duces excellent results (Figure 3) with no electrolyte freezing apparent; (iii) testing Kuznetsov's prediction[14] regarding two-electron processes; and (iv) possible in-situ composition modification at *below* T_c by, e.g., electrochemical Li^+ intercalation, already established[15] as a room temperature process modifying subsequent superconducting behavior.

Acknowledgment. We thank Merck Ltd. and the SERC for funding and Merck Ltd. for materials.

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Fluorimetric Chemodosimetry. Mercury(II) and Silver(I) Indication in Water via Enhanced Fluorescence Signaling

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Fluoroionophores chemically communicate ion concentrations and have been the subject of substantial investigation in aqueous metal ion analysis.[1] For example, salicylidene-*o*-aminophenol, itself nonfluorescent at pH 4.5, forms a yellow-green fluorescent complex with Al(III).[2] However, the vast majority of fluoroionophores signal metal ions via fluorescence quenching (CHEQ) rather than fluorescence enhancement (CHEF).[3] We have observed that anthrylazamacrocycles display CHEF toward Zn(II) and Cd(II) in water, but CHEQ toward all other complexing transition metals, including Hg(II).[4] In fact, there are no reported examples of fluoroionophores that indicate Hg(II) with selectivity, much less with fluorescence enhancement. Because enhancement methods offer sensitivity advantages, mechanisms that signal inherently quenching metals via increasing emission are of interest. Furthermore, novel signal transduction mechanisms also may provide the selectivities unrelated to binding equilibria required for practical ion discrimination in water.[5] We now report the synthesis of a fluorimetric dosimeter[6] that indicates Hg(II), a strongly quenching ion, with fluorescence enhancement in aqueous solution.

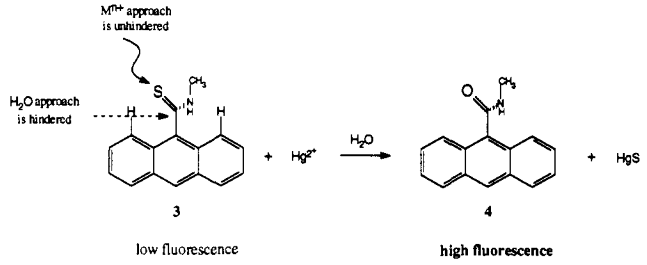


Figure 1.

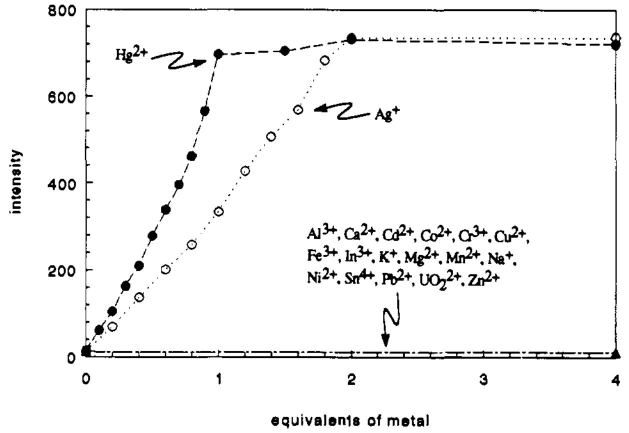
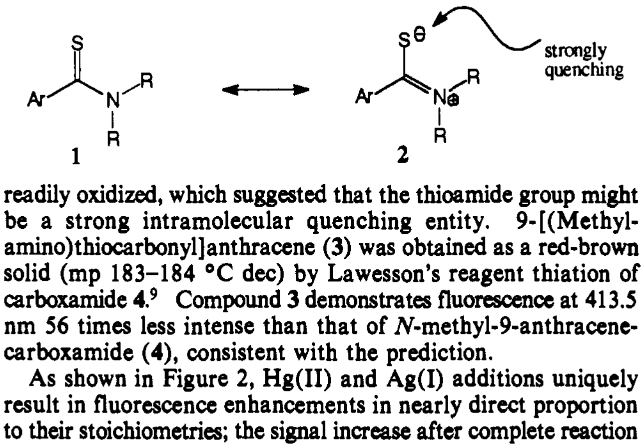


Figure 2. Fluorescence metal titrations of **3**. Solutions are 23 μM **3** in 0.01 M HEPES buffer, pH 7. Measurements shown were made after 70 h, principally to demonstrate the stability of **3** toward nonindicating metals. The Hg(II) reaction is 87% complete and the Ag(I) reaction 73% complete after 10 min under stoichiometric conditions and at room temperature.

