# Observation of Photoinduced Electron Transfer at a Liquid–Liquid Interface by Optical Second Harmonic Generation

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Electron transport across an interface or membrane occurs in a wide variety of chemical and biological systems.[1-10] Control of the overall reaction pathways in these systems is often achieved through the careful design of the interfacial molecular architecture. A simple example of this control is the use of a liquid–liquid interface[11] to separate the products of an oxidation–reduction reaction.[12] For example, placement of an electron donor (D) in an organic medium and an acceptor (A) in an aqueous medium can inhibit the back reaction in a photoinduced electron-transfer process:

$$D(org) + A(aq) \xrightarrow{h\nu} D(org) + A^*(aq) \rightarrow D^+(org) + A^-(aq) \quad (1)$$
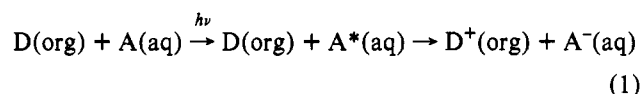
To maintain charge neutrality in the two liquid phases, either counterions must flow across the interface or the compensating charge must be supplied by an external electrical circuit. Observation of the photocurrents associated with electron-transfer reactions across liquid–liquid interfaces has been reported previously.[13] Although it is not stated explicitly in eq 1, the strong distance dependence of the electron-transfer process[1-4,8,10] requires that the molecules D and A* be very close to the liquid–liquid interface.

In this paper we report the first direct spectroscopic observation of a photoinduced electron transfer at a liquid–liquid interface using the surface-sensitive and surface-selective technique of optical second harmonic generation (SHG).[14,15] In order to directly study photoinduced electron transfer at the water/1,2-dichloroethane (DCE) interface, we use a redox-active probe molecule,

trans-1-ferrocenyl-2-[4-(trimethylammonio)phenyl]ethylene tetraphenylborate (1⁺·BPh₄⁻), in which both the affinity to adsorb to the interface and the inherent optical nonlinearity of the molecule depend on its oxidation state. When the ferrocene $1^+\cdot BPh_4^-$ is dissolved in the organic phase and tris(2,2'-bipyridinyl)ruthenium(II) chloride $(Ru(bpy)_3^{2+}\cdot 2Cl^-)$ is dissolved in the aqueous phase, photooxidation of 1^+ occurs at the water/DCE interface upon steady-state illumination. This electron transfer leads to a change in the optical nonlinearity of the interface which we detect by a change in the SHG.
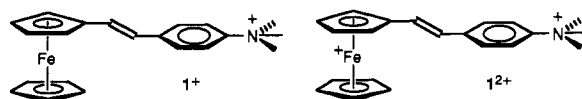
Aromatic molecules with conjugated electron-donating and -accepting groups exhibit large second-order nonlinear optical responses,[16,17] as has been shown for ferrocene derivatives similar to 1^+.[18,19] Compound $1^+\cdot BPh_4^-$ was synthesized by a Wittig coupling,[20-22] followed by methylation of the amine and metathesis of the counterion. Compound $1^{2+}\cdot 2PF_6^-$ was prepared independently by oxidation of 1^+ using benzoquinone in the presence of HCl,[23] followed by metathesis of the counterion. Compound $1^+\cdot BPh_4^-$ is not soluble in water.[24] Liquid–liquid interfaces were prepared by vigorously mixing a 1 mM solution of $1^+\cdot BPh_4^-$ in DCE (20 mL) with Millipore-filtered water (20 mL) and allowing the system to equilibrate. Interfacial tension measurements[15] show that 1^+ adsorbs to the water/DCE interface at a surface concentration of about 10^{13} molecules cm⁻² (corresponding to 3 × 10⁻¹⁰ mol at the interface) at this bulk solution concentration.[26]

