

Heterogeneous Photocatalysis of Poly(4-trifluoromethylpyridine-2,6-diyl)

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Poly(4-trifluoromethylpyridine-2,6-diyl) shows heterogeneous photocatalysis under visible light ($\lambda > 400$ nm), leading to efficient reductions not only of water to H_2 but also of some carbonyl compounds to alcohols in the presence of triethylamine as a sacrificial electron donor.

We recently reported that insoluble linear aromatic polymers such as poly(*p*-phenylene) (PPP)¹⁾ and poly(pyridine-2,5-diyl) (PPy)²⁾ show high photocatalytic activity under visible light irradiation in the presence of triethylamine (TEA) as a sacrificial electron donor, leading to efficient photoreductions of water, some aromatic carbonyl compounds, and alkenes to H_2 , alcohols, and alkanes, respectively. Furthermore, it was found that oligo(*p*-phenylenes) such as *p*-terphenyl and *p*-quaterphenyl show homogeneous photocatalysis under UV light irradiation as well. However, poly(*m*-phenylene) and *m*-terphenyl, whose sequential bonding is at meta position, showed little activity under comparable conditions.³⁾ The case was also true for poly(pyridine-2,6-diyl) (2,6-PPy). We have now found that when CF_3 group is introduced at the 4 position of pyridine unit in 2,6-PPy, efficient photocatalytic activity emerges in the resulting poly(4-trifluoromethylpyridine-2,6-diyl) (CF_3 -2,6-PPy).

According to Yamamoto's method,⁴⁾ CF_3 -2,6-PPy and 2,6-PPy were prepared from 2,6-dichloro-4-trifluoromethylpyridine and 2,6-dibromopyridine, respectively. Since these polymers were insoluble in most organic solvent, they were purified by Soxhlet extraction using toluene as extract and then by refluxing with aq. EDTA solution at pH 3 and pH 9 to eliminate soluble organic compounds and metal ions. CF_3 -2,6-PPy and 2,6-PPy are pale yellow and, as shown in their reflectance spectra (Fig. 1), both have absorption in the visible region and the introduction of CF_3 was found to shift the absorption onset to longer wavelength. The solid state ^{13}C NMR analysis indicated that the structure of CF_3 -2,6-PPy consists of 4-trifluoromethylpyridine rings combined regularly at the 2 and 6 positions. The structure of 2,6-PPy was also supported by the solid ^{13}C NMR.

Photocatalytic reductions were conducted using a 300 W halogen lamp with a sodium nitrite solution filter following the same procedure as reported for PPP¹⁾ and PPy.²⁾ CF_3 -2,6-PPy showed photocatalytic activity for reduction of water to H_2 (H_2 evolved 0.4 μ mol/6 h) and the

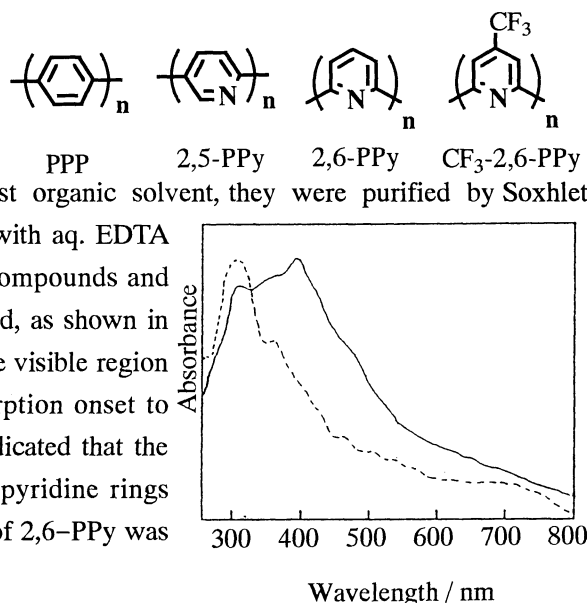


Fig. 1. Absorption spectra taken by reflectance spectrometry: —, CF_3 -2,6-PPy; ---, 2,6-PPy.

presence of RhCl_3 as a source of a cocatalyst, colloidal Rh metal, enhanced the H_2 evolution (H_2 ; 10.9 $\mu\text{mol}/6\text{ h}$, the apparent quantum yield was $\Phi(1/2\text{H}_2)=0.13$ at 405 nm.) as well as the $\text{PPP}/\text{RuCl}_3^{1)}$ and $\text{PPy}/\text{RuCl}_3^{2)}$ systems. On the other hand, 2,6-PPy did not show the activity for the H_2 evolution in the presence of Rh metal colloid. Photoreduction of D_2O with $\text{CF}_3\text{-2,6-PPy}/\text{RhCl}_3$ system gave a mixture of D_2 , DH , and H_2 in a 90 : 7 : 3 ratios. This fact suggests that the major source of H_2 should be water.

Table 1. $\text{CF}_3\text{-2,6-PPy}$ - or 2,6-PPy- Catalyzed Photoreduction of Carbonyl Compounds with TEA under Visible-light Irradiation^{a)}

$\text{R}^1\text{-CO-R}^2$		$-\text{E}_{1/2}^{\text{red b)}}$ /V	Yield ^{c)} / %				
R^1	R^2		Catalyst	Conversion / %	Alcohol	Pinacol	
Ph	CO_2Me	1.13	$\text{CF}_3\text{-2,6-PPy}$	100	100	0	
			2,5-PPy	100	93	0	
			2,6-PPy	29	28	trace	
			PPP	98	74	trace	
4-CNPh	Ph	1.17	$\text{CF}_3\text{-2,6-PPy}$	100	78	0	
			2,5-PPy	100	91	0	
			2,6-PPy	0	0	0	
4-ClPh	4-ClPh	1.24	$\text{CF}_3\text{-2,6-PPy}$	12	86	0	
			2,5-PPy	100	95	0	
			2,6-PPy	0	0	0	
Ph	H	1.48	$\text{CF}_3\text{-2,6-PPy}$	40	96	0	
			2,5-PPy	35	81	trace	
			2,6-PPy	0	0	0	
			PPP	87	trace	100	
4-MeOPh	H	1.56	$\text{CF}_3\text{-2,6-PPy}$	0	0	0	

a) A 2 ml methanolic solution containing the catalyst (10 mg), TEA (1 mol dm^{-3}) and carbonyl compound (1 mmol dm^{-3}) was irradiated at $\lambda > 400\text{ nm}$ for 6 h. b) Polarographic half-wave reduction potential vs. SCE in methanol. See reference 5. c) Based on the substrate converted.

The photocatalytic reduction was extended to some carbonyl compounds with different reduction potential and the results are summarized in Table 1. It has now been found that $\text{CF}_3\text{-2,6-PPy}$ catalyzes photoreduction of the carbonyl compounds whose reduction potentials are more than -1.48 V vs. SCE, leading selectively to the corresponding alcohols. 2,6-PPy was only effective in the photoreduction of methyl benzoylformate. Interestingly, the reducing activity of $\text{CF}_3\text{-2,6-PPy}$ was high enough to reduce benzaldehyde, giving benzyl alcohol while 2,6-PPy was ineffective. When compared with PPP, the selective photoreduction to alcohols is worth noting.

In conclusion, this is the first report of effective photocatalysis induced by a meander aromatic polymer under visible light irradiation.

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