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N-ALKYL-4, 4'-BIPYRIDYL. A NEW EFFICIENT ELECTRON CARRIER IN THE PHOTOCHEMICAL HYDROGEN PRODUCING SYSTEM

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Abstract—Various pyridine derivatives were found to be effective electron carriers in the photochemical hydrogen generating system consisting of ascorbic acid as a reproducible electron donor, zinc *meso*-tetra (4-hydroxysulphophenyl) porphyrin as a photocatalyst, and colloidal platinum. Among them the system using an N-alkyl-4, 4'-bipyridyl, especially the n-hexyl derivative (C_6Py^+Py), was most effective, where the quantum yield for the hydrogen generation was 0.1 and the theoretical recycling number of the photocatalyst reached 100,000. The mechanism of the hydrogen generating reaction is discussed. Based on a number of standard experiments, C_6Py^+Py is shown to be effective only in the specific combination with the present components.

The photochemical production of hydrogen is a primary target in solar energy conversion. A variety of systems have been developed to generate hydrogen under visible light irradiation,[1] but most of the organic electron (hydrogen) donors consumed in these systems are much more valuable than hydrogen evolved and not easily reproduced in any reasonable way. In this sense the processes are less promising from the practical viewpoints. Sutin *et al.* reported the ascorbic acid–$Ru(bpy)_3^{2+}$–Co^{2+} complex system, in which the electron donor was able to readily recycle after appropriate treatments, generating hydrogen with visible light irradiation, although its quantum yield of hydrogen production was relatively low ($\phi_{H_2} = 0.00046$).[2] A recent publication from this laboratory[3] described the efficient hydrogen producing system consisting of ascorbic acid (AsA), Zn meso-tetra (4-hydroxysulphophenyl) porphyrin ($ZnT_{SO_3Na}PP$),[4] methylviologen (MeV^{2+}) and colloidal Pt supported on polyvinylalcohol where the quantum yield ($\phi_{H_2} = 0.005$) was by *ca.* 10 times higher than that of Sutin's system.

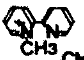
We now wish to report that replacement of MeV^{2+} by various pyridine or monoalkylated pyridine derivatives often caused a remarkable increase in the efficiency of hydrogen generation.

RESULTS AND DISCUSSION

Visible light (≥ 410 nm) irradiation of 5 ml of aqueous solution (pH 4.5) containing AsA (1×10^{-1} M), $ZnT_{SO_3Na}PP$ ($9 \sim 10\times10^{-5}$ M), pyridine or an appropriate N-monoalkylated pyridine derivative ($1 \sim 10\times10^{-3}$ M) and colloidal Pt (1.2×10^{-4} g. equivalent/l) supported on polyvinylalcohol at 0°C leads to H_2 generation which was determined by means of gas chromatography. The results are summarized in Table 1.

All the systems shown in Table 1 produced hydrogen

Table 1. Photochemical H_2 evolution using pyridine or bipyridyl derivative as an electron carrier

run	e-carrier	H_2 evolved(μl)	$ZnT_{SO_3Na}PP$ consumed(%)	H_2 evolved/ $ZnT_{SO_3Na}PP$ consumed
1	 2×10^{-3} M	3100	9 %	6,150
2	 2×10^{-3} M	1850	25 %	1,320
3	 1×10^{-2} M	3650	60 %	1,090
4	 4×10^{-3} M	3000	65 %	820
5	 1×10^{-3} M	7650	10 %	14,800
6	 1×10^{-3} M	7200	2 %	68,000
7 [a]	 1×10^{-3} M	7150	5 %	102,000
8 [b]	 1×10^{-3} M	1600	98 %	310
9	 1×10^{-2} M	2800	76 %	680
10	 2×10^{-3} M	3400	67 %	1,000

AsA 1×10^{-1} M, $ZnT_{SO_3Na}PP$ $9\sim10\times10^{-5}$ M,[a] Pt 1.2×10^{-4} g. equiv/l, 5ml, pH 4.5. irrad. >410 nm, 10h. a) $ZnT_{SO_3Na}PP$ 2.5×10^{-5} M; b) irrad. 3h.

more efficiently than the AsA-$ZnT_{SO_3N_a}PP$-MeV^{2+}-colloidal Pt system but sometimes with a considerable decomposition of the photocatalyst during the irradiation. Among the electron carriers investigated, N-alkyl-4, 4'-bipyridyls[5,6] were most effective and most stable toward irradiation. Interestingly monoalkylated bipyridyl has never been investigated as an electron carrier although viologens (dialkyl-4, 4'-bipyridyls) were very often used. Electrochemical reduction of N-methyl-4, 4'-bipyridyl was reported to form a cation radical which decomposition followed first order kinetics ($k_1 = ca.$ 6.3×10^{-4} sec^{-1} at pH 4.5 10°C).[6b] Based on this kinetic behavior, N-alkyl-4, 4'-bipyridyls are stable enough to relay electrons from the photocatalyst to the redox catalyst and this class of compounds have appropriate oxidation-reduction potentials (e.g., -0.75 volt SCE for the monomethyl derivative).[6]

