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Covalently-Attached Dianions as Sensitizers for Photogalvanic Effects at Semiconductor Electrodes

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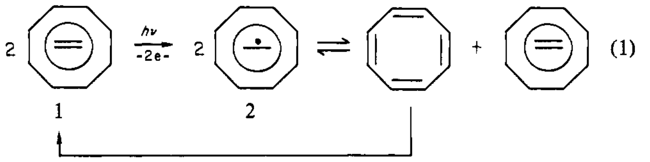
Abstract: Cyclooctatetraene derivatives (mono- and dimethyl alcohols) were attached to antimony-doped tin oxide optically transparent semiconductor electrodes via appropriate linking agents. The resulting modified electrodes give rise to enhanced photocurrents upon illumination of the reduced form (dianions) of the covalently-bound molecules. These results are compared with those obtained with analogous adsorbed sensitizers and a mechanism for the observed photoeffects is suggested. The instability of these covalently-modified visible-light-responsive electrodes under prolonged irradiation detracts from their utility as practical devices.

The use of organic photosensitizers to improve the spectral response to semiconductor electrodes in photoelectrochemical cells has attracted considerable attention.[1-6] The use of neutral organic species for such purposes has been hampered by their general lack of absorption in the visible region and their relatively high oxidation potentials. Our recent studies of the cyclooctatetraenyl dianion (COT^{2-}, **1**) showed that anions can be used to avoid both limitations.[6]

Earlier studies had shown that **1** photoejects an electron efficiently upon UV irradiation[7] and that the disproportionation of the photochemically produced radical anion, **2**, is highly dependent upon solvent and associated cation.[6,8] Control of this disproportionation reaction is important because it provides a means of avoiding both electron recapture (**2** → **1**) at the surface of the illuminated electrode and the numerous side reactions that radical anions can undergo. Our hope of utilizing this dianion in a liquid-phase photoelectrochemical cell was borne out by the experiments in which a photoinduced current of 0.1 to 0.5 $\mu A/cm^2$ (quantum efficiency on the order of 10^{-2}) was observed when **1** was irradiated with a GE 275W sunlamp at single crystal or polycrystalline n-TiO_2 in ammonia.[6] When this irradiation was conducted in an appropriate photoelectrochemical cell, the oxidized photoproduct can be made to revert thermally to starting material. The net chemistry is shown in eq 1. Consistent with this overall conversion, no decrease in the concentration of **1** could be observed after 5 days of irradiation, an observation which demonstrates the stability of this system, a novel anionic photogalvanic cell.



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Chemical modification of electrodes has also excited considerable interest as a means of increasing the visible light responsive range and improving the stability of semiconductor electrodes.[9-13] Our recent success in covalently attaching arenes to semiconductor electrodes[14] showed that such attachment per se has little effect on the properties of the bound species, either electrochemically or spectroscopically. Several methods of covalent bonding are available including direct attachment by ester formation and indirect attachment through such linking agents as silicon tetrachloride and cyanuric chloride.

Described in this present report are our efforts to combine these two concepts, by covalently bonding appropriate COT derivatives to SnO_2 semiconductor electrodes and by studying the modified electrodes so produced. In addition to their possible direct applications in solar energy utilization, these studies may also provide insight into electrode surface phenomena. Our hope was that covalent attachment of a near-monolayer of an appropriate derivative of the cyclooctatetraene dianion would enhance the crucial rate of disproportionation of the radical anion in eq 1, relative to back electron transfer, by removing the requirement for diffusional collision for the necessary electron exchange (Figure 1). Such manipulation of the respective rate constants should be reflected in the relative efficiency for photocurrent production.

