

## ARTICLES

Uphill Photooxidation of NADH Analogues by Hexyl Viologen Catalyzed by Zinc Porphyrin-Linked Fullerenes<sup>†</sup>

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Received: April 27, 2001; In Final Form: June 27, 2001

In the absence of oxygen, the photolytically generated  $C_{60}^{\bullet-}$  moiety in  $ZnP^{\bullet+}-C_{60}^{\bullet-}$  and  $ZnP^{\bullet+}-H_2P-C_{60}^{\bullet-}$  radical ion pairs undergoes one-electron oxidation by hexyl viologen ( $HV^{2+}$ ), whereas the  $ZnP^{\bullet+}$  moiety is reduced by NADH analogues (1-benzyl-1,4-dihydronicotinamide and 10-methyl-9,10-dihydroacridine). Thus, both  $ZnP-C_{60}$  and  $ZnP-H_2P-C_{60}$  donor–acceptor ensembles act in benzonitrile as efficient photocatalysts for the uphill oxidation of NADH analogues by  $HV^{2+}$ . In the case of  $ZnP-C_{60}$ , the quantum yield of the photocatalytic reaction increases with increasing concentration of  $HV^{2+}$  or an NADH analogue to reach a limiting value of 0.99. The limiting quantum yields of  $ZnP-C_{60}$  and  $ZnP-H_2P-C_{60}$  agree well with the quantum yields of radical ion pair formation,  $ZnP^{\bullet+}-C_{60}^{\bullet-}$  and  $ZnP^{\bullet+}-H_2P-C_{60}^{\bullet-}$ , respectively. In the presence of oxygen, the lifetimes of the radical ion pairs are, however, markedly reduced because of an oxygen-catalyzed back electron transfer process between  $C_{60}^{\bullet-}$  and  $ZnP^{\bullet+}$ . Such an impact on the radical ion pair lifetime consequences a significant decrease in the photocatalytic reactivity of the dyad (i.e.,  $ZnP-C_{60}$ ) in the overall photooxidation of an NADH analogue by  $HV^{2+}$ . By contrast, the reactivity of the triad (i.e.,  $ZnP-H_2P-C_{60}$ ) shows little effects upon admitting  $O_2$ .

## Introduction

The spherical shape of  $C_{60}$ , containing sixty delocalized  $\pi$  electrons, renders these carbon allotropes ideal components for the construction of efficient electron transfer model systems. Most importantly, the small reorganization energy, found for  $C_{60}$  in electron transfer processes, results, on one hand, in an overall acceleration of the charge separation (CS) step, whereas on the other hand, a deceleration was noted for the energy-wasting charge recombination (CR) step.<sup>1–3</sup> Thus, efficient stepwise CS, for example, in fullerene-based dyad, triad, and tetrad ensembles, has been accomplished along well-designed and fine-tuned redox gradients.<sup>1–3</sup> The resulting high-energy CS state is converted into electrical energy by constructing integrated artificial photosynthetic assemblies on gold electrodes with the use of self-assembled monolayers (SAMs).<sup>4,5</sup> However, the conversion of the high-energy CS state in fullerene-containing donor–acceptor linked systems into chemical energy has yet to be reported, although there have been some reports on uphill photochemical reactions catalyzed by other photosensitizers.<sup>6–8</sup>

In the biological redox systems, the NADH/NAD<sup>+</sup> system (NAD<sup>+</sup> = nicotinamide adenine dinucleotide; NADH = reduced form of NAD<sup>+</sup>) plays a key role in energy conversion and storage.<sup>9–11</sup> In fact, NADH is a source of two electrons and a proton, which is the equivalent to a hydride ion.<sup>9–11</sup> Once NADH is oxidized to NAD<sup>+</sup>, it is, however, rather difficult to reduce NAD<sup>+</sup> back to NADH by a one-electron reducing entity. The intrinsic stability of NAD<sup>+</sup> relates to its low reduction potential (−1.1 V vs. SCE) although the overall two-electron process is thermodynamically favorable.<sup>10,11</sup> An NADH analogue, 9-phenyl-10-methyl-9,10-dihydroacridine (AcrHPh) has previously been used as an electron source in the direct photochemical oxidation of AcrHPh by *N,N'*-dimethyl-4,4'-bipyridinium dication (methyl viologen,  $MV^{2+}$ ) without a photocatalyst.<sup>12</sup> The amount of energy stored in this photochemical oxidation was estimated as 0.76 eV (73 kJ mol<sup>−1</sup>).<sup>12</sup>

In this study, we wish to report on highly efficient energy conversion systems, based on several  $C_{60}$ -containing donor acceptor ensembles, zinc porphyrin- $C_{60}$  ( $ZnP-C_{60}$ ) and zinc porphyrin-free base porphyrin-fullerene triad ( $ZnP-H_2P-C_{60}$ ). These systems act as novel photocatalysts for the uphill oxidation of NADH analogues by hexyl viologen ( $HV^{2+}$ ) in the absence of oxygen. By contrast, upon admitting oxygen, the rate limiting back electron transfer (BET) process, that is, CR between the fullerene radical anion and the zinc porphyrin radical cation, was accelerated profoundly without forming

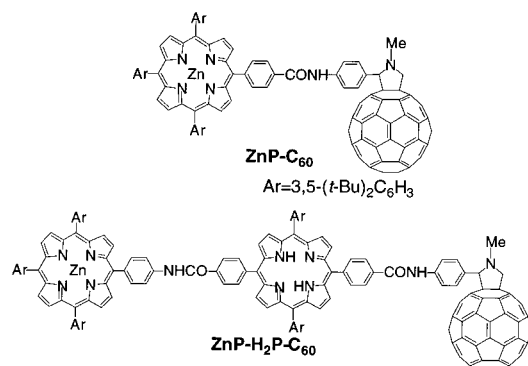
<sup>†</sup> Part of the special issue "Noboru Mataga Festschrift".

