

Itamar Willner* [1] and William E. Ford

Laboratory of Chemical Biodynamics, University of California,
Berkeley, California 94720, U.S.A.

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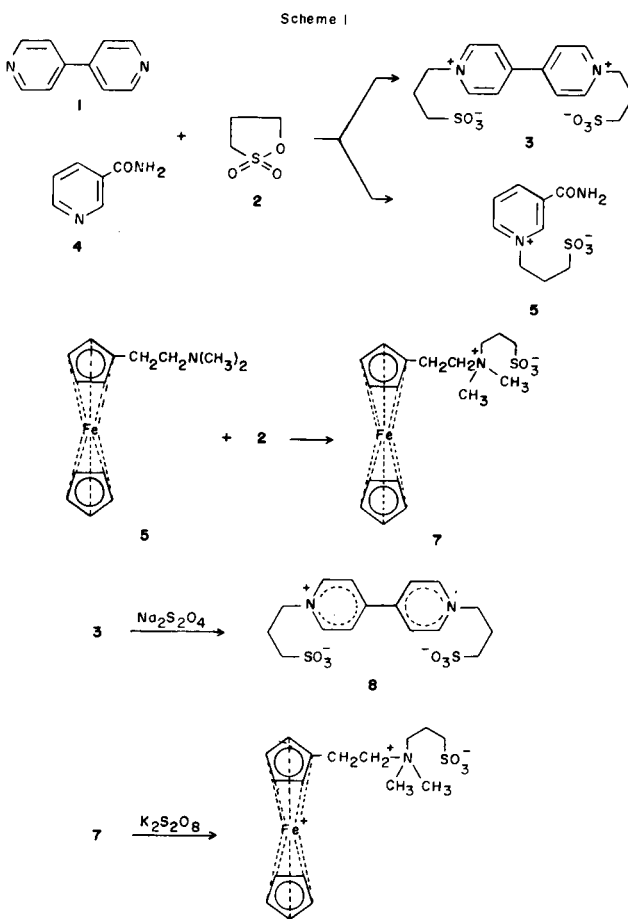
The reactions of 4,4'-bipyridine and nicotinamide with 1,3-propane sultone yields zwitterionic electron acceptors. Reaction of dimethylaminoethyl ferrocene with 1,3-propane sultone yields a zwitterionic ferrocene electron donor. The electron acceptors and donor are reduced and oxidized to the respective radical anions and ferrocenyl cation. Dipropyl-4,4'-bipyridinium disulfonate and the ferrocene derivative quench the excited $\text{Ru}(\text{bipy})_3^{2+}$.

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Photosensitized electron transfer reactions are currently of interest as a means to convert and store solar energy [2,3]. For efficient and long term storage of the energy, the stabilization of the photoproducts is required. Several interfacial systems such as micelles [4], microemulsions [5], vesicles [6] and charged colloidal silicon dioxide particles [7] have been suggested as a means to achieve this goals. In these systems electrostatic and/or hydrophobic interactions of the photoproducts with the interface are utilized in separating the photoproducts and inhibiting their recombination [8]. Of particular interest is the development of electron acceptors and donors capable of being further utilized in useful chemical routes such as the photodecomposition of water [2,3]. In recent years, it has been shown that 4,4'-bipyridinium salts (viologens) and nicotinamides serve as efficient quenchers of excited species, and that their reduced form reduces water to hydrogen in the presence of solid catalysts [9,10]. Unfortunately, these electron acceptors do not change their electrical properties during the electron transfer process, and thus their utilization in energy conversion in interfacial systems is limited.

Here, we wish to report a general route for the preparation of zwitterionic electron acceptors and donors. The zwitterionic structure of these compounds yields neutral reactants that result is negatively or positively charged products (upon reduction or oxidation respectively). Consequently, these compounds can be used in charged interfacial systems such as micelles or colloids and effectively improve the energy conversion and storage process [4,7,8].