Experimental Section

Materials. Tetrahydrofuran (THF) was freshly distilled from potassium under nitrogen. Dimethylformamide was vacuum distilled from P_2O_5 and stored over molecular sieves. The solvent was vacuum transferred to the cell and was deaerated by 3 freeze-thaw cycles. Cyclic voltammetric (CV) scans of the solvent/electrolyte mixture showed no impurity waves. Lithium perchlorate was recrystallized twice and dried overnight in the cell under vacuum over low heat before use. The cyclooctatetraene esters **3** and **4** were prepared by the published methods[15] (except that ethyl propiolate was used in the preparation of the monoester). Reduction of the esters was also effected by published methods.[16]

Analytical Instrumentation. Ultraviolet and visible spectra were obtained on a Cary 210 spectrophotometer. Proton nuclear magnetic resonance spectra were obtrained on a Varian EM390 or a Nicolet NT-200 spectrometer and ^{13}C spectra on a Varian FT-80A spectrometer. Infrared spectra were obtained on a Beckman Acculab-7 and mass spectra were obtained on a DuPont 21-471 or a 21-110C spectrometer. A GE 275-W sunlamp was used as the irradiation source, with or without Corning 3-73 ($\lambda > 400$ nm) or 3-70 ($\lambda > 490$ nm) glass filters to ensure absorption only by the anions, i.e., to eliminate direct excitation of the electrode. Action spectra were taken using a Hanovia 1000-W high-pressure mercury-xenon lamp and a Bausch and Lomb monochromator. Electrochemical experiments were conducted using a PAR Model 173 potentiostat, a Model 179 digital coulometer equipped with positive

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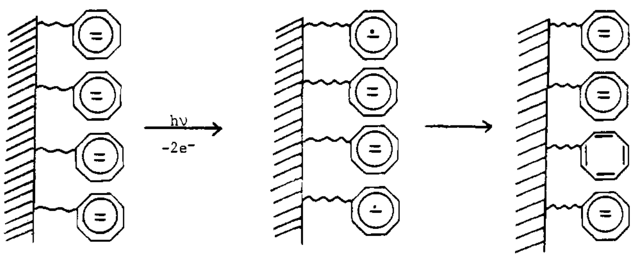


Figure 1. Enhanced disproportionation at a modified electrode.

feedback for IR compensation, a Model 175 universal programmer, and a Houston Instrument Model 2000 X–Y recorder. Currents were measured using a Keithley Model 177 digital multimeter.

General Procedure for Electrochemical Experiments and Photocurrent Measurements. All electrochemical and photocurrent experiments were performed in DMF containing 0.3 M $LiClO_4$ as electrolyte in a vacuum-tight three-electrode cell equipped with a Pyrex optical flat to accommodate irradiation. All cyclic voltammograms and preparative electrolyses were performed using a silver wire quasireference electrode and a platinum wire counter electrode. The potential of the quasireference was determined, after the sample cyclic voltammogram, by adding cyclooctatetraene and observing its known redox behavior. Cyclic voltammograms of dissolved COT derivatives were obtained using a platinum disk working electrode (area: 0.05 cm^2). Preparative electrolyses were performed at a platinum foil working electrode (1 × 1 cm). Photocurrents were measured between the semiconductor electrode and the platinum wire counter electrode for an illumination time of ca. 1 s and are measured as the difference between dark and illuminated current. Metal electrodes were polished before use with 0.5 μm alumina polishing powder. Semiconductor electrodes were thoroughly rinsed with distilled water and with acetone and were dried in the cell overnight before use.

Preparation of (Methoxymethyl)cyclooctatetraene (7). A solution of cyclooctatetraenylcarbinol[16a] (**5**, 0.99 g, 7.5 mmol) in THF (5 mL) was added to a stirred suspension of potassium *tert*-butoxide (1.52 g, 13.5 mmol) in THF (30 mL) under nitrogen. After 5 min, methyl iodide (1 mL, 2.3 g, 16 mmol) was added and stirring was continued for 2 h. Water was then added and the reaction mixture was extracted twice with ether. The aqueous layer was then continuously extracted with ether for 17 h and the recombined ether layers were washed sequentially with water and saturated aqueous sodium chloride and were dried over $MgSO_4$. After removal of solvent, the entire crude reaction mixture (0.99 g) was passed through a neutral alumina column (ca. 4.5 in. high × 20 mm in diameter) by eluting with CH_2Cl_2. The first fraction (150 mL) after removal of solvent (rotovapor), yielded a yellow oil (0.6 g, 55%): IR (neat) 3000, 2960, 2815, 1689, 1636, 1447, 1369, 1267, 1188, 1146, 1095, 921, 686, 803, 778, 739, 697, 689, 639 cm^{-1}; mass spectrum, *m/e* 103, 117, 148 (M^+); the NMR spectrum was identical with that previously reported for (methoxymethyl)cyclooctatetraene.[17] High-resolution mass spectrum: calcd for $C_{10}H_{12}O$, 148.0888; found, 148.0885.