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**Figure 1.** Structures of  $\text{ZnP-C}_{60}$  and  $\text{ZnP-H}_2\text{P-C}_{60}$ .

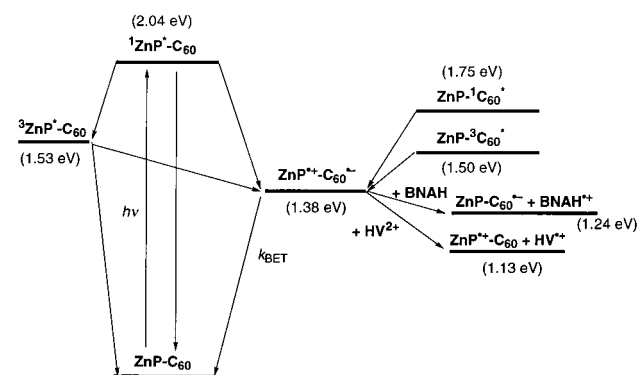
reactive oxygen species, such as singlet oxygen or superoxide anion.<sup>13</sup> The effects of  $\text{O}_2$  on the photocatalytic reactivity of  $\text{ZnP-C}_{60}$  and  $\text{ZnP-H}_2\text{P-C}_{60}$  are also examined in relation with the catalytic effects of  $\text{O}_2$  on the BET reactions.<sup>13</sup>

## Experimental Section

**Materials.** The synthesis and characterization of the porphyrin-fullerene linked molecules ( $\text{ZnP-C}_{60}$ <sup>3,14</sup> and  $\text{ZnP-H}_2\text{P-C}_{60}$ <sup>3</sup>) have been described previously (see Figure 1). Preparation of 1-benzyl-1,4-dihydronicotinamide (BNAH) and the BNA dimer was described previously.<sup>15</sup> 10-Methyl-9,10-dihydroacridine ( $\text{AcrH}_2$ ) was prepared from 10-methylacridinium iodide ( $\text{AcrH}^+\text{I}^-$ ) by the reduction with  $\text{NaBH}_4$  in methanol and purified by recrystallization from ethanol.<sup>15</sup>  $\text{AcrH}^+\text{I}^-$  was prepared by the reaction of acridine with methyl iodide in acetone and was converted to the perchlorate salt ( $\text{AcrH}^+\text{ClO}_4^-$ ) by the addition of magnesium perchlorate to the iodide salt ( $\text{AcrH}^+\text{I}^-$ ) and purified by recrystallization from methanol.<sup>16</sup> Tetrabutylammonium hexafluorophosphate used as a supporting electrolyte for the electrochemical measurements was obtained from Tokyo Kasei Organic Chemicals. Benzonitrile was purchased from Wako Pure Chemical Ind., Ltd. and purified by successive distillation over calcium hydride. The synthesized 1,1-dihexyl-4,4'-dipyridinium dibromide and the corresponding diperchlorate salt ( $\text{HV}^{2+}$ ) were described previously.<sup>13,17</sup>

**Quantum Yield Determinations.** A standard actinometer (potassium ferrioxalate)<sup>18</sup> was used for the quantum yield determination of the photochemical reactions of NADH analogues with hexyl viologen in the presence of  $\text{ZnP-C}_{60}$  or  $\text{ZnP-H}_2\text{P-C}_{60}$ . Typically, a square quartz cuvette (10 mm i.d.) which contained a deaerated PhCN solution ( $3.0 \text{ cm}^3$ ) of  $\text{ZnP-C}_{60}$  ( $3.0 \times 10^{-6} \text{ M}$ ), BNAH ( $4.0 \times 10^{-4} \text{ M}$ ), and  $\text{HV}^{2+}$  ( $8.0 \times 10^{-4} \text{ M}$ ) was irradiated with monochromatized light of  $\lambda = 433 \text{ nm}$  from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, the actinometer and  $\text{ZnP-C}_{60}$  absorbed essentially all of the incident light of  $\lambda = 433 \text{ nm}$ . The light intensity of monochromatized light of  $\lambda = 433 \text{ nm}$  was determined as  $9.22 \times 10^{-9} \text{ einstein s}^{-1}$  with the slit width of 20 nm. The photochemical reaction was monitored using a Hewlett Packard 8452A diode-array spectrophotometer. The quantum yields in the absence of oxygen were determined from increase in absorbance of  $\text{HV}^{\bullet+}$  at 615 nm ( $\epsilon = 10\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ). The  $\epsilon$  value was determined by the quantitative reduction of  $\text{HV}^{2+}$  by tetramethylsemiquinone radical anion which was prepared by the disproportionation reaction of tetramethylhydroquinone and the dianion obtained by deprotonation with tetrabutylammonium hydroxide.<sup>19</sup> In the presence of oxygen, the quantum yields of the photooxidation of  $\text{AcrH}_2$  by  $\text{HV}^{2+}$  were determined from increase in absorbance

## SCHEME 1



of  $\text{AcrH}^+$  at 358 nm ( $\epsilon = 18\,000 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>20</sup> In order to avoid the contribution of light absorption of the products, only the initial rates were used for determination of the quantum yields.

