The high-energy absorption bands are, for all n, largely unaffected by HCl protonation (Figure 1). The spectra of the protonated forms are very similar to those of the diphenylpolyynes, particularly for **3**, reported by Kobayashi et al.[5] and are attributable to $\pi \rightarrow \pi^*$ transitions.

These molecules show a strong emission from the charge-transfer state. The lifetime of the emission is short, less than the response function of our transient emission system (<5 ns), indicating a fluorescence. We have not been able to observe any phosphorescence even at 77 K. The emission maxima are highly solvent sensitive which is typical of emissive charge-transfer states which experience large dipole changes between the ground and the excited state.[9,10] For compound **2** the emission maximum is at 536 nm in toluene and 590 nm in ether.[11] The emission maxima show little change for the series of molecules in a given solvent, and both the emission half width ($\sim$4000 cm^{-1}) and Stokes shift ($\sim$7000 cm^{-1}) are likewise insensitive to n. However, the emission intensity decreases dramatically (Figure 2) in going from compound **1** to **3**. The pertinent spectroscopic data are summarized in Table I.

Corrected excitation spectra of these compounds reproduce the strong ICT band in all cases, but the higher energy features which are associated with $\pi \rightarrow \pi^*$ transitions of the diphenylpolyyne[5] appear to be much weaker than in the absorption spectra. The overlap of $\pi \rightarrow \pi^*$ transitions with the ICT band for **3** results in a strong wavelength dependence of the emission quantum yield for that molecule.

Taken as a whole the spectroscopic data suggest several things about the nature of these charge-transfer excited states. The significant observations from this series are the relative invariance in energy and intensity of the ICT band as the distance between the donor and acceptor is varied and the strong dependence of the emission quantum yield on n. The results from absorption spectroscopy indicate that while interaction between the donor and acceptor is efficient, as suggested by the large extinction coefficients, it remains relatively constant as the delocalized π system which connects the D/A pair is lengthened.

To a first approximation the ICT band can be thought of as a weak aniline $n(NH_2) \rightarrow \pi^*$ transition which gains intensity as a result of mixing π^* orbitals with the π^* orbitals on the nitro group.[6] Equivalently, this mixing may be described as a result of coupling an $n\pi^*$ state with a diphenylpolyyne state and a state with a charge-transfer configuration (ICT). Our results indicate that while the delocalized π/π^* orbitals are necessary for communication between the donor and acceptor, large changes in the energy of the diphenylpolyyne $\pi \rightarrow \pi^*$ transitions do not alter greatly the energy and intensity of the ICT electronic transition.

This suggests a relatively small amount of mixing of the diphenylpolyyne $\pi\pi^*$ state with the $n\pi^*$ and ICT states. This is reasonable since diphenylpolyyne $\pi\pi^*$ states and the ICT state differ by two one-electron promotions. Despite the small mixing, the fact that the ICT band intensity remains high for all n suggests that charge transfer through the conjugated linker is very efficient even for $n = 3$. Qualitatively the diphenylpolyyne linking group is acting as a molecular wire.

As previously mentioned the emission quantum yields (Figure 3) decrease precipitously as n goes from one to three. This, taken with the observation that the extinction coefficients for the ICT band remain relatively constant, suggests that the rate constant for nonradiative decay increases with polyyne length. This enhanced nonradiative decay could be due to intersystem crossing or internal conversion of the singlet ICT state.[12]

In summary, we have prepared a series of new donor-acceptor molecules in which the energies and intensities of the ICT electronic transitions are relatively independent of the length of the polyyne linking chain while the nonradiative decay rate shows dramatic enhancement with increasing linker length.

Acknowledgment. We thank Dr. David Beratan for helpful discussions. The research reported in this paper was performed by the Jet Propulsion Laboratory, California Institute of Technology, as part of its Innovative Space Technology Center, which is sponsored by the Strategic Defense Initiative Organization/Innovative Science and Technology through an agreement with the National Aeronautics and Space Administration (NASA).

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(10) Twisting of the two phenyl rings of these molecules may be an important factor in describing the excited state and its dynamics, as it is in the ICT states of some other molecules (Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971-988. Bonacic-Koutecky, V.; Koutecky, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170-189).

(11) A detailed study of the solvent dependence is currently underway. We have not been able to detect any emission from solution in more polar solvents such as acetonitrile.

(12) As n increases the higher density of vibrational states in the ground electronic state could yield faster internal conversion. However, increases in n could also be expected to yield faster intersystem crossing. This could be due to the greater charge separation in the ICT allowing rapid spin decorrelation from singlet to triplet ICT state or due to a decreased energy gap between ICT and $^3\pi\pi^*$ as a result of the lowering of the energy of $^3\pi\pi^*$ with increasing n.