Preparation of 1,2-Bis(methoxymethyl)cyclooctatetraene (8). A solution of 1,2-bis(hydroxymethyl)cyclooctatetraene[16b] (**6**, 1.0 g, 6.1 mmol) in THF (3 mL) was added to a stirred suspension of sodium hydride (1.5 g, 63 mmol) in THF (30 mL) under nitrogen. The solution was warmed for 2 h with a water bath (~50 °C) before the reaction was quenched with methyl iodide (7.0 mL, 16 g, 0.11 mol). Water was then added and the reaction mixture was extracted twice with ether. The aqueous layer was continuously extracted for 24 h with ether and the recombined ether layers were washed sequentially with water and saturated aqueous sodium chloride solution and dried over $MgSO_4$. After removal of solvent, the crude reaction mixture (0.96 g) was passed through a neutral alumina column (ca. 12 in high × 20 mm in diameter), eluting with CH_2Cl_2. The first fraction (250 mL), after removal of solvent, yielded **8** as a viscous yellow oil (0.69 g, 59%): ^1H NMR ($CDCl_3$) δ 5.8 (s, 6 H), 3.95 (dd, J = 13 Hz, 4 H), 3.3 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 140.0, 131.3, 130.9, 130.3, 74.1, 57.2; IR (neat) 2990, 2925, 2880, 2810, 1455, 1375, 1355, 1275, 1192, 1127, 1088, 970, 882, 833, 797, 722, 642 cm^{-1}; mass spectrum; *m/e* 103, 115, 129, 147, 161, 192 (M^+). High-resolution mass spectrum: calcd for $C_{12}H_{16}O_2$, 192.1150; found, 192.1154.

Pretreatment for Unmodified Electrodes. Antimony-doped (density 10^{18}) SnO_2-coated glass plates (0.5 × 2 in., all cut from the same large sheet supplied by PPG Industries) were washed thoroughly (using a mechanical shaker or ultrasonic bath) with Alconox detergent and rinsed with an organic solvent (isopropyl alcohol or Skelly B) and with triply-distilled water. The plates were then soaked in 40% aqueous NaOH for 15 h, carefully rinsed with triply-distilled water, and dried in a 140 °C oven for 24 h before further treatment.