The present experiments showed at the first time that some of monoalkylated 4, 4'-bipyridyls gave considerably better results in hydrogen production than viologen. Especially, N-n-hexyl-4, 4'-bipyridyl (C_6Py^+Py) was found to be the best carrier when it was used with $ZnT_{SO_3N_a}PP$ and colloidal Pt supported on PVA, where the hydrogen production was very efficient and undesirable decomposition of $ZnT_{SO_3}N_aPP$ during the hydrogen production was minimum as shown in Table 1.

Control experiments in which one of the components was omitted clearly demonstrates that every component used is essential and the efficient emmision quenching of $ZnT_{SO_3N_a}PP$ with C_6Py^+Py but not AsA gives similar conclusion to that for the AsA-$ZnT_{SO_3N_a}PP$-MeV^{2+}-colloidal Pt system; i.e. the first photo-induced charge separation is occuring between $ZnT_{SO_3N_a}PP^*$ and C_6Py^+Py.[3] On the basis of this information, a simple mechanism can be postulated for the photocatalyzed H_2 generation.

The rate of hydrogen production was reduced for the prolonged irradiation (Fig. 1). This reduction seems to be due not only to the decrease of AsA causing deceleration of the charge separation but also to the so-called "back electron transfer" between $RPyPyH^{\dagger}$ and dehydroascorbic acid as ascertained by the following experiments. A remarkable reduction in the initial hydrogen production rate was observed by the initial addition of dehydroascorbic acid into the system and the rate reduction was dependent on the dehydroascorbic acid concentraion (Table 2), giving estimated value of k_f/k_b (ratio of forward and backward electron transfer) 0.43 at 1×10^{-1} M dehydroascorbic acid (average).[7] Other components, i.e. $ZnT_{SO_3N_a}PP$, C_6Py^+Py and colloidal Pt were stable under the H_2 generation conditions, and the H_2 generation activity which was reduced by the accumulation of dehydroascorbic acid during the reaction was easily recovered (although not completely) by the further addition of AsA into the reaction mixture.

The quantum yield of hydrogen production (number of

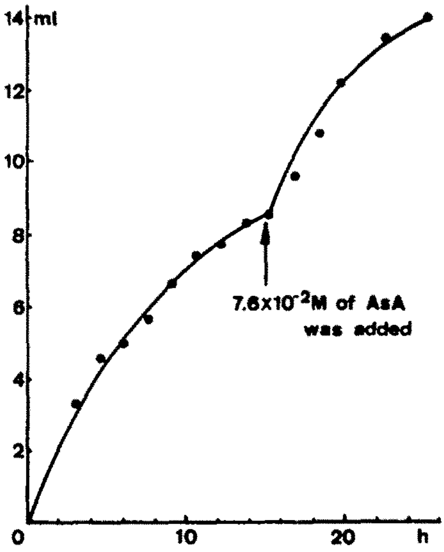
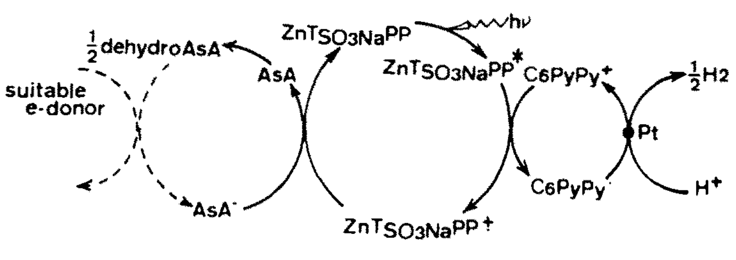


Fig. 1. Hydrogen evolution as a function of time (run 6, Table 1).



Scheme 1.

Table 2. The initial H_2 production rate in the presence of dehydroascorbic acid

dehydro AsA initially added (M)	H_2 generation (µl/h)
0	1100
5×10^{-2}	553
10×10^{-2}	300

AsA = 1×10^{-1} M, $ZnT_{SO_3Na}PP$ = 1×10^{-4} M, C_6Py^+Py = 1×10^{-3} M,
Pt = 6×10^{-7} g.equiv/l. 5 ml

utilized electron for hydrogen production per absorbed photon) is 0.1 at the early stage of the reaction (for at least 3 hr). This value is about 200 times higher than that of Sutin's system and comparable to those of the most effective photochemical hydrogen producing systems[1c, d] using such a nonrecoverable electron donor as EDTA or triethylamine.