High Surface Area Catalysts for H_2 Reduction of an Enzyme: Reduction of NAD^+ to NADH

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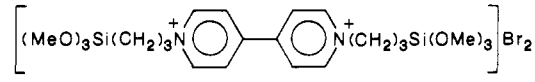
We report results which show that enzymes, formate dehydrogenase (FDH, MW $\approx$ 320 000)[1] and lipoamide dehydrogenase (LipDH, MW$\approx$100,000)[2] can equilibrate with the redox polymer derived from I[3] anchored to high surface area SiO_2,



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$[SiO_2]$-$(PQ^{2+})_n$,[4] eq 1 and 2. Further, by impregnating the

$$[SiO_2]\text{-}(PQ^{2+})_n + {}^1/_2n HCO_2^- \overset{FDH}{\rightleftharpoons} [SiO_2]\text{-}(PQ^{+})_n + {}^1/_2n CO_2 + {}^1/_2n H^+ \quad (1)$$

$$[SiO_2]\text{-}(PQ^{2+})_n + {}^1/_2n NADH \overset{LipDH}{\rightleftharpoons} [SiO_2]\text{-}(PQ^{+})_n + {}^1/_2n NAD^+ + {}^1/_2n H^+ \quad (2)$$

(1) Thauer, R. K.; Fuchs, G.; Jungermann, K. in *Iron-Sulfur Proteins*; Lowenberg, W., Ed.; Academic Press: New York, 1977; Vol. 3, p 121. FDH was obtained commercially from Sigma Chemical Co. (FDH, ECl. 1.2.1.2., from *Pseudomonas oxalaticus*, $\sim$0.3 unit activity per mg protein).

(2) (a) Barman, T. E., *Enzyme Handbook*; Springer Verlag: New York, 1969; Vol. 1, p 203. (b) Massey, V. In *The Enzymes*, 2nd ed.; Boyer, P. D., Lardy, H., Myrback, K., Eds.; Academic Press: New York, 1963; Vol. 7, p 279. LipDH was obtained commercially from Sigma Chemical Co. (LipDH, EC1.4.6.3, Type III from porcine heart, $\sim$100 units activity per mg protein, or Type V from Torula yeast, $\sim$25 units activity per mg protein).

(3) Bookbinder, D. C.; Wrighton, M. S. *J. Electrochem. Soc.* **1983** *130*, 1080.

(4) (a) Chao, S.; Stalder, C. S.; Summers, D. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 2723. (b) Bookbinder, D. C.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 7656 for modification of Pyrex glass with $(PQ^{2+}\cdot Pt)_n$. (c) SiO_2 used is from Alfa, 330 m^2/g, pretreated by heating to 300 °C for 48 h prior to refluxing with I in CH_3CN to effect formation of $[SiO_2]$-$(PQ^{2+})_n$, $\sim$70% by weight ($PQ^{2+}\cdot 2Br^-$). Partial exchange of Br^- by $PtCl_4^{2-}$ followed by H_2 reduction in aqueous solution gives $[SiO_2]$-$(PQ^{2+}\cdot xPt)_n$ with a Pt loading of $\sim$0.5% by weight. $[SiO_2]$-$(DA^{2+}\cdot xPt)_n$ was prepared similarly where $(DA^{2+})_n$ is derived from hydrolysis of the nonredox active diammonium reagent *N,N'*-bis[3-(trimethoxysilyl)propyl]-*N,N,N',N'*-tetramethyl-1,6-hexanediammonium. Details of catalyst preparation are reported in a full paper: Chao, S.; Simon, R. A.; Mallouk, T. E.; Wrighton, M. S., submitted for publication.

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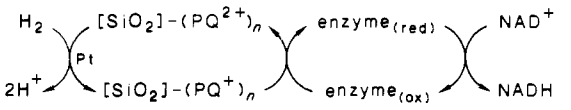
Table I. Catalyzed Reduction of NAD^+ to NADH

catalyst (amount used, mg)		starting sol[a] (vol, mL)	Δ absrbnce[b] (λ = 340 nm)	NADH[c] concn, mM	reactn time, h
$[SiO_2]$-$(PQ^{2+}\cdot x Pt\cdot 2Cl^-)_n$[d]	(10)	0.5 mM NAD^+/100 units LipDH	0.07	0.01	0.2
		pH 8.0/1 atm H_2	0.19	0.03	0.4
		(4.0)	0.31	0.05	0.7
			0.44	0.07	0.9
	(20)	1 mM NAD^+/200 units LipDH	1.3	0.21	0.2
		pH 8.0/1 atm H_2	0.20[e]	0.32	0.5
		(2.5)	0.29[e]	0.47	1.3
	(10)	0.5 mM NAD^+/no LipDH	0	0	0.4
		pH 8.0/1 atm H_2	0	0	0.9
		(3.0)	0	0	2.1
			0	0	3.2
$[SiO_2]$-$(DA^{2+}\cdot x Pt\cdot 2Cl^-)_n$[f]	(10)	0.5 mM NAD^+/100 units LipDH	0	0	1.0
		pH 8.0/1 atm H_2	0	0	2.0
		(3.0)	0	0	3.0

