

## Efficient Visible-light-driven Photocatalysis. Poly(pyridine-2,5-diyl)-catalysed Hydrogen Photoevolution and Photoreduction of Carbonyl Compounds

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Poly(pyridine-2,5-diyl), an insoluble yellow powder, shows efficient photocatalysis under visible light ( $\lambda > 400$  nm) towards water and some carbonyl compounds in the presence of triethylamine as a sacrificial electron donor, yielding  $H_2$  and corresponding alcohols, respectively.

In recent years, a number of organic polymers with conjugated  $\pi$ -electrons have been synthesized and some novel properties have been successfully developed.<sup>1,2</sup> We previously reported that under visible light, poly(*p*-phenylene) (PPP) works as a heterogeneous photocatalyst, inducing not only *cis-trans* photoisomerizations of some alkenes<sup>3</sup> but also photoreductions of water, ketones and alkenes with triethylamine (TEA) as a sacrificial electron donor.<sup>4</sup> Recently, Yamamoto *et al.* reported that the dehalogenation polycondensation of 2,5-dibromopyridine with zerovalent Ni complexes gave poly(pyridine-2,5-diyl) (PPy) with a molecular weight corresponding to a polymer with 16 to 25 monomer units.<sup>5,6</sup> Since the proposed linear structure is comparable with that of PPP, we attempted to clarify the photocatalytic properties of PPy. We report here that PPy shows more efficient visible light-induced photocatalysis than PPP, leading to the reduction of water to  $H_2$  and the reduction of some carbonyl compounds to alcohols.

Taking into account the possibility of random polycondensation of 2,5-dibromopyridine and slight solubility, PPy prepared according to Yamamoto's method<sup>6</sup> was analysed by field desorption (FD)-mass and solid state  $^{13}C$  NMR spectrometry (CMX-360 MHz, Chemagnetics inc.). FD-mass analysis revealed that the PPy consisted of 5 to 19 monomer

units and was terminated at each end with hydrogen atoms. The solid state  $^{13}C$  NMR spectrum with a normal cross polarization consists of four peaks. The cross polarization experiment, however, demonstrated the presence of three protonated carbons and the dipolar dephasing experiment revealed the presence of only two non-protonated carbons. These facts led to the conclusion that the polymer consists of a linear structure of pyridine rings combined regularly at the 2 and 5 positions and that the photoinduced charge separation should also be comparable with that of PPP.

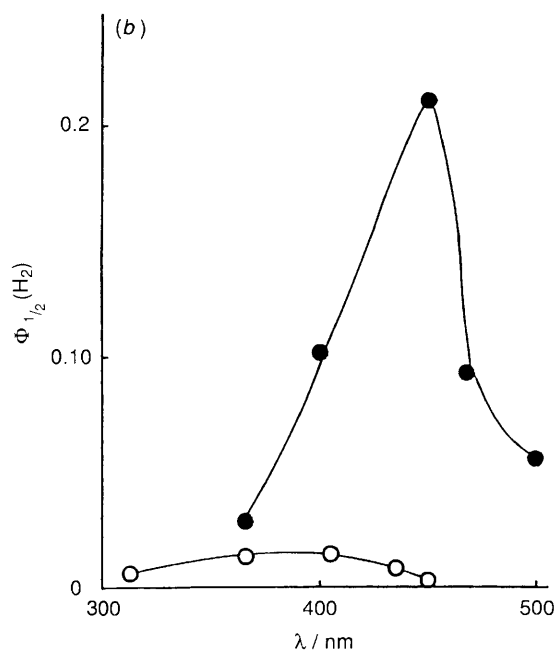
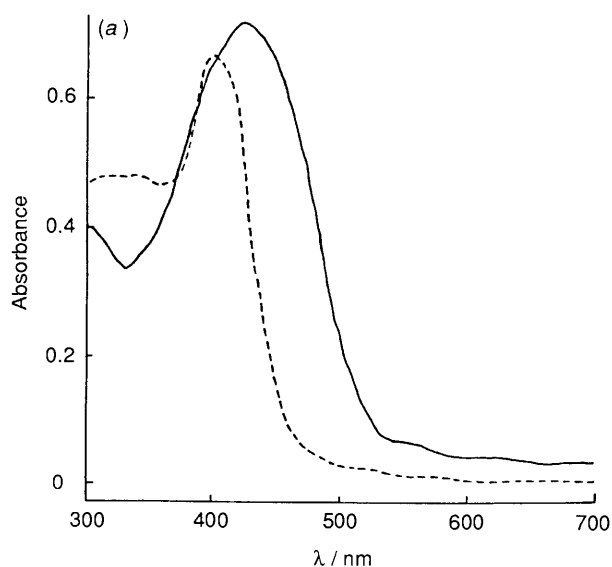
Fig. 1(a) shows the reflectance spectra, measured by a multi-channel photodiode system (MCPD), of the solid states of PPy and PPP. The spectra indicate how the onset and the maximum of the absorption of PPy shift to a longer wavelength than those of PPP, suggesting that PPy could have advantages for visible light energy conversion. Furthermore, based on its absorption and fluorescence spectra, the band gap was estimated to be 2.4 eV, which is smaller than that of PPP, 2.9 eV.<sup>4</sup>

