saturating response. The peri hydrogens in **3** effectively slow water attack on the orthogonal thiocarbonyl carbon while not impeding access to the thioamide group by metals. Thus, thioamide **3** shows no (<5%) fluorescence change in metal-free pH 7 solution over 3 days. Because **3** and **4** are not ionizable, their fluorescence spectra are unaffected by pH.

In summary, we report (1) a previously undescribed inorganic reaction resulting in dosimetric metal ion determination; (2) the first wholly aqueous fluorescence detection scheme with selectivity for Hg(II) vs most other transition metals; and (3) a novel and perhaps generalizable signal transduction scheme for achieving enhanced fluorescence from a quenching metal.

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Supplementary Material Available: Experimental details for the synthesis and characterization of **3** (2 pages). Ordering information is given on any current masthead page.

Vectorial Electron Transfer from an Interfacial Photoexcited Porphyrin to Ground-State C_{60} and C_{70} and from Ascorbate to Triplet C_{60} and C_{70} in a Lipid Bilayer

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With the advent of techniques to produce C_{60}[1,2] in large quantites,[3] many of its properties[4] have been determined. Electron transfer from various amines[5-7] and semiconductor colloids[8] to photoexcited singlet and triplet C_{60} has been reported. Cast films of C_{60} on metal electrodes were observed[9] to behave as n-type semiconductors. Herein, we report evidence of interfacial electron transfer to both ground-state and excited triplet C_{60} and C_{70} in self-organized planar lipid bilayers. Electrical measurements used in this study provide absolute proof of the direction of electron transfer and identify the kinetics of interfacial electron transfer.

A planar lipid bilayer was formed[10] across a 0.8-mm-diameter hole in a thin Teflon sheet which divided two aqueous compartments. The photovoltage across the lipid bilayer was measured by a differential amplifier (Tektronix Model P6046) and a digital oscilloscope (Tektronix TDS 540). In the absence of C_{60} or any other electron acceptors, photoexcitation of an amphoteric porphyrin absorbed to the bilayer–water interface causes fast voltage transients (Figure 1a and the upper trace of the inset). These fast transients (18-ns positive rise, data not shown, and ~5-μs negative decay) involve inter-porphyrin electron transfer with motion of the porphyrin ion radicals at the interface[11] and a recombination half-time of ~230 μs. The photovoltage is small because the reactants are located at the bilayer–water interface (high dielectric).[12]

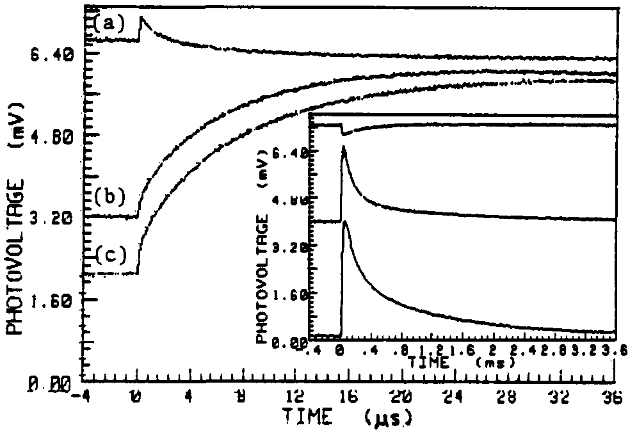

Figure 1. Photovoltage across a planar lipid bilayer. Amphoteric zinc deuteroporphyrin IX bis(ethylenediamine) (Porphyrin Products, Inc.) was added to the positive electrode side of the aqueous compartment at 5 μM, a saturating concentration. The bilayer-forming solution contains (a) no fullerenes, (b) 0.9 mM C_{60}, and (c) 0.9 mM C_{70}. The aqueous phase consists of 1 M NaCl, 10 mM Hepes, pH 7.0, and is deoxygenated enzymatically (ref 21). The excitation wavelength is 532 nm (50 μJ, 7.5 ns, 1 Hz, Continuum Nd:YAG laser, Surelite 10). The decay traces of a, b, and c are shown in the inset: upper, middle, and lower, respectively. Each trace is an average of 16 shots.

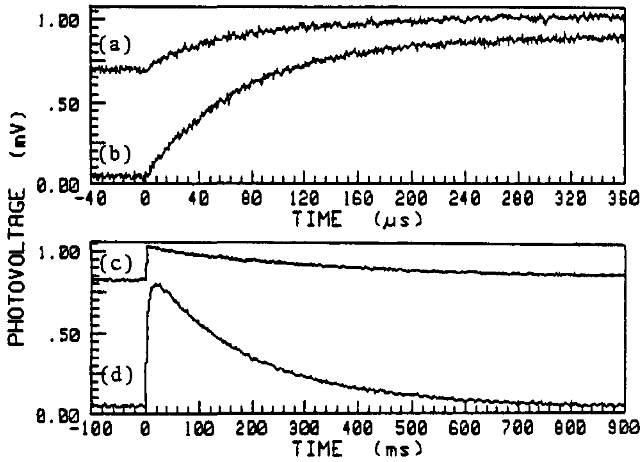

Figure 2. Photovoltage rises and decays observed from planar lipid bilayers containing (a and c) 0.8 mM C_{60} and (b and d) 0.8 mM C_{70} in the lipid solution and with 60 mM ascorbate in the positive electrode side of the aqueous compartment. The excitation wavelength is 532 nm (120 μJ, 1 Hz). Each trace is an average of 100 shots. The decay traces were obtained with a high-impedance differential amplifier (Stanford Research System, Model 560, 10^8 Ω) with a bandwidth of 1 MHz ~1 Hz.

