellow.

On the other hand, PPy has a lower coordination ability toward metal ions,[6b] and only about half of the $[Pt(bpy)]^{2+}$ seems to be trapped by PPy. PPP has no nitrogen for the coordination and in this case $[Pt(bpy)_2]^{2+}$ is considered to be regenerated by a reaction of the photochemically produced $[Pt(bpy)]^{2+}$ and bpy.

EDX analysis of the catalysts separated from the reaction system after the photoreaction between PBpy and $[Pt(bpy)_2]$-$(NO_3)_2$ indicates that Pt exists all over the surface of the particles of PBpy and PPy. On the other hand, no clear signal of Pt was observed at the surface of the PPP particle.

Once Pt(bpy) is trapped on the surface of the PBpy particle, the PBpy catalyst having fixed Pt(bpy) shows the photocatalytic activity, even in the absence of $[Pt(bpy)_2](NO_3)_2$ in solutions. As shown by curve a in Figure 6, its catalytic activity observed without $[Pt(bpy)_2](NO_3)_2$ in the solution is comparable to that in the presence of $[Pt(bpy)_2](NO_3)_2$ in the solution (curve a in Figure 3).

4. Characterization by XPS. XPS spectrum of PBpy having fixed Pt(bpy) shows a peak of Pt 4f in addition to those of C 1s and N 1s. A relative peak area of Pt 4f against that of N 1s indicates that PBpy contains 2 mol % of fixed Pt per bpy unit of PBpy on the surface. This Pt content roughly agrees with a fed amount of $[Pt(bpy)_2](NO_3)_2$ per bpy unit of PBpy. The N 1s region gives a strong peak at 398.4 eV and a weak peak at 400.2 eV, which are assigned to the uncoordinated nitrogen in the bpy unit of PBpy and the nitrogen coordinated with Pt-(bpy), respectively. The latter peak is compared with that of bpy in $[Pt(bpy)_2](NO_3)_2$ at 399.7 eV.

Figure 7a shows Pt 4f (Pt $4f_{5/2}$ and Pt $4f_{7/2}$) XPS spectrum of PBpy bearing fixed Pt(bpy). For comparison, reported positions of the XPS signals of the $TiO_2-Pt(bpy)$[8e] and TiO_2-Pt[19] catalysts and two Pt complexes[8e] are shown in Figure 7b. It has been reported that the $TiO_2-Pt(bpy)$ system gives two sets of doublets with higher binding energy (76.2 and 73.1 eV shown by bars in Figure 7b-i) and low binding energy (74.5 and 70.9 eV; broken bar in Figure 7b-i), and they are considered to be in virtual charge states of +1 and 0, respectively.[8e] The PBpy−Pt(bpy) catalyst also gives two sets of doublets at almost the same position, indicating that Pt species fixed by PBpy are in an electronic state similar to those of the Pt species trapped by TiO_2 which has high activity toward the H_2 evolution.

5. Use of Na_2EDTA as Sacrificial Reagent. When Na_2EDTA (pH = about 4.5) was used instead of NEt_3 as the sacrificial reagent, the PBpy−$[Pt(bpy)_2](NO_3)_2$ catalyst prepared by simple mixing of PBpy and $[Pt(bpy)_2](NO_3)_2$ evolves only a trace amount of H_2. Since Na_2EDTA gives an acidic medium, the low activity of the PBpy−$[Pt(bpy)_2](NO_3)_2$ catalyst suggests that protonation of the nitrogen of PBpy prevents PBpy from trapping $Pt(bpy)^{2+}$. On the other hand, the PBpy catalyst having fixed Pt(bpy) prepared by the process shown above exhibits catalytic activity for H_2 evolution even in the acidic medium containing Na_2EDTA, although the catalytic activity is lower than that observed in the presence of NEt_3 (curve b in Figure 6), presumably due to lower electron-donating properties of Na_2-EDTA as sacrificial reagent.

Conclusion

The PBpy−Pt(bpy)$_2$ system exhibits the highest activity for the photoevolution of H$_2$ among the catalysts so far reported based on π-conjugated polymers. The high activity is related to the high coordinating ability of PBpy against Pt, and chemical analysis as well as spectroscopic analysis (e.g., EDX and XPS) supports this view. Although the importance of the transition metal cocatalyst in the photoevolution of H$_2$ has been pointed out, such clear identification of Pt trapped on the surface of organic semiconductor has not been reported.

References and Notes

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(5) It is reported in refs 2b and 4 that NEt$_3^{\bullet+}$ is converted to ethanol and diethylamine in the photoreaction.

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(11) The amount of bpy was determined from the standard calibration curve. The calibration curve was obtained by using [Fe(bpy)$_3$]SO$_4$ (λ_{max} = 520 nm, ϵ = 8510 M^{-1} cm^{-1}) solution prepared by addition of various amounts (3.1, 6.3, 9.4, 12.6 × 10^{-4} mmol) of bpy to FeSO$_4$ solution (1.0 × 10^{-3} mmol). On the other hand, the intensity of the absorption band of [Fe(bpy)$_3$]SO$_4$ (λ_{max} = 520 nm, ϵ = 8510 M^{-1} cm^{-1}) increased with an increase in the amount of added FeSO$_4$ reaching a saturated absorbance, from which the amount of bpy was determined.

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(16) The conduction band edge potential (E_{CB}) of TiO$_2$ particle shifts cathodically with pH according to the equation E_{CB}(TiO$_2$) = E_{CB}(−0.13 V at pH = 0) − 0.059 pH (vs NHE), which is given in the following references: (a) Grätzel, M.; Frank, A. J. *J. Phys. Chem.* **1982**, *86*, 2964. (b) Duonghong, D.; Ramsden, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977. On the other hand, the potential (E_0(H$_2$/H$^+$)) of the normal hydrogen electrode (NHE) locates at 4.5 eV relative to the vacuum level [Lohmann, F. *Z. Naturforsch., Teil A* **1967**, *22*, 843. Noyes, R. M. *J. Am. Chem. Soc.* **1962**, *84*, 513]. Therefore, E_{CB}(TiO$_2$) at pH = 10 is estimated to be 3.78 eV.

(17) The hydrogen evolution potential (E(H$_2$/H$^+$)) at pH = 10 is estimated as 3.91 eV from the following equation, E(H$_2$/H$^+$) = E_0(H$_2$/H$^+$) − 0.059 pH, and the E_0(H$_2$/H$^+$) value of 4.5 eV.

(18) The hydrophilicity of PPP, PPy, and PBpy can be evaluated by contact angle θ of the polymer films against water. Cast films of PPy and PBpy give θ values of 64.7 and 65.0°, respectively, whereas the θ value of vacuum-deposited PPP film[6b] is 117.0°. The θ value of PPP is larger than those of polypropylene and polyethylene (θ = 94−95°).

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