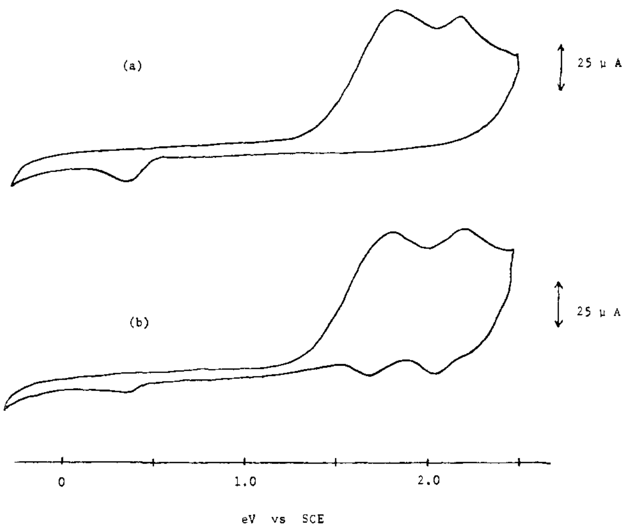
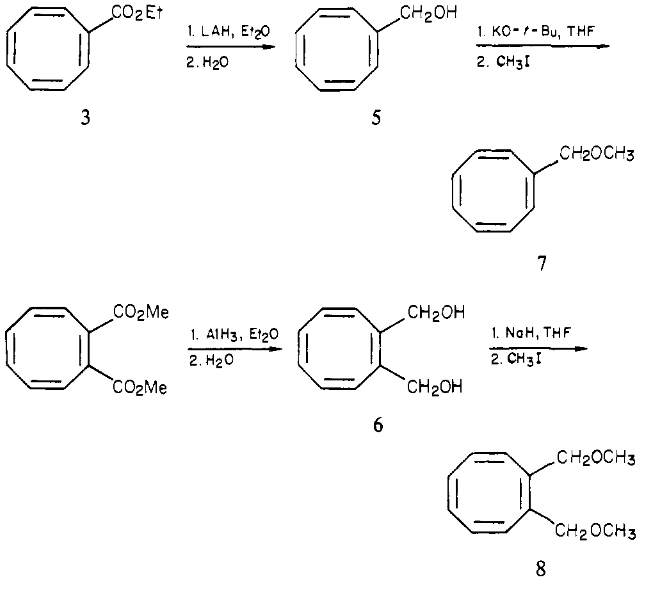


Figure 2. Cyclic voltammogram of (methoxymethyl)cyclooctatetraene (**7**): (a) anhydrous dimethylformamide, 0.3 M $LiClO_4$, room temperature, scan rate 500 mV/s; (b) as in (a) with added rigorously anhydrous neutral alumina.

Modification Using Cyanuric Chloride. Pretreated electrodes (from above) were modified by treatment with cyanuric chloride (Aldrich) by the method of Kuwana et al.[18] These were suspended in a solution of the appropriate cyclooctatetraene alcohol (ca. 0.30 g) in anhydrous acetone (40–50 mL) in a small screw cap jar. With the cap in place, the jar and its contents were shaken mechanically for 20 h. The electrodes were thoroughly rinsed (by Soxhlet extraction with benzene). Immediately before use, the electrode was further rinsed with triply-distilled water and acetone.

Modification Using Tetrachlorosilane. Pretreated electrodes (from above) were modified by treatment with tetrachlorosilane by the method of Haller.[19] Freshly distilled tetrachlorosilane was substituted for (3-aminopropyl)triethoxysilane in Haller's procedure. These electrodes were suspended in a solution of the appropriate cyclooctatetraene alcohol (0.1–0.3 g) in THF (40–50 mL) in a small screw cap jar. The jar and its contents were subjected to mechanical shaking for 24 h. The electrodes were then rinsed thoroughly with ethanol. Immediately before use, they were again rinsed with triply-distilled water and with acetone.



Results

COT derivatives, **7** and **8**, were first studied as model systems for the modified electrodes. By cyclic voltammetry (in DMF at

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Table I. Photocurrent Production Sensitized by 8^{2-} at a SnO_2-Coated Glass Electrode[a]

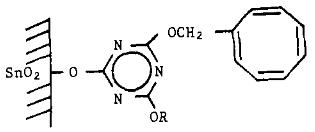
	photocurrent,[b] μA/cm²		
conditions	no filter	Corning 3-73 filter	Corning 3-70 filter
before reduction of 8	0.005	0.004	0.003
after reduction of 8[c]	0.027	0.007	0.004

[a] At cleaned but unmodified SnO_2-coated glass, in DMF, $[LiClO_4] = 0.23$ M. [b] Difference between illuminated and dark photocurrents at 0 V vs. SCE, upon illumination with a thermostated 275 W sunlamp. [c] 6.8% reduction to dianion.