[a] The starting solutions (in 0.1 M $NaClO_4$/0.05 M NaH_2PO_4) were reduced under active H_2 purge in a septum-sealed 1-cm pathlength quartz cuvette. The solutions also contained 3 mM dithiothreitol that inhibits NAD^+ reduction at the trace Pt surfaces. [b] Monitored as a well-defined absorption band (λ_{max} = 340 nm). Samples were analyzed after centrifuging to remove suspended catalyst from the beam. [c] Calculated with ϵ_M = 6.2×10^3 M^{-1} cm^{-1} at 340 nm.[17] [d] Catalyst prepared as described in ref 4c. [e] A 0.30-mL sample was withdrawn from the reaction mixture and diluted to 3.0 mL before making the measurement. [f] This "control" system is made as in ref 4c except the $(DA^{2+})_n$ is derived from hydrolysis of nonredox active *N,N'*-bis[3-(trimethoxylsilyl)propyl]-*N,N,N',N'*-tetramethyl-1,6-hexanediammonium dibromide instead of I. This polymer system contains no viologen mediator and shows that the Pt alone is ineffective in producing NADH.

Scheme I. Catalytic H_2 Reduction of NAD^+ to NADH



surface-bound polymer with Pt[4b] it is possible to effect reduction of the coenzyme NAD^+ to enzymatically active NADH according to Scheme I.[5,6] It is noteworthy that the NAD^+/NADH[7] and $(PQ^{2+/+})_n$ redox potentials[3] are nearly the same, ~ −0.55 V vs. SCE at pH 7, making the $(PQ^{2+/+})_n$ redox system a good candidate as a redox mediator for enzymes employing the NAD^+/NADH coenzyme. Reduction of NAD^+ may be important in situations where NADH regeneration is required, as in enzyme-catalyzed organic transformations requiring NADH as a coenzyme.[8-14] Generally, NADH regeneration has been effected by using glucose-6-phosphate,[9] HCO_2^-,[10] or EtOH[11] and an appropriate enzyme, giving C-containing products in the mixture. Molecular H_2 has been reported[12,13] as a reducing agent but requires two enzymes and an extra flavin as a coenzyme. Certain hydrogenase enzymes can utilize NAD^+ as a substrate[14] and hence might serve as catalysts for regeneration of NADH with H_2, but lack of a commercial source and difficulties in obtaining the purified enzymes impede their routine use. Recently, modified Pd and Pt catalysts for reduction of methylviologen with H_2 have been used in regeneration of NADH.[15] Our new results suggest that a "synthetic hydrogenase", $[SiO_2]$-$(PQ^{2+}\cdot x Pt)_n$, can be useful to effect reduction of NAD^+ to NADH with H_2 with use of one enzyme. The $[SiO_2]$-$(PQ^{2+}\cdot x Pt)_n$ is novel, because the viologen mediator *and* the H_2 activation center are immobilized onto a suspended solid. The Pt is "buried" by the mediator polymer from I and is not directly exposed to enzymes or NAD^+.

$[SiO_2]$-$(PQ^{2+})_n$ and $[SiO_2]$-$(PQ^{2+}\cdot x Pt)_n$ can be prepared as previously described.[4] Equilibration of FDH or LipDH with the bound $(PQ^{2+/+})_n$ redox system is established by demonstrating that the reduction processes represented by eq 1 and 2 occur. Typical starting conditions for reaction according to eq 1 involve use of 50 mL of pH 7.0 (0.05 M NaH_2PO_4 buffer) 0.1 M $NaClO_4$ aqueous solution in a round-bottomed flask (under Ar) containing 20 mg of suspended $[SiO_2]$-$(PQ^{2+}\cdot 2Br^-)_n$, 5 mM $NaHCO_2$, and ~3 units of FDH.[1] Starting conditions for the reaction according to eq 2 are the same except 0.5 mM NADH[5] replaces the $NaHCO_2$ and ~100 units LipDH[2] replace the FDH. Reactions were run at 298 K. LipDH and FDH were assayed by using standard procedures[16] immediately prior to use. Reduction of $[SiO_2]$-$(PQ^{2+})_n$ to $[SiO_2]$-$(PQ^+)_n$ is detected by observing the change in color of the suspended powder from off-white to blue-violet.[3,4] Quantitative studies of the rate of reduction of PQ^{2+} by $FDH_{(red)}$ or $LipDH_{(red)}$ have not been made, but the blue-violet coloration accompanying $PQ^{2+} \rightarrow PQ^+$ reduction occurs in <5 min with the enzyme, whereas attempted reduction in the absence of enzyme shows no change in color of $[SiO_2]$-$(PQ^{2+})_n$ even after >1 h. Qualitative observations associated with eq 1 and 2 show that large enzymes can equilibrate with the surface-bound viologen mediator derived from I.