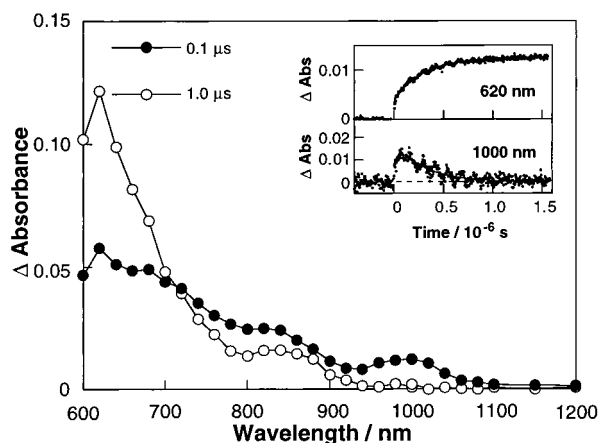
**Laser Flash Photolysis.** Nanosecond transient absorption measurements were carried out using SHG (532 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, fwhm 6 ns) as an excitation source. For transient absorption spectra in the near-IR region (600–1600 nm), monitoring light from a pulsed Xe lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834). Photoinduced events in micro- and millisecond time regions were estimated by using a continuous Xe lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu Photonics, G5125-10) as a probe light and a detector, respectively. Details of the transient absorption measurements were described elsewhere.<sup>3</sup> All of the samples in a quartz cell ( $1 \times 1 \text{ cm}$ ) were deaerated by bubbling argon through the solution for 15 min.

**Electrochemical Measurements.** The cyclic voltammetry (CV) measurements were performed on a BAS 50 W electrochemical analyzer in a deoxygenated PhCN solution containing 0.10 M  $n\text{-Bu}_4\text{NPF}_6$  as a supporting electrolyte at 298 K. The differential pulse voltammetry measurements were also performed on a BAS 50 W electrochemical analyzer in a deaerated PhCN solution containing 0.10 M  $n\text{-Bu}_4\text{NPF}_6$  as a supporting electrolyte at 298 K ( $10 \text{ mV s}^{-1}$ ). The glassy carbon working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgCl (saturated KCl) reference electrode. Ferrocene/ferricenium was used as an external standard.

## Results and Discussion

**Photocatalytic Oxidation of BNAH by  $\text{HV}^{2+}$ .** The energy levels of the singlet and triplet excited states of the investigated  $\text{ZnP-C}_{60}$  dyad in PhCN are summarized in Scheme 1, illustrating the different relaxation pathways following the initial photoexcitation event of  $\text{ZnP-C}_{60}$ .<sup>3</sup> Time-resolved techniques, including fluorescence lifetime and transient absorption measurements, have been employed to probe the CS and CR dynamics in this donor-acceptor array, disclosing the formation of the  $\text{ZnP}^{\bullet+}\text{-C}_{60}^{\bullet-}$  pair in a variety of solvents.<sup>3,13</sup> With the help of these time-resolved studies we determined the quantum yield of the radical ion pair formation as  $\Phi_1 = 0.99$ .<sup>3</sup> The rate of intramolecular back electron transfer ( $k_{\text{BET}}$ ) from  $\text{C}_{60}^{\bullet-}$  to  $\text{ZnP}^{\bullet+}$  in  $\text{ZnP}^{\bullet+}\text{-C}_{60}^{\bullet-}$ , is  $1.3 \times 10^6 \text{ s}^{-1}$  in oxygen-free PhCN solutions.<sup>3</sup>

The photophysics of the second compound, namely,  $\text{ZnP-H}_2\text{P-C}_{60}$ , in PhCN are well-studied.<sup>3</sup> An initial singlet-singlet energy transfer from the  $^1\text{ZnP}^*$  moiety (2.04 eV) to the  $\text{H}_2\text{P}$



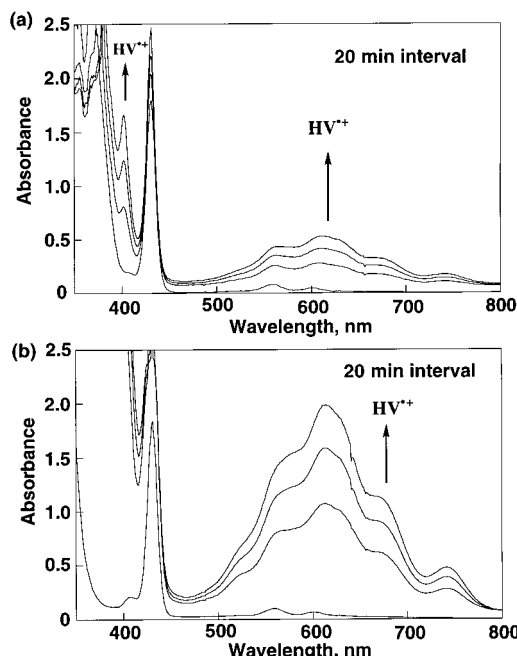
**Figure 2.** Transient absorption spectra of a PhCN solution containing  $\text{ZnP-C}_{60}$  ( $1.0 \times 10^{-4}$  M) and  $\text{HV}^{2+}$  ( $3.5 \times 10^{-3}$  M) after laser excitation (0.1 and 1  $\mu\text{s}$ ) in deaerated PhCN. Inset: Absorption-time profiles at 620 and 1000 nm.