Photoreductions of water and carbonyl compounds were conducted using a 500 W halogen lamp fitted with a sodium nitrite solution filter in the same way as reported for PPP.<sup>4</sup> For the catalytic reduction of water and  $H_2$  evolution, PPy (hydrogen evolved 1.0  $\mu\text{mol}$  over 6 h) was found to be more

**Table 1** PPy-catalysed photoreduction of carbonyl compounds with TEA<sup>a</sup>

R <sup>1</sup> COR <sup>2</sup>		Catalyst	$-E_{1/2}^{\text{red}}/V$	Conversion (%)	Yield <sup>c</sup> (%)	
R <sup>1</sup>	R <sup>2</sup>				Alcohol	Pinacol
Ph	CO <sub>2</sub> Me	PPy	1.16	100	93	0
Ph	CO <sub>2</sub> Me	PPP	1.16	98	74	trace
<i>p</i> -CNC <sub>6</sub> H <sub>4</sub>	Ph	PPy	1.17	100	91	0
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	PPy	1.24	100	95	0
Ph	H	PPy	1.48	35	81	trace
Ph	H	PPP	1.48	87	trace	~100

<sup>a</sup> A 2 ml methanolic solution containing PPy (10 mg), TEA (1 mol dm<sup>-3</sup>) and carbonyl compound (1 mmol dm<sup>-3</sup>) was irradiated at >400 nm for 6 h. <sup>b</sup> Polarographic halfwave reduction potential vs. standard calomel electrode (SCE) in methanol. See: T. Shiragami, C. Pac and S. Yanagida, *J. Phys. Chem.*, 1990, **94**, 505. <sup>c</sup> Based on the substrate converted.



**Fig. 1** (a) Absorption spectra taken by reflectance spectrometry using a Photal: —, PPy; ---, PPP. (b) Action spectra for photoevolution H<sub>2</sub> in the presence of RuCl<sub>3</sub>: ●, catalysed by PPy; ○, catalysed by PPP.

efficient than PPP (H<sub>2</sub>: 0.5 μmol/6 h) and the presence of RuCl<sub>3</sub> considerably enhances the H<sub>2</sub> evolution (H<sub>2</sub>: 14 μmol/6 h). This enhancement is due to photoreductive formation of colloidal Ru<sup>0</sup> as was observed for PPP, probably owing to the strong interaction between PPy and Ru ions. The photolysis in a D<sub>2</sub>O-TEA-CD<sub>3</sub>OD-RuCl<sub>3</sub> system gave a mixture of D<sub>2</sub>, HD and H<sub>2</sub> in a 73:23:4 ratio determined by mass spectroscopy, indicating that the major source of H<sub>2</sub> should be water. Figure 1(b) shows an action spectrum of the PPy-catalysed H<sub>2</sub> evolution in the presence of RuCl<sub>3</sub> based on the apparent quantum yields determined at an appropriate wavelength. Surprisingly, the quantum yields were almost ten times as high as those of PPP. It is interesting to note that the action spectrum is almost identical with the absorption spectrum [Figure 1(a)] and that the maximum quantum yield (0.21) was obtained approximately around the band-gap excitation (450 nm) by assuming that two photons produce one molecule of H<sub>2</sub>.

The photoreductions of carbonyl compounds are summarized in Table 1. It has now been found that the carbonyl compounds examined were all photoreduced to the corresponding alcohols in good yields. As was observed in the PPP-catalysed photoreductions, the presence of RuCl<sub>3</sub> was not favourable for the photoreduction of carbonyl compounds. It is worth noting that benzaldehyde was exclusively reduced to benzyl alcohol without the production of pinacol, while its PPP-catalysed photoreduction gave the pinacol.<sup>4</sup>

In conclusion, this is the first communication on the photoredox reactions by means of polypyridine not as a ligand of metal-complexes but as a photocatalyst.

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## References

- C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Kouis, S. C. Gau and A. G. MacDiarmid, *Phys. Rev. Lett.*, 1977, **39**, 1098.
- P. J. Nigrey, D. MacInnes, Jr., D. P. Nairns, A. G. MacDiarmid and A. J. Heeger, *J. Electrochem. Soc.*, 1981, **128**, 1651; L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, J. M. Sowa, D. M. Ivory, G. G. Miller and R. H. Baughman, *J. Chem. Soc., Chem. Commun.*, 1982, 361; S. Dong, Z. Sun and Z. Lu, *J. Chem. Soc., Chem. Commun.*, 1988, 993.
- S. Yanagida, M. Hanazawa, A. Kabumoto and C. Pac, *Synthetic Metals*, 1987, **18**, 785.
- S. Yanagida, A. Kabumoto, K. Mizumoto, C. Pac and K. Yoshino, *J. Chem. Soc., Chem. Commun.*, 1985, 474; T. Shibata, A. Kabumoto, T. Shiragami, O. Ishitani, C. Pac and S. Yanagida, *J. Phys. Chem.*, 1990, **94**, 2068.
- T. Yamamoto, T. Ito and K. Kubota, *Chem. Lett.*, 1988, 153; T. Yamamoto, T. Ito, K. Sanechika and M. Hishinuma, *Chem. Ind. (London)*, 1988, 337.
- T. Yamamoto, T. Maruyama and K. Kubota, *Chem. Lett.*, 1989, 1951; T. Yamamoto, T. Maruyama, T. Ikeda and M. Sisido, *J. Chem. Soc., Chem. Commun.*, 1990, 1306.