The reaction for preparing these compounds consists of the nucleophilic substitution of 1,3-propane sultone by a tertiary amine in acetone or methanol [11]. By this method, two zwitterionic electron acceptors have been prepared. The reaction of 4,4'-bipyridine (**1**) with 1,3-propane sultone (**2**) yields dipropyl-4,4'-bipyridinium disulfonate (**3**), and nicotinamide (**4**) reacts with (**2**) to form *N*-propyl-nicotinamide sulfonate (**5**) (Scheme 1). Similarly, by reacting dimethylaminoethyl ferrocene (**6**) with 1,3-propane sultone (**2**) the zwitterionic electron donor (**7**), is obtained (Scheme 1). The products were characterized by ^1H -nmr spectroscopy and gave correct elementary analysis. The



zwitterionic products are very soluble in water, and insoluble in organic solvents such as acetone, toluene, and dichloromethane. Thus, their utilization in aqueous colloids or micellar solutions is feasible. Dipropyl-4,4'-bipyridinium disulfonate (**3**) is reduced [12] under an inert atmosphere by sodium dithionite to the respective blue viologen radical anion (**8**); ϵ (602 nm) = $12,800 \text{ M}^{-1}\cdot\text{cm}^{-1}$ and ϵ (735 nm) = $3200 \text{ M}^{-1}\cdot\text{cm}^{-1}$. This radical anion **7** is reoxidized by air. The electron donor **7** is oxidized by potassium persulfate to the corresponding ferrocenyl cation **9**; $\lambda = 622 \text{ nm}$ ($\epsilon = 300 \text{ M}^{-1}\cdot\text{cm}^{-1}$).

Dipropyl-4,4'-bipyridinium sulfonate, (**3**), quenches the luminescence of the excited sensitizers $\text{Ru}(\text{bipy})_3^{2+}$ or Zn-porphyrins. For $^*\text{Ru}(\text{bipy})_3^{2+}$ the quenching rate constant is $k_q = 1.5 \times 10^9 \text{ M}^{-1}\cdot\text{sec}^{-1}$. In turn, the nicotinamide derivative **4** does not quench the luminescence of these sensitizers. Similarly, laser flash experiments with the zwitterionic ferrocene **7**, indicate that $^*\text{Ru}(\text{bipy})_3^{2+}$ is quenched by this electron donor ($k_q \approx 10^9 \text{ M}^{-1}\cdot\text{sec}^{-1}$), although no separation of intermediate photoproducts could be observed. Photosensitized electron transfer reactions using the zwitterionic electron acceptors **3** and **5** were accomplished. With dipropyl-4,4'-bipyridinium disulfonate, (**3**), as electron acceptor, $\text{Ru}(\text{bipy})_3^{2+}$ as sensitizer and triethanolamine as electron donor the photoinduced formation of **8** is substantially enhanced in negatively charged interfacial systems (*i.e.* silicon dioxide colloids and NaLS micelles) as compared to homogeneous solutions [7,8]. This has been attributed to the stabilization of **8** against its recombination with the oxidized intermediate photoproduct, $\text{Ru}(\text{bipy})_3^{3+}$.

EXPERIMENTAL

Emission spectra and fluorescence quenching studies were performed on a Perkin-Elmer (MPF-2A) fluorescence spectrophotometer equipped with a 150-W xenon arc lamp and a red-sensitive type R-136 photomultiplier tube. The uv-visible spectra were recorded with a UVIKON-820 (KONTRON) spectrophotometer. ^1H -nmr spectra were recorded on a Bruker WH-300 pulsed FT spectrometer operating at 300.133 MHz.