moiety (1.89 eV) is followed by a sequential ET relay starting with the  $\text{ZnP-H}_2\text{P}^+-\text{C}_{60}$  via the transient  $\text{ZnP-H}_2\text{P}^+-\text{C}_{60}^{\bullet-}$  (1.63 eV) to yield finally the  $\text{ZnP}^{++}-\text{H}_2\text{P-C}_{60}^{\bullet-}$  (1.34 eV). The individual charge shift reactions are, however, in competition with the back ET to the ground state and triplet excited states, resulting in only a moderate quantum yield (0.40) for the final radical ion pair formation ( $\text{ZnP}^{++}-\text{H}_2\text{P-C}_{60}^{\bullet-}$ ).<sup>3</sup> On the other hand, the large distance, separating the donor and acceptor moieties, is beneficial with respect to increasing the lifetime ( $k_{\text{BET}} = 4.8 \times 10^4 \text{ s}^{-1}$ ) of the  $\text{ZnP}^{++}-\text{H}_2\text{P-C}_{60}^{\bullet-}$  pair by a factor of 27 relative to that noted for the  $\text{ZnP}^{++}-\text{C}_{60}^{\bullet-}$  pair.<sup>3,13</sup>

A comparison between the one-electron oxidation potential of  $\text{C}_{60}^{\bullet-}$  ( $E_{\text{ox}}^0 = -0.67$  V vs SCE, which is equivalent to the one-electron reduction potential of  $\text{C}_{60}$ ) and the one-electron reduction potential of  $\text{HV}^{2+}$  ( $E_{\text{red}}^0 = -0.42$  V vs SCE) unravels that an electron transfer from  $\text{C}_{60}^{\bullet-}$  to  $\text{HV}^{2+}$  is exergonic by 0.25 eV (Scheme 1). In fact, when  $\text{HV}^{2+}$  is added to the  $\text{ZnP-C}_{60}$  system, a direct electron transfer from  $\text{C}_{60}^{\bullet-}$  in the radical ion pair ( $\text{ZnP}^{++}-\text{C}_{60}^{\bullet-}$ ) to  $\text{HV}^{2+}$  occurs, producing  $\text{HV}^{++}$  ( $\lambda_{\text{max}} = 615$  nm) as shown in Figure 2. Importantly, the decay of the  $\text{C}_{60}^{\bullet-}$  absorption at 1000 nm<sup>21</sup> coincides with the appearance of  $\text{HV}^{++}$  at 615 nm (see inset of Figure 2), and furthermore, the decay rate varies linearly with  $\text{HV}^{2+}$  concentration. These findings serve as crucial testimony for the existence of a one-electron transfer between the photolytically generated  $\text{C}_{60}^{\bullet-}$  (i.e.,  $\text{ZnP}^{++}-\text{C}_{60}^{\bullet-}$ ) and  $\text{HV}^{2+}$  to form the stable  $\text{HV}^{++}$ .

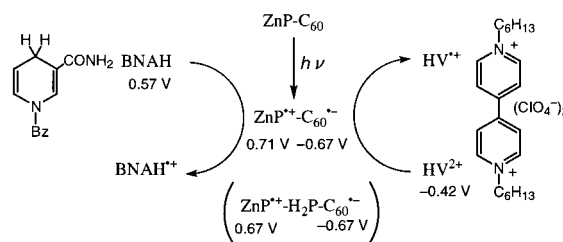
The transient features of  $\text{ZnP}^{++}$  are not affected by this reaction and remain virtually stable on the monitored time scale shown in Figure 2.<sup>13</sup> The second-order rate constant of the intermolecular electron transfer is determined from the formation rate of  $\text{HV}^{++}$  as  $(7 \pm 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Thus, the rate of intermolecular electron transfer from  $\text{C}_{60}^{\bullet-}$  to  $\text{HV}^{2+}$  ( $2.5 \times 10^6 \text{ s}^{-1}$  at  $3.5 \times 10^{-3}$  M of  $\text{HV}^{2+}$ ) competes well with the rate of intramolecular back electron transfer from  $\text{C}_{60}^{\bullet-}$  to  $\text{ZnP}^{++}$  in  $\text{ZnP}^{++}-\text{C}_{60}^{\bullet-}$  ( $k_{\text{BET}} = 1.3 \times 10^6 \text{ s}^{-1}$ ).<sup>3</sup>

If  $\text{ZnP}^{++}$  is indeed reduced by an external electron donor such as BNAH, separately added to the  $\text{ZnP-C}_{60}/\text{HV}^{2+}$  or  $\text{ZnP-H}_2\text{P-C}_{60}/\text{HV}^{2+}$  systems,  $\text{ZnP-C}_{60}$  or  $\text{ZnP-H}_2\text{P-C}_{60}$  may, in fact, photocatalyze the overall oxidation of BNAH by  $\text{HV}^{2+}$  (Scheme 2). An electron transfer from BNAH to  $\text{ZnP}^{++}$  is expected to be exothermic, considering the one-electron oxidation potential of BNAH ( $E_{\text{ox}}^0 = 0.57$  V vs SCE),<sup>15</sup> which is 0.14 V less positive than the one-electron reduction potential of  $\text{ZnP}^{++}$  (0.71 V vs SCE, which is equivalent to the one-electron oxidation potential of  $\text{ZnP}$ ).<sup>13</sup> Thus, once the CS state is obtained



