Photo-splitting of Water to Dihydrogen and Hydroxyl Radicals Catalysed by Rhodium-deposited Perfluorinated Poly(*p*-phenylene)

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Perfluorinated poly(*p*-phenylene) with deposited colloidal rhodium metal catalyses photo-splitting of water to dihydrogen and hydroxyl radicals scavenged by benzene to give phenol under UV irradiation.

Photochemical splitting of water to dihydrogen and dioxygen using inorganic semiconductors[1–5] or organometallic compounds[6,7] has been studied as one of the simplest methods for the chemical conversion and storage of photon energy. Most organic molecular systems, however, seem to be inappropriate for water-splitting photocatalysts or photosensitizers, because they are subject to photooxidation themselves. We recently reported that perfluorination of poly(*p*-phenylene) chains induces appropriate redox potentials for water-splitting in its excited states and enhances its stability against the severe oxidation conditions in the photocatalytic oxidation of water.[8–10] This led us successfully to photo-split water to dihydrogen and hydroxyl radicals (scavenged by benzene to give phenol) by using perfluorinated poly(*p*-phenylene) combined with rhodium as an electron mediator for dihydrogen evolution.

Perfluorinated poly(*p*-phenylene) (F-PPP-*n*; *n* denotes the number of phenyl rings in the chain and $n \geqslant 3$) was synthesized by condensation polymerization of pentafluorophenylmagnesium bromide and decafluorobiphenyl.[10] It was found by MS that F-PPP-*n* consisted of oligomers with $n = 3$–10, mainly 5 and 6. Subsequent rhodium deposition on F-PPP-*n* (F-PPP-*n*–Rh) was conducted by the photodeposition method.†

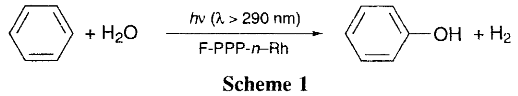
In a Pyrex tube (i.d. = 8 mm), the catalyst (F-PPP-*n*–Rh or F-PPP-*n*; 1 mg) was dispersed in an acetonitrile solution (2 ml) containing water (2 vol%; 0.04 ml) and benzene (20 vol%; 0.4 ml), then the suspension was irradiated with a 500 W high-pressure mercury arc lamp ($\lambda > 290$ nm) while being stirred with a magnetic stirrer at 25 °C. Only when F-PPP-*n*–Rh was used as a photocatalyst under deoxygenated conditions was the simultaneous formation of phenol and dihydrogen recognized (Table 1, Runs 1 and 2). On GLC [column; Shimadzu capillary column HiCap-CBP20 (PEG-20M type), $\phi = 0.2\ \text{mm} \times 25\ \text{m}$] examination of the liquid phase, trace amounts of cyclohexane and cyclohexene were detected, probably due to hydrogenation of benzene.

By assuming the average molecular weight of F-PPP-*n* as that of a hexamer ($n = 6$; $M_w = 926$) and the stoichiometry of the photolysis (Scheme 1), the turnover numbers (TN) for the formation of phenol and dihydrogen after irradiation for 5 h in Run 1 were estimated to be 4 and 2, respectively.‡ These values suggest that photo-splitting of water induced by F-PPP-*n*–Rh is catalytic. In the presence of dioxygen (Runs 5 and 6), a good electron acceptor, however, the present photosystem led to effective photooxidation of benzene to phenol and photoreduction of dioxygen to hydrogen peroxide with nearly equal TN's, while the quantity of dihydrogen was as low as in the control experiments (Runs 4 and 7).

In order to confirm the source of the dihydrogen, and the oxygen atom in phenol, two isotope tracer experiments were conducted and the photoproducts analysed by MS under degassed conditions. When the photolysis was carried out using D_2O, the ratio of the intensity of the mass numbers 2, 3 and 4, which corresponded to H_2, HD, and D_2, was 13 : 29 : 58. When the photolysis was carried out using $H_2{}^{18}O$, the parent ion peak due to $C_6H_5{}^{18}OH$ was observed exclusively, and that of $C_6H_5{}^{16}OH$ could not be detected. These facts clearly show that both the dihydrogen and the oxygen atom in phenol originate from the water molecule.

A positive shift of 300 mV in the oxidation potential due to perfluorination was observed in comparison with *p*-terphenyl and perfluorinated *p*-terphenyl.[8] The oxidation potentials of water[11] and benzene[12] in acetonitrile were reported to be 0.8 V *vs.* NHE and 2.30 V *vs.* SCE, respectively. These facts suggest that water should be more susceptible to oxidation than benzene in acetonitrile, and that phenol should be formed through photooxidation of water to a hydroxyl radical and its electrophilic attack on benzene (photoinduced Fenton's reagents reaction[8,9,13]). In order to detect directly the formation of the intermediary hydroxyl radical, EPR analysis was conducted using the spin trapping technique.[14] Using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a probe for radical species, the reaction suspension containing water, benzene, and F-PPP-*n* (comparable to Run 3) was irradiated for 1 min under degassed conditions.§ The quartet EPR signal which appeared with the intensity ratio of 1 : 2 : 2 : 1, as shown in Fig. 1, was assigned to the adduct of the hydroxyl radical with DMPO, proving that the hydroxyl radical is formed from water in the photocatalysis.