The other important parameter describing the efficiency of the artificial photosystem is, as Lehn has pointed out,[1b] the observed recycling number of each catalyst. The practical recycling number of the present photocatalyst (number of electrons utilized for hydrogen production per molecule of catalyst used) under conditions was already extremely high, being *ca.* 5100 on $\mathrm{ZnT_{SO_3Na}PP}$ and 128 on $\mathrm{C_6Py^+Py}$ after only 10 hr irradiation. This recycling number is further increasing almost monotonously with time. Therefore the following theoretical recycling number is also considered. At the above stage after the 10 hr irradiation, *ca.* 5% of $\mathrm{ZnT_{SO_3Na}PP}$ was destroyed and the theoretical recycling number (number of electrons utilized for hydrogen production per number of catalyst molecule destroyed) was more than 100,00 on the consumed $\mathrm{ZnT_{SO_3Na}PP}$. This value further was raised to *ca.* 200,000 when an appropriate amount of AsA (*loc cit*) was added at every 3 h. This value seems to indicate that the present photocatalyst is a very long-lived species, although in most of the reported photochemical hydrogen producing systems only quantum yield and practical recycling number were described without referring to stability of catalyst.[8]

We have performed a number of modifications on the AsA-$\mathrm{ZnT_{SO_3Na}PP}$-$\mathrm{C_6Py^+Py}$-colloidal Pt system, replacing a given component by another one in order to investigate the scope and limitation of the present photosystem. No detectable amount of H_2 ($< 5\ \mu l$) was produced when AsA is replaced by EDTA (5×10^{-2} M pH 5.5) probably because the reduction of $\mathrm{ZnT_{SO_3Na}PP^{\dot{+}}}$ with EDTA is slower than with AsA. Replacement of $\mathrm{ZnT_{SO_3Na}PP}$ by $\mathrm{Ru(bpy)_3^{2+}}$, a well-known and widely used photocatalyst, also caused a remarkable decrease of H_2 generation ($< 5\ \mu l$). This situation was also encountered with $\mathrm{MeV^{2+}}$ as an electron carrier[3] in the system of AsA-$\mathrm{ZnT_{SO_3Na}PP}$-$\mathrm{MeV^{2+}}$-colloidal Pt. From the EDTA (2×10^{-2} M)-Ru $\mathrm{(bpy)_3^{2+}}$ (1×10^{-4} M)-$\mathrm{C_6Py^+Py}$ (1×10^{-2} M)-colloidal Pt system H_2 was generated at the rate of 620 μl/10 h. The latter system is less effective than the EDTA Ru $\mathrm{(bpy)_3^{2+}}$-$\mathrm{MeV^{2+}}$-colloidal Pt system (1100 μl/10 hr). Therefore, interestingly, $\mathrm{C_6Py^+Py}$ is effective only in the specific combination with AsA, $\mathrm{ZnT_{SO_3Na}PP}$, and colloidal Pt.

In summary, two important findings are newly made; (1) N-monoalkyl-4, 4'-bipyridyl such as $\mathrm{C_6Py^+Py}$ is an efficient electron carrier in the photochemical hydrogen producing system; (2) AsA-$\mathrm{ZnT_{SO_3Na}PP}$-$\mathrm{C_6Py^+Py}$-colloidal Pt combination affords the most efficient and stable hydrogen producing system using AsA as a "recoverable" electron donor.[9]

EXPERIMENTAL

Materials. Photocatalyst $\mathrm{H_2T_{SO_3Na}PP}$ was prepared as described by Fleisher *et al.*[10] and was converted to the corresponding zinc complex according to Herrmann's procedure.[3, 11] Anhydrous dehydroascorbic acid was prepared as described by Kenyon *et al.*[12] Colloidal Pt supported on polyvinylalcohol (n = 1500) was prepared according to Rampino's procedure.[13] Monoalkylated pyridine derivatives were prepared by alkylation of the corresponding pyridine derivatives with appropriate alkyl halides. For the syntheses of monoalkylated bipyridyls the equivalent amount of alkyl halides were used and the products were isolated by fractional crystallization. The details of the reactions are as follows (starting materials, solvent, reaction temp, reaction time, solvent for recrystallization, yield, m.p.).