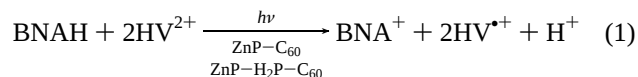
**Figure 3.** (a) Spectral change observed in the steady-state photolysis of a PhCN solution of BNAH ( $4.0 \times 10^{-4}$  M),  $\text{HV}^{2+}$  ( $8.0 \times 10^{-4}$  M), and  $\text{ZnP-C}_{60}$  ( $3.0 \times 10^{-6}$  M) under irradiation with monochromatized light of  $\lambda = 433$  nm. (b) Spectral change observed in the steady-state photolysis of a PhCN solution of BNAH ( $4.0 \times 10^{-4}$  M),  $\text{HV}^{2+}$  ( $8.0 \times 10^{-4}$  M), and  $\text{ZnP-H}_2\text{P-C}_{60}$  ( $3.0 \times 10^{-6}$  M) under irradiation with monochromatized light of  $\lambda = 433$  nm.

## SCHEME 2



via photoirradiation of  $\text{ZnP-C}_{60}$  or  $\text{ZnP-H}_2\text{P-C}_{60}$ , the oxidation of BNAH and the reduction of  $\text{HV}^{2+}$  should be accomplished by a reaction with  $\text{ZnP}^{++}$  and  $\text{C}_{60}^{\bullet-}$ , respectively (Scheme 2).<sup>22</sup> Hereby, the longer lifetime of the  $\text{ZnP}^{++}$ -spacer- $\text{C}_{60}^{\bullet-}$  state in the triad as compared to that in the dyad (vide supra) may result in facilitated redox reactions involving the CS state, BNAH and  $\text{HV}^{2+}$ .

In fact, this pathway was experimentally confirmed by photolysis of the  $\text{ZnP-C}_{60}/\text{BNAH}/\text{HV}^{2+}$  and  $\text{ZnP-H}_2\text{P-C}_{60}/\text{BNAH}/\text{HV}^{2+}$  systems with visible light (433 nm) in deoxygenated PhCN. For instance, Figure 3a,b depicts the steady state photolysis in deoxygenated PhCN, in which the  $\text{HV}^{++}$  absorption band ( $\lambda_{\text{max}} = 402$  and 615 nm) increases progressively with irradiation time. By contrast, no reaction occurs in the dark or in the absence of the photocatalyst (i.e.,  $\text{ZnP-C}_{60}$  or  $\text{ZnP-H}_2\text{P-C}_{60}$ ) under photoirradiation. Once  $\text{HV}^{++}$  is generated in the photochemical reaction, it was found to be stable in deoxygenated PhCN. The stoichiometry of the reaction is established by employing eq 1,

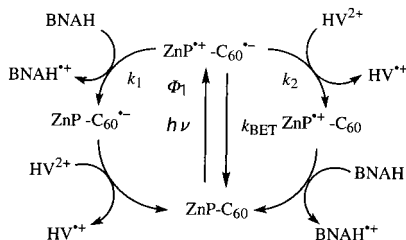


where BNAH acts as a two-electron donor to reduce two equivalents of  $\text{HV}^{++}$ .

**TABLE 1: Quantum Yields ( $\Phi_{\text{obs}}$ ) of Photocatalytic Oxidation of BNAH ( $4.0 \times 10^{-3}$  M) by  $\text{HV}^{2+}$  in the Presence of  $\text{ZnP-C}_{60}$  ( $3.0 \times 10^{-6}$  M) or  $\text{ZnP-H}_2\text{P-C}_{60}$  ( $3.0 \times 10^{-6}$  M) in Deoxygenated PhCN**

| catalyst                        | $[\text{HV}^{2+}]/\text{mM}$ | $\Phi_{\text{obs}}$ |
|---------------------------------|------------------------------|---------------------|
| $\text{ZnP-C}_{60}$             | 2                            | 0.65                |
|                                 | 4                            | 0.76                |
|                                 | 8                            | 0.87                |
|                                 | 10                           | 0.90                |
| $\text{ZnP-H}_2\text{P-C}_{60}$ | 2                            | 0.40                |
|                                 | 8                            | 0.40                |

### SCHEME 3



The quantum yields ( $\Phi_{\text{obs}}$ ) for the photochemical reaction of BNAH with  $\text{HV}^{2+}$  in the presence of  $\text{ZnP-C}_{60}$  or  $\text{ZnP-H}_2\text{P-C}_{60}$  were determined using a ferrioxalate actinometer<sup>18</sup> under irradiation with monochromatic light of  $\lambda = 433$  nm. The  $\Phi_{\text{obs}}$  value in the presence of  $\text{ZnP-C}_{60}$  ( $3.0 \times 10^{-6}$  M) increases with increasing  $\text{HV}^{2+}$  concentration at a fixed BNAH concentration ( $4.0 \times 10^{-3}$  M). Conversely, the  $\Phi_{\text{obs}}$  value in  $\text{ZnP-H}_2\text{P-C}_{60}$  is invariant, irrespective of the chosen  $\text{HV}^{2+}$  concentration (Table 1). We ascribe this difference in concentration dependence to effects that evolve from the different lifetimes of radical ion pair in  $\text{ZnP}^{+\bullet}\text{-C}_{60}^{\bullet-}$  and  $\text{ZnP}^{+\bullet}\text{-H}_2\text{P-C}_{60}^{\bullet-}$  (vide infra).