In conclusion, perfluorinated poly(*p*-phenylene) is the first organic compound which shows water-splitting photocatalysis under UV-light irradiation. Rhodium, as an effective mediator



Scheme 1

Table 1 Photolysis of water in the presence of benzene catalysed by perfluorinated poly(*p*-phenylene)[a]

Run	Catalyst	Conditions[c]	Photoproducts/μmol (TN[b]) PhOH[d]	H_2[d]	H_2O_2[e]
1	F-PPP-*n*–Rh	*Vacuo*	4.0 (4)	1.8 (2)	<0.1
2	F-PPP-*n*–Rh	Ar	5.0 (5)	0.5–1.0 (1)	<0.1
3	F-PPP-*n*	Ar	2.7 (3)	<0.05	0.1–0.3
4	None	Ar	0	<0.05	<0.1
5	F-PPP-*n*–Rh	O_2	14.2 (13)	<0.05	12.4 (11)
6[f]	F-PPP-*n*	O_2	17.4 (16)	<0.05	18.7 (17)
7	None	O_2	trace	<0.05	0.4–0.7

[a] After 5 h irradiation. [b] Turnover number. [c] The system was degassed by the freeze–pump–thaw technique, purged with argon gas, or saturated by dioxygen gas before irradiation. [d] Determined by GC. [e] Determined by colorimetry by monitoring the absorbance at $\lambda = 402$ nm due to the absorption of a complex of H_2O_2 with $Ti(SO_4)_2$ in aqueous methanolic solution. [f] Under the same conditions as ref. 9.

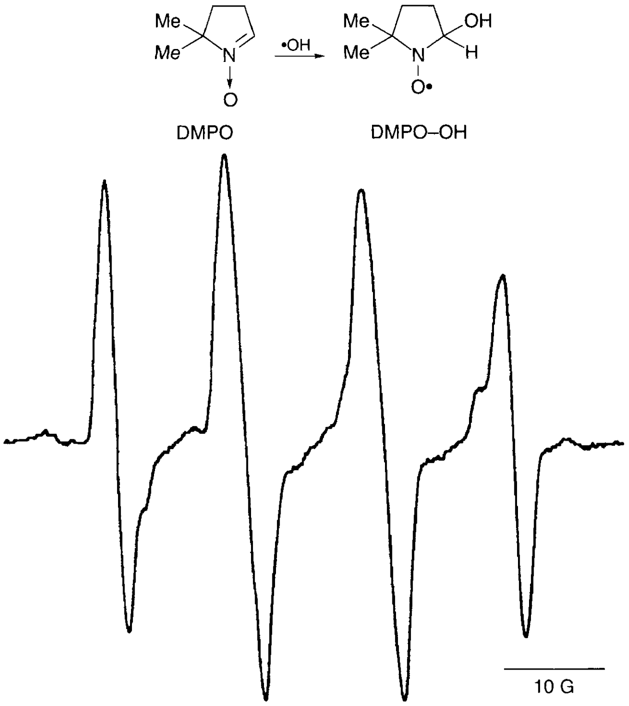


Fig. 1 EPR spectrum observed in the F-PPP-*n*-catalysed photolysis of water in the presence of DMPO: g = 2.006, a^N = 13.2, a^H = 13.2

for irreversible electron transfer from F-PPP-*n*, and benzene, as an efficient scavenger of reactive hydroxyl radicals, also play a decisive role in the present heterogeneous photocatalytic water-splitting reaction.

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Footnotes

† In a Pyrex tube (i.d. = 8 mm), an aqueous methanolic suspension containing triethylamine, $RhCl_3$ and insoluble F-PPP-*n* was irradiated with a 500 W high-pressure mercury arc lamp (λ > 290 nm) for 3 h under stirring with a magnetic stirrer at 25 °C. F-PPP-*n*–Rh was obtained by evaporation of the photolysate to dryness.

‡ The higher TN for the formation of phenol than dihydrogen was ascribed to partial reductive degradation of the photocatalyst. In particular, the lower molecular-weight oligomers readily underwent reductive defluorination as was observed in the F-PPP-*n*-catalysed photoreduction of water with triethylamine as a sacrificial electron donor.[8,10] In other words, the partial reductive defluorination of the photocatalyst may explain the shortage of reductive dihydrogen evolution. Furthermore, formation of cyclohexane and cyclohexene indicated the existence of other reduction channels through the rhodium catalyst. In Run 2, the amount of dihydrogen was less than that in Run 1. This shortage was caused by electron trapping by dioxygen gas which could not be removed completely from the reaction system by purging with argon.

§ The acetonitrile suspension containing water (2 vol%), benzene (20 vol%), F-PPP-*n*, and DMPO (6.7×10^{-2} mol dm^{-3}) was placed in an EPR tube (i.d. = 2.6 mm) and degassed by the freeze–pump–thaw technique. After the system had been irradiated with a 350 W high-pressure mercury arc lamp with a 290 nm interference filter for 1 min, the spectrum was measured at room temp. under the following conditions: magnetic field, 327.5 ± 7.5 mT; field modulation width, 0.25 mT; microwave power, 4 mW.

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