Dipropyl-4,4'-bipyridinium Disulfonate (**3**)

4,4'-Dipyridyl dihydrate (**1**) (Aldrich) (0.810 g, 5 mmoles) was dissolved in 60 ml of acetone. 1,3-Propane sultone (**2**) (Aldrich) (1.28 g, 10.5 mmoles) dissolved in 5 ml of acetone was added to the reaction mixture. The solution was stirred under nitrogen for 10 minutes and then refluxed for 30 minutes. A white precipitate developed in the flask. The mixture was cooled to room temperature, and stirred for an additional 10 hours. The precipitate was filtered, washed with 30 ml of acetone and dried to yield product **2**, 1.4 g (51% yield). The product was hygroscopic and was kept anhydrous over calcium chloride; ^1H nmr (deuterium oxide, carbon tetrachloride, TMS): δ (ppm) 2.39 (tt, 4H, $J_1 = 7.9 \text{ Hz}$, $J_2 = 7.0 \text{ Hz}$), 2.88 (t, 4H, $J = 7.0 \text{ Hz}$), 4.78 (t, 4H, $J = 7.9 \text{ Hz}$), 8.42 (d, 4H, $J = 6.6 \text{ Hz}$), 9.01 (d, 4H, $J = 6.6 \text{ Hz}$).

Anal. Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$: C, 53.88; H, 4.49; N, 5.71; S, 13.06. Found: C, 53.74; H, 4.27; N, 6.03; S, 12.92.

Propyl Nicotinamide Sulfonate (**5**)

Nicotinamide (**4**) (2.4 g, 20 mmoles) and 1,3-propane sultone (2.68 g, 22 mmoles) were dissolved by stirring in 10 ml of methanol. The solution was mixed at room temperature. Within 15 minutes a white precipitate appeared. The mixture was stirred for an additional 8 hours. The precipitate

was filtered, washed with methanol and dried. The product **5** mp $>300^\circ$ dec, 3.1 g (63% yield); ^1H nmr (deuterium oxide, carbon tetrachloride, TMS): δ (ppm) 2.36 (tt, 2H, $J_1 = 7.4 \text{ Hz}$, $J_2 = 5.1 \text{ Hz}$), 2.88 (t, 2H, $J = 7.4 \text{ Hz}$), 4.72 (t, 2H, $J = 5.1 \text{ Hz}$), 8.08 (t, 1H, $J = 7.8 \text{ Hz}$), 8.79 (d, 1H, $J = 8.2 \text{ Hz}$), 8.93 (d, 1H, $J = 6.2 \text{ Hz}$), 9.24 (s, 1H).

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{N}_2\text{SO}_4$: C, 44.26; H, 4.92; N, 11.48; S, 13.11. Found: C, 44.18; H, 4.96; N, 11.49; S, 13.06.

Propyl Dimethylammoniumethyl Ferrocene Sulfonate (**7**)

Dimethylaminoethyl ferrocene (**6**) (Aldrich) (2.4 g, 10 mmoles) was dissolved in 100 ml of acetone. To the stirred solution was added 1,3-propane sultone (1.33 g, 11 mmoles) dissolved in 15 ml of acetone. The solution was stirred for 18 hours. After 45 minutes a yellow precipitate developed in the flask. At the end of the reaction, the yellow precipitate was filtered, washed with acetone and dried. The product **7**, 3.1 g, was hygroscopic (81% yield), mp $>300^\circ$.

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{NSO}_3\text{Fe}$: C, 53.68; H, 6.84; N, 3.68; S, 8.42. Found: C, 53.23; H, 6.33; N, 3.90; S, 8.88.

Chemical Oxidation of **7**

A stock solution of **7** (0.1 M) was prepared by dissolving 38 mg of **7** in 1 ml of water. Sixty μl of this stock solution were diluted to 3 ml and introduced into a glass cuvette. A solution of potassium persulfate, ($\text{K}_2\text{S}_2\text{O}_8$, 0.3 M) was added in 5 μl portions to the cuvette solution and the spectrum was recorded. The solution turned green. Addition of the oxidizing agent was continued until no additional increase in the absorption at $\lambda = 622 \text{ nm}$ was observed; the extinction coefficient corresponded to $\epsilon = 300 \text{ M}^{-1}\cdot\text{cm}^{-1}$.

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