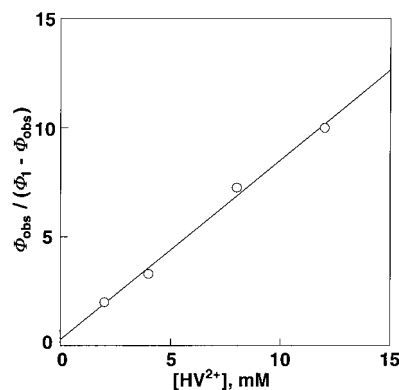
BNAH is oxidized by the  $\text{ZnP}^{+\bullet}$  moiety in the radical ion pair ( $k_1$ ), whereas  $\text{HV}^{2+}$  is reduced by the  $\text{C}_{60}^{\bullet-}$  moiety ( $k_2$ ) as shown in Scheme 3. These individual electron transfer processes compete, however, with the BET in the radical ion pair ( $k_{\text{BET}}$ ).  $\text{BNAH}^{+\bullet}$  thus produced may disproportionate to give BNAH,  $\text{BNA}^+$ , and  $\text{H}^+$ ,<sup>23</sup> when the overall redox reaction is given by eq 1.

By applying the steady-state approximation to the concentrations of the  $\text{ZnP}^{+\bullet}$  and  $\text{C}_{60}^{\bullet-}$  moieties in Scheme 3, the dependence of  $\Phi_{\text{obs}}$  on  $[\text{BNAH}]$  and  $[\text{HV}^{2+}]$  can be derived as given by eq 2

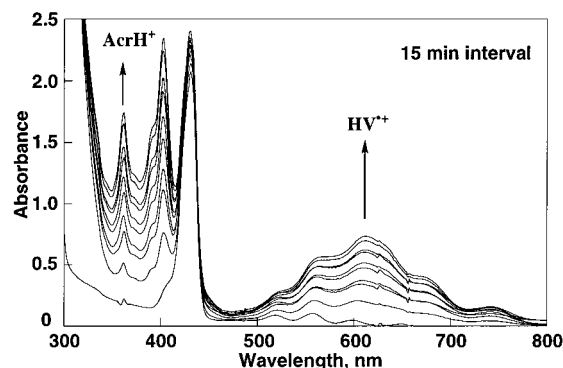
$$\Phi_{\text{obs}} = \frac{\Phi_1(k_1[\text{BNAH}] + k_2[\text{HV}^{2+}])}{k_{\text{BET}} + k_1[\text{BNAH}] + k_2[\text{HV}^{2+}]} \quad (2)$$

where  $\Phi_1$  is the quantum yield of the radical ion pair formation. Under the experimental conditions (i.e.,  $k_1[\text{BNAH}]$  or  $k_2[\text{HV}^{2+}] \gg k_{\text{BET}}$ ), the limiting quantum yield ( $\Phi_{\infty}$ ) corresponds to  $\Phi_1$ . The dependence of  $\Phi_{\text{obs}}$  on  $[\text{HV}^{2+}]$  in the case of  $\text{ZnP-C}_{60}$  (Table 1) agrees with eq 2 from which the  $\Phi_{\infty}$  value is determined as 0.99. This value agrees well with the  $\Phi_1$  value obtained independently from the direct kinetic analysis of the radical ion pair formation (0.99).<sup>3</sup> In the case of  $\text{ZnP-H}_2\text{P-C}_{60}$ , the  $\Phi_{\infty}$  value agrees also with the  $\Phi_1$  value (0.40) obtained from the transient absorption spectrum.<sup>3a</sup> Such agreements confirm the validity of Scheme 3.

Equation 2 is reformulated to eq 3, which predicts, in principle, a linear correlation between  $\Phi_{\text{obs}}/(\Phi_1 - \Phi_{\text{obs}})$  and  $[\text{HV}^{2+}]$ . With the help of Figure 4 this linear correlation was



**Figure 4.** Plot of  $\Phi_{\text{obs}}/(\Phi_1 - \Phi_{\text{obs}})$  vs  $[\text{HV}^{2+}]$  for the photocatalytic oxidation of BNAH ( $4.0 \times 10^{-4}$  M) by  $\text{HV}^{2+}$  with  $\text{ZnP-C}_{60}$  ( $3.0 \times 10^{-6}$  M).