The experimental geometry for measuring the SHG response from 1^+ adsorbed at the water/DCE interface is shown schematically in Figure 1a. The fundamental laser light at 610 nm was linearly polarized at 45° with respect to the plane of incidence and impinged onto the liquid–liquid interface at an incident angle of 32° with respect to the surface normal. SHG at 305 nm reflected from the liquid–liquid interface was detected with a polarization perpendicular to the plane of incidence (s-polarization). For photoinduced electron-transfer experiments, the 488-nm line of an argon ion laser was used to irradiate the interface. The 488-nm laser beam overlapped the 610-nm laser beam on the interface as depicted in Figure 1a. Details of the SHG experimental apparatus have been published elsewhere.[27]

We observe SHG from 1^+ adsorbed at the water/DCE interface, and the position of the electronic absorption of $1^+\cdot BPh_4^-$ (λ_{max} = 318 nm in DCE, 312 nm in CH₃CN) suggests that the SHG at 305 nm is resonance-enhanced. The amount of surface SHG depends on the oxidation state of the ferrocene moiety. Introduction of 1 drop of concentrated nitric acid to the aqueous medium resulted in a 10-fold increase in the surface SHG signal due to the oxidation of the adsorbed ferrocene 1^+ to ferrocenium 1^{2+}. This quantity of nitric acid is more than sufficient to oxidize

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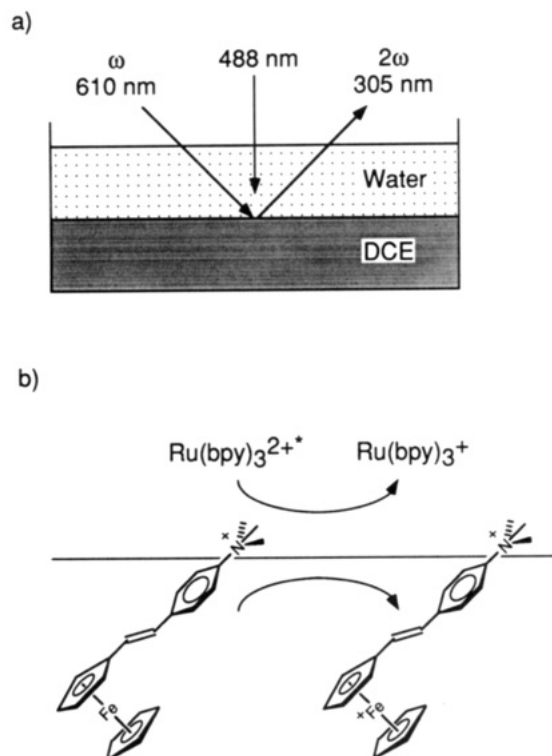(25) Hanzlik, J.; Samec, Z.; Hovorka, J. *J. Electroanal. Chem.* 1987, 216, 303–308.

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a)

b)

Figure 1. (a) Surface SHG experiment for monitoring the photoinduced electron-transfer reaction from **1**$^+$ to Ru(bpy)$_3$$^{2+}$$^\bullet$ at the water/DCE interface. (b) Schematic representation of the photoinduced electron-transfer reaction at the water/DCE interface.

Figure 2. SHG at 305 nm from **1**$^+$ adsorbed at the water/DCE interface in the presence of Ru(bpy)$_3$$^{2+}$ without illumination ("OFF") and with illumination ("ON") from the argon ion laser (488 nm). The increased SHG during illumination arises from the production of **1**$^{2+}$ at the interface by the photoinduced electron-transfer reaction depicted in Figure 1b.

the 3 × 10^{-10} mol of **1**$^+$ at the interface. Interfacial tension measurements indicate that **1**$^{2+}$ is more strongly adsorbed to the water/DCE interface than **1**$^+$.[26] The UV/vis spectrum of **1**$^{2+}$·2PF$_6$$^-$ (λ_{max} = 300 nm in DCE, 298 nm in CH$_3$CN) suggests an increase in the resonance enhancement of the SHG.[24] Thus the increased surface SHG response upon oxidation of **1**$^+$ to **1**$^{2+}$ can be attributed to a combination of increased surface coverage and increased resonance enhancement of the molecular nonlinear polarizability.