More detailed studies with $[SiO_2]$-$(PQ^{2+}\cdot x Pt)_n$ show that H_2 can be used to effect reduction of NAD^+ to NADH at pH 8, Table I. $[SiO_2]$-$(PQ^{2+}\cdot x Pt)_n$ is a "synthetic hydrogenase" in that H_2 is converted to two, one-electron outer sphere reducing equivalents capable of equilibrating with large biological redox reagents.[4b]

(5) NADH, nicotinamide adenine dinucleotide (reduced form), MW = 709.4 g/mol, Grade III from yeast, 98% purity, was purchased from Sigma Chemical Co. as the disodium salt and NAD^+, nicotinamide adenine dinucleotide (oxidized form), MW = 663.4 g/mol, Grade III from yeast, 98% purity, was purchased from Sigma Chemical Co. as the free acid.

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Data in Table I show that the reduction process occurs according to Scheme I. Control experiments, catalysis of H_2 reduction with $[SiO_2]$-$(PQ^{2+}\cdot xPt)_n$ but without LipDH or use of a Pt-containing, cationic, nonredox active polymer $(DA^{2+})_n$,[4c] without the redox mediator show that all components of the catalyst system are necessary: (1) Pt to "activate" the H_2, (2) $PQ^{2+/+}$ to accept reducing equivalents from H_2 and transfer them to $LipDH_{(ox)}$ to form $LipDH_{(red)}$, and (3) enzyme to effect reduction of NAD^+ to NADH.

NADH produced according to Scheme I is typically monitored in solution by the growth of characteristic absorbance at 340 nm (ϵ = 6200 M^{-1} cm^{-1}).[17] HPLC retention time and the complete UV–vis spectrum of the NADH found are the same as the authentic (enzymatically active) NADH obtained commercially. Further, the NADH produced shows strong fluorescence at 457 nm, characteristic of NADH.[18] Importantly, NADH produced has been shown to be enzymatically active for the reduction of lipoamide disulfide by using LipDH as the enzyme.[16] As shown by data in Table I, significant conversion of $\sim 10^{-3}$ M NAD^+ to NADH can be effected. HPLC and UV–vis spectra do not show evidence for formation of 1,2- or 1,6-dihydro NADH isomers that could form by nonenzymatic reduction at the Pt under H_2.[19] During prolonged reaction a decomposition product with λ_{max} = 290 nm does appear, but this may be due to the instability of NADH itself.[20] The important point is that the $[SiO_2]$-$(PQ^{2+}\cdot xPt)_n$ serves as a system capable of equilibrating the H_2O/H_2 redox system with catalytically active redox enzymes, establishing the viability of using H_2 as a reductant in enzymatic reduction processes.

Acknowledgment. We thank the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences for support of this research.

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Additions and Corrections

Electron Density Analysis of the Reaction of Aldehydes with Lithium Hydride. The General Importance of HOMO–HOMO Interaction [*J. Am. Chem. Soc.* **1986**, *108*, 3946–3951]. STEVEN M. BACHRACH and ANDREW STREITWIESER, JR.*

The relative force constants attributed to Komornicki et al. (ref 15) in the transition state for the reaction of acetylene with fuminic acid are actually the reverse of their assignment. In fact, as detailed earlier in our paper, the orbital composition of the transition-state HOMO has no necessary relationship to the bonding or energy properties that derive from *all* of the occupied MOs. Accordingly, the final paragraph of this section of our paper (p 3951) should be deleted. We are indebted to Professor K. Houk for pointing out this error.

Chirality of Intermediates in Thiamin Catalysis: Structure of (–)-2-(-1-Hydroxyethyl)-3,4-dimethyl-5-(2-hydroxyethyl)thiazolium Iodide, the Absolute Stereochemistry of the Enantiomers of Hydroxyethylthiamin, and Enzymic Reaction of the Diphosphates [*J. Am. Chem. Soc.* **1987**, *109*, 618–620]. RONALD KLUGER,* KHASHAYAR KARIMIAN, GERALD GISH, WALTER A. PANGBORN, and GEORGE T. DETITTA*

The title and the caption to Figure 1 in the published paper indicate a (+) enantiomer; however, both should indicate that the (–) enantiomer of HETI was the subject of our analysis, as is correctly indicated in the text as well as Scheme I.