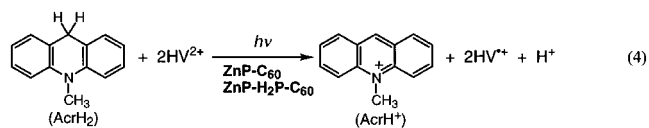
**Figure 5.** Spectral change observed in the steady-state photolysis of a PhCN solution of  $\text{AcrH}_2$  ( $4.0 \times 10^{-4}$  M),  $\text{HV}^{2+}$  ( $8.0 \times 10^{-4}$  M), and  $\text{ZnP-H}_2\text{P-C}_{60}$  ( $3.0 \times 10^{-6}$  M) under irradiation with monochromatized light of  $\lambda = 433$  nm.

confirmed for the  $\text{ZnP-C}_{60}$  system. With  $k_{\text{BET}}$  ( $1.3 \times 10^6 \text{ s}^{-1}$ ),<sup>3</sup>  $k_2$  is derived from

$$\frac{\Phi_{\text{obs}}}{\Phi_1 - \Phi_{\text{obs}}} = \frac{k_2}{k_{\text{BET}}}[\text{HV}^{2+}] + \frac{k_1[\text{BNAH}]}{k_{\text{BET}}} \quad (3)$$

the slope as  $(1.0 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>24</sup> This value agrees within experimental error with the value determined directly from the time-resolved experiment in Figure 2 [ $(7 \pm 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ].

**Photocatalytic Oxidation of  $\text{AcrH}_2$  by  $\text{HV}^{2+}$ .** Upon replacing BNAH with  $\text{AcrH}_2$  ( $4.0 \times 10^{-3}$  M), photoinitiated ( $\lambda = 433$  nm) oxidation by  $\text{HV}^{2+}$  ( $8.0 \times 10^{-3}$  M) produces  $\text{AcrH}^{+\bullet}$  ( $\lambda_{\text{max}} = 358$  nm) and  $\text{HV}^{+\bullet}$  ( $\lambda_{\text{max}} = 402$  and 615 nm) in the presence of  $\text{ZnP-H}_2\text{P-C}_{60}$ , as shown in Figure 5. The stoichiometry of the photocatalytic  $\text{AcrH}_2$  oxidation (eq 4) is the same as established above for the BNAH oxidation (eq 1).



As is the case of the photocatalytic BNAH oxidation, the quantum yields were determined from an increase in absorbance due to  $\text{HV}^{+\bullet}$  at 615 nm (Table 2). Hereby, the  $\Phi$  values ( $\Phi = 0.25$  ( $\text{ZnP-C}_{60}$ ) and 0.15 ( $\text{ZnP-H}_2\text{P-C}_{60}$ )) are markedly reduced relative to the corresponding values obtained for the oxidation of BNAH ( $\Phi = 0.87$  ( $\text{ZnP-C}_{60}$ ) and 0.40 ( $\text{ZnP-H}_2\text{P-C}_{60}$ )). We ascribe this decrease to the higher oxidation

**TABLE 2: Quantum Yields ( $\Phi_{\text{obs}}$ ) of Photocatalytic Oxidation of AcrH<sub>2</sub> ( $4.0 \times 10^{-3}$  M) by HV<sup>2+</sup> ( $8.0 \times 10^{-3}$  M) in the Presence of ZnP–C<sub>60</sub> ( $3.0 \times 10^{-6}$  M) or ZnP–H<sub>2</sub>P–C<sub>60</sub> ( $3.0 \times 10^{-6}$  M) in the Absence and Presence of O<sub>2</sub> in PhCN**

| catlyst                              | $\Phi_{\text{obs}}$  |                                         |
|--------------------------------------|----------------------|-----------------------------------------|
|                                      | O <sub>2</sub> = 0 M | O <sub>2</sub> = $8.5 \times 10^{-3}$ M |
| ZnP–C <sub>60</sub>                  | 0.25                 | 0.02                                    |
| ZnP–H <sub>2</sub> P–C <sub>60</sub> | 0.15                 | 0.14                                    |

potential of AcrH<sub>2</sub> ( $E_{\text{ox}}^0$  vs SCE = 0.81 V)<sup>23</sup> compared to that of BNAH ( $E_{\text{ox}}^0$  vs SCE = 0.57 V).<sup>13</sup> In this case, electron transfer from AcrH<sub>2</sub> to ZnP<sup>+</sup> is endergonic by 0.10 eV and, in turn, thermodynamically unfavorable. However, AcrH<sub>2</sub><sup>+</sup> is known to undergo a rapid deprotonation to produce subsequently AcrH<sup>•</sup>.<sup>23</sup> Following this deprotonation step, an electron transfer from AcrH<sup>•</sup> to ZnP<sup>+</sup>, forming AcrH<sup>+</sup>, becomes now highly exergonic judging from the low oxidation potential of the AcrH<sup>•</sup> species ( $E_{\text{ox}}^0 = -0.46$  V, which is equivalent to the one-electron reduction potential of AcrH<sup>+</sup>).<sup>25,26</sup> Thus, the overall stoichiometry implies also a two-electron oxidation of AcrH<sub>2</sub> by two equivalents of HV<sup>2+</sup> (eq 4), although the actual electron transfer event involving AcrH<sub>2</sub> is much slower than the corresponding oxidation of BNAH, leading consequently to the smaller quantum yields.