Pt) **7** was found to have two quasireversible reduction waves (Epc = −1.85, −2.15 V vs. SCE, Figure 2). Similarly, **8** displayed quasireversible reductions (Epc = −1.90, −2.2 V). These waves appear in the expected range, assuming a close analogy with the known electrochemisity of cyclooctatetraene.[20] During the course of preparative-scale reduction (at Pt foil) of **8** in DMF, the solution was observed to turn steadily darker, showing an increased absorption in the visible range. Finally, a solution containing a mixture of the neutral and reduced COT derivatives at an unmodified SnO_2 glass electrode was found to produce modest photocurrents (Table I) upon illumination with a visible light source in our previously described apparatus.

Covalent Modification of SnO_2 Electrodes. COT derivatives **5** and **6** were attached to antimony-doped tin oxide coated NESA glass plates (PPG Industries) using either cyanuric chloride (by the method of Kuwana et al.[18]) or tetrachlorosilane (by a procedure similar to that used by Haller[19]). The modified electrodes so produced (**9**–**12**) exhibited electrochemical properties similar to those of **7** and **8**, i.e., quasireversible reduction waves near −2.0 V. Surface analysis by ESCA revealed approximately monolayer coverage by the covalent modifications. Such monolayer coverage produces a site density compatible with neighbor–neighbor interactions.

In order to establish that chemical attachment had really occurred, i.e., to ensure that the observed waves were not attributable solely to chemisorption of **5** and **6**, a set of SnO_2-coated glass plates were treated with **5** and **6** without preliminary attachment of the linking agent. After washing the electrodes, no waves could be observed in the region expected for reduction of **5** or **6** when the electrodes were examined by cyclic voltammetry. Nor were nonnegligible photocurrents generated upon irradiation at wavelengths longer than 420 nm.



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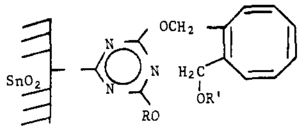

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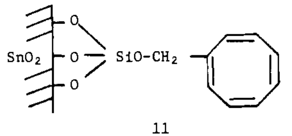

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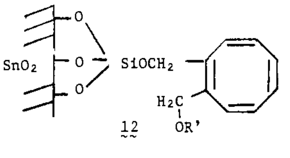

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Electrochemical reduction (ca. 2 e/mol of attached COT derivative) of these COT-derivatized electrodes proved facile. Following reduction, significant photocurrents were produced upon illumination (Table II) in our previously described cell.[6] These photocurrents dropped off slowly after short periods of illumination (>15 s), implying that some partly irreversible process was taking place at the surface of the electrode. Since electrochemical reduction could partially restore the photocurrent to its previous levels, the observed diminution of photocurrent may have been caused by depletion of the dianion at the electrode surface.

Table II. Photocurrent Production at Reduced Modified Electrodes

modified electrode		photocurrent, μA/cm²		
COT alcohol	linking agent	no filter	Corning 3-73 filter	Corning 3-70 filter
5	cyanuric chloride	2.4	0.35	0.13
5	cyanuric chloride	2.1	0.11	0.06
6	cyanuric chloride	1.9	0.09	0.021
6	cyanuric chloride	2.9	0.16	0.03
5	tetrachlorosilane	2.5	0.20	0.05
6	tetrachlorosilane	1.8	0.18	0.05
none	cyanuric chloride	0.008	0.0	0.0
none	none	0.13	0.008	0.0

Table III. Effect of Neutral and Reduced COT Ether on Photocurrent

		photocurrent, μA/cm²		
modified electrode	conditions	no filter	Corning 3-73 filter	Corning 3-70 filter
9[a]	after reduction of electrode coating	2.8	0.35	0.13
	after addition of 7	0.45	0.15	0.042
	after partial reduction of 7 at Pt	0.60	0.18	0.060
11	after reduction of electrode coating	0.12	0.008	0.006
	after addition of 7	0.016	<0.005	<0.005
	after partial reduction of 7 at Pt	0.031	0.005	<0.005
11	after reduction of electrode coating	0.23	<0.005	<0.005
	after addition of 7	0.016	<0.005	<0.005
	after partial reduction of 7 at Pt	0.025	<0.005	<0.005

[a] Slight oxidation preceded reduction at this modified electrode and hence the photocurrents were substantially higher than in the other two cases (vide supra).