Because Hg(II) is a thiophilic metal ion, sulfur-based intramolecular quenching functional groups were considered. While thioethers do quench anthracene fluorescence by photoinduced electron transfer (PET), that process is not as efficient as quenching by amines.[7] Thus, we chose the thioamide group (**1**); because the C=S double bond is weak, resonance structure **2** is the dominant resonance contributor.[8] Thiolates are in general readily oxidized, which suggested that the thioamide group might be a strong intramolecular quenching entity. 9-[(Methylamino)thiocarbonyl]anthracene (**3**) was obtained as a red-brown solid (mp 183–184 °C dec) by Lawesson's reagent thiation of carboxamide **4**.[9] Compound **3** demonstrates fluorescence at 413.5 nm 56 times less intense than that of *N*-methyl-9-anthracenecarboxamide (**4**), consistent with the prediction.



1 **2**

As shown in Figure 2, Hg(II) and Ag(I) additions uniquely result in fluorescence enhancements in nearly direct proportion to their stoichiometries; the signal increase after complete reaction is 55-fold. Al(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), In(III), K(I), Mg(II), Mn(II), Na(I), Ni(II), Pb(II), Sn(IV), UO_2(II), and Zn(II) yield no change in emission intensity under identical conditions. The observed stoichiometries, 1:1 for Hg(II) and 2:1 for Ag(I), are as predicted by the signal transduction mechanism shown in Figure 1. Both ions effect the desulfurization of **3**, yielding anthryl amide **4** and the insoluble metal sulfides as products. Because the amide group does not efficiently quench fluorescence, and (importantly) because it does not complex metals in aqueous solution, the conversion of **3** to **4** results in a net fluorescence enhancement with linear and

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(9) We synthesized **3** from 9-anthracenecarboxylic acid by conversion to the acid chloride, reaction with methylamine, and thiation with Lawesson's reagent. Full synthetic and characterization details are available as supplementary material.

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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.

Acknowledgment. The financial support of the National Science Foundation is acknowledged with gratitude. Shared resources, including the use of a fluorometer, were made available by Prof. Matthew Platz of this department. NMR spectra were obtained by using equipment funded in part by NIH Grant 1 S10 RR01458-01A1. A.W.C. thanks the A. P. Sloan and Dreyfus Foundations for support in the form of fellowships and Eli Lilly and Company for support in the form of a granteeship.

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]

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

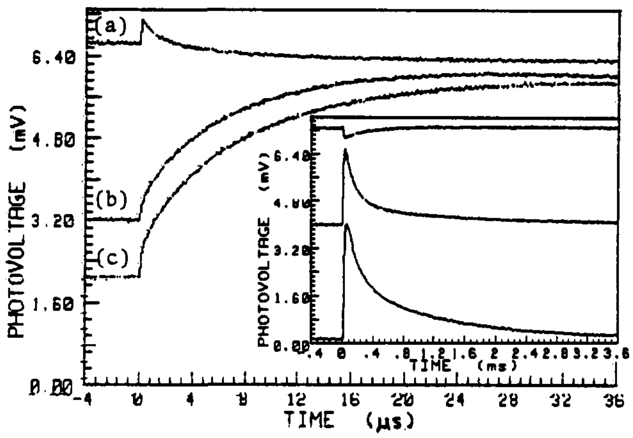

Figure 1. Photovoltage across a planar lipid bilayer. Amphoteric zinc deuteroporphyrin IX bis(ethylenediamine) (Porphyrin Products, Inc.) was added to the positive electrode side of the aqueous compartment at 5 μM, a saturating concentration. The bilayer-forming solution contains (a) no fullerenes, (b) 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.

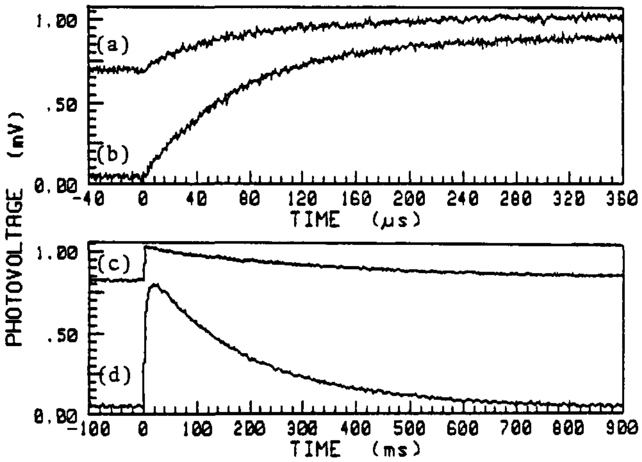

Figure 2. Photovoltage rises and decays observed from planar lipid bilayers containing (a and c) 0.8 mM C_{60} and (b and d) 0.8 mM C_{70} in the lipid solution and with 60 mM ascorbate in the positive electrode side of the aqueous compartment. The excitation wavelength is 532 nm (120 μJ, 1 Hz). Each 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.

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