The amount of free energy ( $\Delta G$ ), stored in the photochemical oxidation of AcrH<sub>2</sub> by HV<sup>2+</sup>, is obtained as 1.28 eV (124 kJ mol<sup>-1</sup>) based on the difference between the redox potentials of the AcrH<sub>2</sub>/AcrH<sup>+</sup> (0.22 V vs SCE)<sup>26</sup> and HV<sup>2+</sup>/HV<sup>•+</sup> (−0.42 V vs SCE) redox couples (eq 5). In the case of BNAH ( $E^0(\text{BNAH}/\text{BNA}^+) = 0.02$  V),<sup>27</sup> the corresponding value is obtained as 0.88 eV (85 kJ mol<sup>-1</sup>). In the dark, the back reaction

$$\Delta G = 2F[E^0(\text{AcrH}_2/\text{AcrH}^+) - E^0(\text{HV}^{2+}/\text{HV}^{\bullet+})] \quad (5)$$

is extremely slow because of the kinetic barrier for a highly endergonic electron transfer from HV<sup>•+</sup> ( $E_{\text{ox}}^0 = -0.42$  V vs SCE) to BNA<sup>+</sup> ( $E_{\text{red}}^0 = -1.08$  V vs SCE),<sup>15</sup> although the overall two-electron process is exergonic.<sup>28,29</sup>

**Effects of O<sub>2</sub> on the Photocatalytic Systems.** In the presence of oxygen, the lifetimes of both radical ion pairs (i.e., ZnP<sup>•+</sup>–C<sub>60</sub><sup>•−</sup> and ZnP<sup>•+</sup>–H<sub>2</sub>P–C<sub>60</sub><sup>•−</sup>) are reduced significantly because of an oxygen-catalyzed back electron transfer (BET) processes between C<sub>60</sub><sup>•−</sup> and ZnP<sup>•+</sup>.<sup>13</sup> An intermolecular ET from C<sub>60</sub><sup>•−</sup> to O<sub>2</sub> occurs via the coordination of O<sub>2</sub> to ZnP<sup>•+</sup> to yield O<sub>2</sub><sup>•−</sup> bound to ZnP<sup>•+</sup>, followed by a rapid intramolecular ET from O<sub>2</sub><sup>•−</sup> to ZnP<sup>•+</sup> in the O<sub>2</sub><sup>•−</sup>–ZnP<sup>•+</sup> complex to regenerate O<sub>2</sub>.<sup>13</sup> Such a binding of the radical anion to metal ion is known to accelerate the ET process.<sup>30,31</sup> The impact that such a reduction in lifetimes of the radical ion pairs has on the photocatalytic AcrH<sub>2</sub> oxidation was examined by deriving the quantum yield of formation of AcrH<sup>+</sup> from O<sub>2</sub>-saturated PhCN solutions (see the Experimental Section).<sup>32</sup> The quantum yields under O<sub>2</sub>-saturated conditions are also listed in Table 2.<sup>33</sup>

Surprisingly, the  $\Phi_{\text{obs}}$  value (0.14) of the triad (ZnP–H<sub>2</sub>P–C<sub>60</sub>) system is little affected by molecular oxygen as compared to the value (0.15) found in the absence of O<sub>2</sub>. In contrast to the triad, the  $\Phi_{\text{obs}}$  value (0.02) of the dyad (ZnP–C<sub>60</sub>) system becomes significantly smaller than the corresponding value (0.25) in the absence of O<sub>2</sub>. It should be noted that the  $k_{\text{BET}}$  value of the triad increases from  $4.8 \times 10^4$  s<sup>-1</sup> to  $3.2 \times 10^5$  s<sup>-1</sup> in the absence and presence of O<sub>2</sub>, respectively. This value is, however, still significantly smaller than the  $k_{\text{BET}}$  value of the dyad, even in the absence of O<sub>2</sub> ( $1.3 \times 10^6$  s<sup>-1</sup>).<sup>13</sup> Furthermore, in the case of the triad (ZnP–H<sub>2</sub>P–C<sub>60</sub>), the rate of inter-

molecular electron transfer from C<sub>60</sub><sup>•−</sup> to HV<sup>2+</sup> ( $5.6 \times 10^6$  s<sup>-1</sup> at  $8.0 \times 10^{-3}$  M HV<sup>2+</sup>) is much faster than the BET rate ( $3.2 \times 10^5$  s<sup>-1</sup>) in an O<sub>2</sub>-saturated PhCN. This can be regarded as a potential rationale for the observation that the  $\Phi_{\text{obs}}$  value of the triad (ZnP–H<sub>2</sub>P–C<sub>60</sub>) system is little affected by the presence of oxygen. Conversely, in the case of dyad (ZnP–C<sub>60</sub>) the BET rate, especially in an O<sub>2</sub>-saturated PhCN solution ( $1.5 \times 10^7$  s<sup>-1</sup>)<sup>13</sup> is much faster than the electron transfer rate, C<sub>60</sub><sup>•−</sup> / HV<sup>2+</sup>.

In conclusion, we have demonstrated that ZnP-linked–C<sub>60</sub> systems act as efficient photocatalysts for the uphill oxidation of NADH analogues by HV<sup>2+</sup>. The catalytic performance of the triad (ZnP–H<sub>2</sub>P–C<sub>60</sub>) system, which exhibits a much longer lifetime of the radical ion pair, is little affected by O<sub>2</sub>, whereas the catalytic reactivity of the dyad (ZnP–C<sub>60</sub>) is reduced significantly by the pure presence of O<sub>2</sub>.

**Acknowledgment.** This work was supported by a grant-in-aid for Scientific Research Priority Area (No. 11228205) from the Ministry of Education, Science, Sports and Culture, Japan, the Sumitomo Foundation, and the Office of Basic Energy Sciences of the U.S. Department of Energy (contribution No. NDRL-4295 from the Notre Dame Radiation Laboratory).

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