Finally, action spectra taken using electrodes **10** and **12** showed reasonable correspondence with the combined visible absorption spectra of the dianion of **8** and a clean unmodified SnO_2-coated glass electrode. In particular, maxima at 360 nm tailing up to 440 nm in the action spectra correspond with a similar feature in the absorption spectrum of the dianion of **8**.

Discussion

The data in Table II clearly show an increase (by approximately an order of magnitude) in photocurrent production at SnO_2-coated glass electrodes upon covalent modification of the surface by these COT derivatives[8] (compared with currents produced by reversibly adsorbed sensitizers). The photocurrent yields thus obtained ($\Phi \sim 7 \times 10^{-2}$; net power conversion $\sim 10^{-4}$) are competitive with the most efficient of sensitized photogalvanic cells but are still an order of magnitude less efficient than liquid photovoltaic devices employing band gap irradiation.

A comparison of the results obtained using the modified electrodes **9**–**12** with those obtained from the control experiments (the last two entries) demonstrates that a COT derivative rather than a linking agent is responsible for this photocurrent enhancement (i.e., neither the unmodified SnO_2-coated glass electrode nor the electrode modified with cyanuric chloride alone can produce the photocurrents observed at the COT-modified electrodes). The photocurrents persist, albeit diminished, upon filtering the excitation wavelengths (Corning 3-73 [$\lambda > 400$ mm] and Corning 3-70 [$\lambda > 490$ nm] glass filters) demonstrates that ultraviolet light (band gap irradiation) is not required to produce significant photocurrents. Finally, neutral density filter experi-

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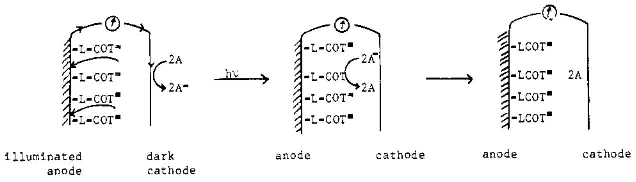
(20) See, for example: (a) Jensen, B. S.; Ronlan, A.; Parker, V. D. *Acta. Chem. Scand., Ser. B*, **1975**, *B29*, 394. (b) Rieke, R. D.; Copenhafer, R. A. *J. Electroanal. Chem.* **1974**, *56*, 409 and references cited therein.

(21) Quantum efficiencies were obtained by measuring relative photocurrents produced at our modified electrodes vis-a-vis those reported[22] for RhB–ZnO photosensitization.

(22) Spitler, M.; Calvin, M. *J. Chem. Phys.* **1977**, *67*, 5193.

Scheme I



ments have shown that photocurrent yield is directly dependent upon light intensity.

Apparently anomalous was the observation that minor oxidation (10^{-4}–(2×10^{-2}) C at 0–1 V vs. SCE) of the electrode coating appeared to be necessary prior to reduction in order to obtain the highest and most consistent photocurrent yields. If this oxidation were avoided, the photocurrents that could be generated (after reduction) were approximately 90% less. We conjecture that this oxidation eliminated small amounts of impurities present on the electrode or in the solution which would otherwise interfere with electrode processes since the potential range (0 to +1 V) for this prior oxidation does not correspond to any observable cyclic voltammetric waves. An alternative explanation is that a thin insulating oxide at the interface inhibits back electron transfer.