To demonstrate that the adsorbed **1**$^+$ could be converted to **1**$^{2+}$ by a photoinduced electron-transfer reaction, a 1 mM solution of **1**$^+$ in DCE was equilibrated with a 20 μM aqueous solution of Ru(bpy)$_3$Cl$_2$ (which is not soluble in DCE). Illumination of the water/DCE interface with 488-nm light (500 mW cm^{-2}) from an argon ion laser resulted in a 5-fold increase in the surface SHG at 305 nm (Figure 2). We attribute this increase to the formation of excited Ru(bpy)$_3$$^{2+}$$^\bullet$ in the aqueous phase which diffuses to the interface and oxidizes the adsorbed **1**$^+$ to **1**$^{2+}$ (as depicted in Figure 1b).[28] This produces a steady-state concentration of **1**$^{2+}$ in the argon ion laser spot at the interface. The rise time for the observed increase in SHG was approximately 13 ± 4 s. This relatively long rise time is consistent with the proposed mechanism which requires diffusion of Ru(bpy)$_3$$^{2+}$$^\bullet$ to the interface for the reaction to occur. Control experiments in which the interface was illuminated (488 nm) in the absence of Ru(bpy)$_3$Cl$_2$ did not reveal any changes in the surface SHG at 305 nm, demonstrating that the increased SHG from the interface

under illumination is not simply due to an excited state of **1**$^+$ formed by direct excitation. Illumination of the water/DCE interface in the absence of **1**$^+$, with Ru(bpy)$_3$Cl$_2$ present in the aqueous phase, yields no detectable SHG.

When the 488-nm illumination was discontinued, the surface SHG signal decayed back to the level observed for **1**$^+$ with a time constant on the order of 20 ± 4 s. The relatively long decay time indicates that the increased SHG is not due to an excited state of **1**$^+$ (whether formed by energy transfer from Ru(bpy)$_3$$^{2+}$$^\bullet$ or by direct excitation). We postulate several possible mechanisms for the decay of the SHG of **1**$^{2+}$ adsorbed at the interface: (i) back electron transfer from any Ru(bpy)$_3$$^+$ that remained at the interface, (ii) lateral diffusion of **1**$^{2+}$ at the interface out of the laser spot, (iii) desorption of **1**$^{2+}$ from the interface into either the aqueous or organic phase, and (iv) reduction of **1**$^{2+}$ to **1**$^+$.[24,25] These mechanisms for removal of **1**$^{2+}$ from the interface involve diffusion and are consistent with the observed decay time.

In summary, we spectroscopically observed the photoinduced electron-transfer reaction from ferrocene **1**$^+$ adsorbed at a water/DCE interface to excited Ru(bpy)$_3$$^{2+}$$^\bullet$ in the aqueous phase by monitoring the SHG response from the interface. These results demonstrate the utility of surface SHG in monitoring photoinduced electron transfer and other photochemical reactions at liquid–liquid interfaces. The successful use of immiscible liquid systems to control the reaction pathways in electron-transfer processes requires a detailed understanding of the interfacial electron-transfer reaction mechanisms; future studies will focus on time-resolved measurements of the electron-transfer kinetics and measurements of interfacial electron-transfer reactions in the presence of an external applied potential.

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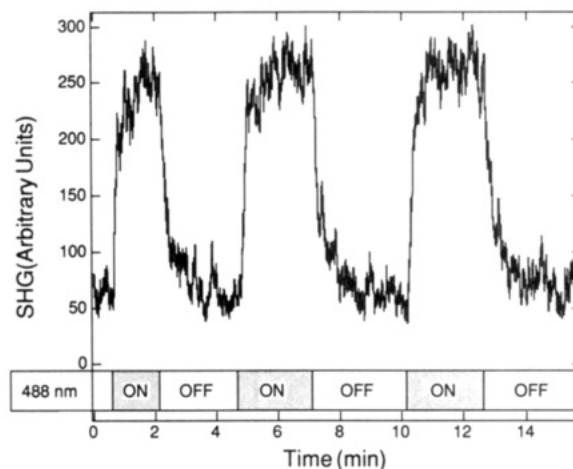
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