The presence of C_{60} in the lipid bilayer[13] dramatically increases the positive photovoltage (Figure 1b and the middle trace of the

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inset on different time scales). The sign of the photovoltage, porphyrin side positive, proves that the direction of electron transfer is from the surface-bound porphyrins to ground-state C_{60} molecules inside the lipid bilayer. The formation of porphyrin cation[14] and C_{60} anion[15] from the excited state is highly favored ($\Delta G \sim -0.7$ eV) over the formation of porphyrin anion[14b] and C_{60}^+ cation[15b] ($\Delta G \geq +0.6$ eV). The photovoltage[16] rise (Figure 1b) consists of two components: a fast component with the same half rise time (18 ns, data now shown) and magnitude as that in Figure 1a, and is thus assigned to the inter-porphyrin electron transfer, and a slow component fit by a single exponential with $\tau = 6.0$ μs. The latter is assigned to the electron transfer from the interfacial porphyrin radical anion to C_{60} in the lipid core. The photovoltage decay (the middle trace of the inset in Figure 1) is fit by second-order kinetics; the observed half decay time decreases in photovoltages of higher amplitudes (obtained by increasing the laser power), confirming second-order kinetics.[17] Similar photovoltage rise and decay kinetics (Figure 1c and the lower trace of the inset) were observed from a porphyrin–C_{70} system.[18]

The contribution of the porphyrin absorption to the photovoltage far exceeds that of C_{60} on the basis of excitation wavelength. When the excitation wavelength is changed to 355 nm with a comparable photon flux, the observed photovoltage is 0.9 of that at 532 nm. This is close to the ratio (1.1) of the absorption coefficients of the zinc deuteroporphyrin at 355 nm to that at 532 nm and is far different from the corresponding ratio (17)[15a] of C_{60}. For C_{70}, the ratio of photovoltage at these wavelengths is 1.2 versus 3.2[15a] for absorption.

When a ground-state aqueous electron donor, ascorbate, replaced the porphyrin in the C_{60} bilayer system, a small photovoltage (Figure 2a) was observed. The free energy difference, $\Delta G \sim -1.3$ eV, between ascorbate and $^3C_{60}$[6] highly favors the formation of C_{60}^- anion. The rise time of the photovoltage is essentially a single exponential and is consistent with slow electron transfer at the interface ($\tau = 74$ μs) producing a small voltage and a much faster ($\sim$1 μs) escape of negative charges deeper into the bilayer, thus producing a large voltage. The order of magnitude slower rise time as compared to that with amphoteric porphyrin may reflect the increased average distance between the reactants. The photovoltage decay (Figure 2c) is fit with a single exponential decay with a surprisingly long τ of 400 ms.[19] The first-order decay is probably due to a small amount of oxidized ascorbate since the rate varies with the freshness of the ascorbate solution. The ascorbate–C_{70} system (Figure 2b,d) produces larger photovoltages than those in the C_{60} system, but with the same rate constants. The larger photovoltages of the ascorbate–C_{70} system are consistent with an 8-fold-higher absorption coefficient of C_{70} than of C_{60} at 532 nm.[15a] These results, in agreement with previous work,[5,6] show that photoexcited triplet C_{60} and C_{70} can serve as electron acceptors. The slow photovoltage rises in Figure 2a,b must be caused by the triplet state, since the lifetime, τ, of $^1C_{60}$ is 1.2 ns and of $^1C_{70}$ is 0.67 ns,[20a] while $\tau(^3C_{60})$ = 410 μs and $\tau(^3C_{70})$ = 51 ms.[20b]

In summary, we report unambiguous electrical evidence showing that both the ground-state and triplet C_{60} and C_{70} can serve as interfacial electron acceptors in a self-organized lipid bilayer system.

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(19) Since the system relaxation (RC) time is $\sim$500 ms, the true decay time may be as long as 2 s, indicating that the C_{60}^- anion is very stable under our experimental conditions. The photovoltage is not saturated by the pulsed light and can be increased several fold at higher incident light intensity.

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Energy Dependence and Dynamics of Gas-Phase Ion–Molecule Reactions

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We report here the generation and unimolecular dissociation of reaction intermediates for two classes of gas-phase ion–molecule reactions: proton transfer and S_N2 displacement. The intermediates are generated in two distinct and widely separated internal energy regimes, with both high and low angular momentum. Thus we are able to initiate chemical reactions starting from energized reactive intermediates and examine directly the effects of large changes of energy and angular momentum on the product branching for both proton-transfer and S_N2 reactions. The chemical sequence which relates the two reactions is shown in Scheme I.

Proton-transfer reactions are a simple and general system in which temperature or energy dependences can be studied. The temperature dependence and dynamics of proton-transfer reactions in the gas phase have been the subject of numerous investigations[1-12] and have been reviewed by Magnera and Kebarle.[13] The proton-transfer reaction shown in Scheme I has recently been studied using high-pressure mass spectrometry by Mautner.[5] The overall enthalpy ($\Delta H°$) and entropy[14] ($\Delta S°$) changes for the reaction $(NC)_2CH^- + HCl \rightarrow (NC)_2CH_2 + Cl^-$, were found to be -2.3 kcal mol^{-1} and -8 cal deg^{-1} mol^{-1}, respectively, making the free energy change ($\Delta G°$) at room temperature very close to zero.[15]

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