Table III presents the results obtained upon addition (and subsequent reduction) of **7** to the anodic half cell after reduction of the coating on the corresponding modified electrode. Clearly, the addition of the neutral COT caused a drastic drop in the initial photocurrent. Its subsequent reduction at Pt partially restored the photocurrent. This result can be explained by invoking a rapidly established equilibrium between the electrode-bound COT derivative (COT_b) and the solution-phase COT (COT_s), eq 2. Addition of neutral COT to solution shifts the equilibrium to the right, causing a depletion of dianion bound to the electrode surface and resulting in a sharp drop in photocurrent. Reduction of the solution-phase COT species at Pt displaces the equilibrium to the left again resulting in a partial restoration of photocurrent. The addition of **7** to the cathodic half cell caused a similar drop in photocurrent production.

$$COT_b^{2-} + COT_s \rightleftharpoons COT_b + COT_s^{2-} \qquad (2)$$

Mechanism of Photocurrent Production. The processes occurring at the electrode surface can be described as shown in Scheme I (where L = linking agent, COT = an appropriate COT derivative, and A = some electron accepting mobile charge carrier). Illumination of the modified electrode causes electron ejection into the semiconductor producing a current flow through the external circuit. Simultaneously, at the cathode, an acceptor A, e.g., cyclooctatetraene, **7**, **8**, or benzoquinone, is reduced and the circuit is completed thereby. At this point, disproportionation of the radical anions on the electrodes surface may take place. Subsequent reduction of the resulting neutral COT moieties by A^- can restore the modified electrode to its initial state, for the lifetime for photocurrent production by the irradiated modified electrodes is extended by a factor of 4–10 by the presence of reducible, mobile, charge carriers. This requires some reversibility of the species formed by the photooxidation in the presence of reducing agent. This photoproduct could be either the radical anion or the neutral hydrocarbon formed by disproportionation. Quasireversibility in the cyclic voltammogram (Figure 2) is permissible of either interpretation, but the persistence of the photooxidized species implies some barrier to energy-dissipating back electron transfer. A barrier is certainly expected for electron transfer to neutral hydrocarbon since a geometry change is known to accompany the reduction (tub shaped hydrocarbon to planar radical anion). Electron transfer to the radical anion requires no such geometry change and a kinetic retardation would not be anticipated (if the linking agent provides no barrier). For this reason, we have depicted the photoconversion in Scheme I as involving the disproportionation product of the primary photoproduct.

Either the disproportionation or the reduction of the photoproduct by the reduced charge carrier is probably inefficient since the photocurrent decays slowly upon extended illumination. Such photocurrent decay is also consistent with the only quasireversibility observed in model systems for these modified electrodes. Since the photocurrent can be restored to its previous levels by further reduction, the last reaction (reduction of the electrode coating by A^-) is most likely the limiting process. Nonetheless, the ultimate decay of light responsiveness in these modified electrodes represents the most serious difficulty to their use as practical devices for solar energy utilization.

Conclusions. Covalent attachment of COT derivatives to semiconductor electrodes can be achieved by the use of linking agents such as cyanuric chloride and tetrachlorosilane. Such attachment does not alter dramatically the electrochemical properties of these species. Following electrochemical reduction at these modified electrodes, substantial enhancement of photocurrent over that produced at unmodified electrodes can be observed upon illumination with visible light. The photocurrent so produced is proportional to light intensity and is dependent on the equilibrium concentration of bound dianionic senisitizers at the surface of the illuminated modified electrode. The mechanism for this photocurrent generation may involve photoinduced electron transfer into the semiconductor followed by disproportionation of the radical anion so formed. Reduction of this oxidation product (neutral COT derivative) by a mobile redox system restores the electrode surface to its initial state. This last reaction is apparently less efficient than in the previously studied systems employing unbound sensitizers and so limits, at least in part, the stability, and hence the utility of covalently-bound anionic sensitizers in such devices.

Acknowledgment. This research was sponsored by the U.S. Department of Energy, Fundamental Interactions Branch, Division of Chemical Sciences. M.A.F. gratefully acknowledges support as an A.P. Sloan Research Fellow (1980–1982) and as a Camille and Henry Dreyfus Teacher–Scholar (1980–1985).

Registry No. 5, 56900-54-0; **6**, 3205-28-5; **7**, 30844-13-4; **8**, 79972-71-7; cyanuric chloride, 108-77-0; tetrachlorosilane, 10026-04-7; SnO_2, 18282-10-5; Sb, 7440-36-0.