1-Methyl-4, 4'-bipyridyl iodide; 4, 4'-bipyridyl and methyl iodide, $\mathrm{CH_3CN}$, 60°, 5 hr, $\mathrm{CH_3CN}$ and EtOH, 50%, 248 ~ 249°, 1-Hexyl-4, 4'-bipyridyl bromide; 4, 4-bipyridyl and n-hexyl bromide, $\mathrm{CH_3CN}$, reflux, 26 hr, $\mathrm{CH_3CN}$, 62%, 187 ~ 189°, 1-Methyl-2, 2'-bipyridyl iodide; 2, 2'-bipyridyl and methyl iodide, $\mathrm{CH_3CN}$, 60°, 5 hr, $\mathrm{CH_3CN}$ and EtOH, 69%, 144.5 ~ 146° (lit[14] 145 ~ 146°), 1-Methyl-3-phenylaminocarbonylpyridinium iodide; 3-phenylaminocarbonylpyridine and methyl iodide, MeOH, 60°, 6 hr, EtOH, 91%, 179.5 ~ 180.5° (lit[15] 181°).

1-Methyl-4-phenylaminocarbonylpyridinium iodide was prepared from 4-phenylaminocarbonylpyridine and methyl iodide in MeOH, at 60°, for 6 hr. Recrystallization from $\mathrm{CH_3CN}$ and EtOH gave a pure compound in 93% yield melted at 190–191°; IR: 3250, 3030, 1665, 1635, 1600 $\mathrm{cm^{-1}}$; NMR: ($\mathrm{CD_3OD}$) 4.12 (3H, s) 7.0 ~ 7.7 (5H, m) 8.32 (2h, d J = 6) 8.92 (2H, d J = 6) Calc. for $\mathrm{C_{13}H_{13}ON_2I}$: C, 45.90; H, 3.85; O, 4.70; N, 8.23; Found: C, 46.00; H, 3.74; O, 4.50; N, 8.28.

Hydrogen generation. In a typical photochemical hydrogen producing experiment, 5 ml of aqueous solution containing $\mathrm{ZnT_{SO_3Na}PP}$ ($9 \sim 10 \times 10^{-5}$ M), AsA (1.0×10^{-1} M), $\mathrm{C_6Py^+Py}$ (1.0×10^{-3} M) and colloidal Pt (6×10^{-7} g equivalent/l) (pH 4.5) was placed in a 10 ml test tube and air was carefully replaced by N_2 through repeated deaeration followed by N_2 introduction. The test tube was then closed and into the tube 1.00 ml of Ar was introduced as an internal standard with a syringe through a rubber seal. The tube was irradiated, with ice cooling, with a National RF-11OV 500 watt tungsten lamp. A filter to cut off below 430 nm (Toshiba VY-43) was used. After irradiation a small amount of gas present in the tube was sampled out by a 50 μl micro-syringe though a rubber seal and the amount of hydrogen produced was determined by gas chromatography (shimadzu GC-3BT) with a molecular sieve 13X column (Yanagimoto MFG Co. Ltd., 1 m) using N_2 as a carrier gas at room temperature. Control experiments were carried out in a similar manner.

Emission spectra. The emission spectra of $\mathrm{ZnT_{SO_3Na}PP}$ in aqueous solution were recorded with Union FS-301 high sensitivity fluorescence spectrophotometer. $\mathrm{ZnT_{SO_3Na}PP}$ (3.5×10^{-7} M) and an appropriate amount of a possible quencher (either AsA Na or $\mathrm{C_6Py^+Py}$) were dissolved in a phosphate buffer (3.3×10^{-2} M) at pH 4.5. The solution was irradiated at the Soret band of $\mathrm{ZnT_{SO_3Na}PP}$ (420 nm). The solution containing CTAB was prepared by adding 1 ml of 1.0×10^{-2} M CTAB (cmc 9×10^{-4} M) to 2 ml of the solution containing 5.3×10^{-7} M $\mathrm{ZnT_{SO_3Na}PP}$, 5.0×10^{-2} M phosphate, and an appropriate amount of quencher. The emission intensity were monitored from 550 to 750 nm. The intensity of the $\mathrm{ZnT_{SO_3Na}PP}$ emission at 605 nm in the presence of a quencher relative to that in the absence of the quencher (100) were measured. These intensity ratios observed were: in the absence of CTAB, 1×10^{-3} M $\mathrm{C_6Py^+Py}$, 8; 1×10^{-1} M AsA (Na), 93; in the presence of 3.3×10^{-3} M CTAB, 1×10^{-3} M $\mathrm{C_6Py^+Py}$, 99; 1×10^{-1} M $\mathrm{C_6Py^+Py}$, 25; 1×10^{-1} M AsA (Na), 26.

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