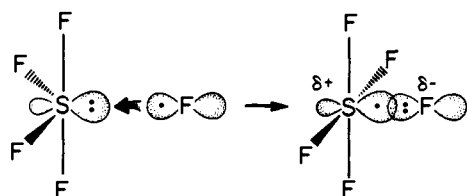


three-electron F⁻-SF₄⁺ bond. At the same time, an electron rearrangement occurs in the SF₄⁺ part of the molecule so that there are two three-center four-electron bonds, giving SF₅ the structure of a tetragonal pyramid.³⁰



SF₆ is built up from SF₅ and F by the formation of a strong three-center four-electron bond when F approaches SF₅ from the opposite side of the F⁻-SF₄⁺ bond. In SF₆ the maximum number of ligands is reached and by symmetry all S-F bonds are equivalent; i.e., SF₆ has three orthogonal three-center four-electron bonds.

Thus this transformation of lone-pair electrons on the central sulfur atom to at first a weak two-center three-electron bond and then to a strong three-center four-electron bond permits sulfur to have a hypervalent character without introducing the concepts of valence excitation and d-orbital hybridization. Moreover, this simple picture also accounts for the observed alternation of the stepwise bond dissociation energies in going from SF₆ to SF₂. It may be expected that similar behavior will be found in the successive bond dissociation energies of other hypervalent compounds.

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Covalent Attachment of Arenes to SnO₂-Semiconductor Electrodes

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Abstract: The synthesis and chemical and physical properties of some arene-derivatized tin oxide semiconductor electrodes are described. Several techniques for attachment are employed (esterification, silanation, silanation/amidation, and the use of cyanuric chloride as a linking agent) and the merits of each are evaluated. The relationship between the observed properties of the attached arenes and the potential utility of the derivatized electrodes as anodes in photogalvanic cells is discussed.

Introduction

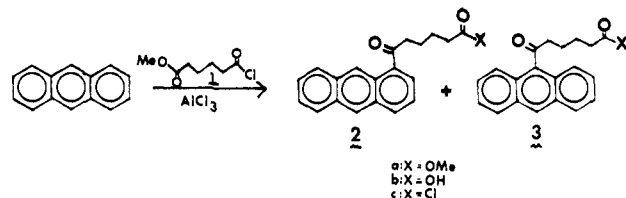
Covalent modification of semiconductor electrodes used in photoelectrochemical cells has been studied recently as a

method for improving electrode stability,¹ for opening new electrocatalytic pathways,^{1,2} and for attaching absorptive sensitizing dyes.³⁻⁶ Our own interest in electron injection from

excited carbanions⁷ prompted us to compare several methods for attaching arenes to semiconductors. If reliable methods for varying the separation between an attached molecule and a flat electrode surface become available, valuable information on the geometry required for efficient dye sensitization would become accessible. We describe in this paper our efforts at attaching several model aromatic compounds of varying reduction potential to a tin oxide semiconductor electrode.

Results

Arene Derivatives. The photochemistry and electrochemistry of appropriate arene derivatives were first examined. Friedel-Crafts acylation of anthracene with the half-ester acid chloride of adipic acid (**1**) afforded a mixture of methyl ester **2a** (60%) and its 9-anthryl isomer **3a** (5%).



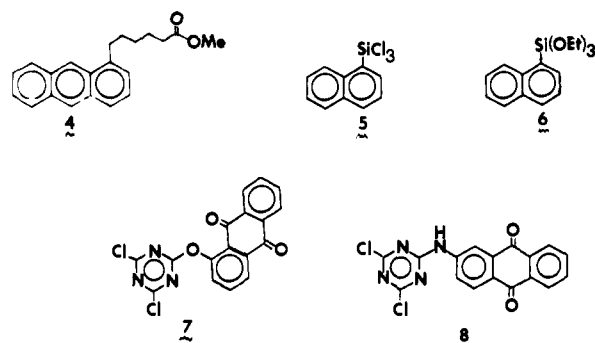
The phosphorescence spectrum of **2a** shows an intense band at 42.6 kcal/mol and a highly structured band at 69.5 kcal/mol. These were assigned as normal phosphorescence⁸ and delayed fluorescence,⁹ respectively, by analogy to reported anthryl derivatives. The fluorescence spectrum of **2a** ($\lambda_{em} = 454$ nm, $t_{1/2} = 220$ ps) confirmed the latter assignment. The triplet lifetime of **2a** (2-MeTHF, 77 K) was 23.5 ms.

Upon photolysis at 254 or ca. 300 nm, **2a** gave a mixture of at least three dimers¹⁰ by a low quantum yield pathway. Irradiation with longer wavelength light (>350 nm) gave no detectable reaction and attempts to sensitize a triplet reaction in **2a** with benzil, eosin, or pyrene led to no discernible reaction.

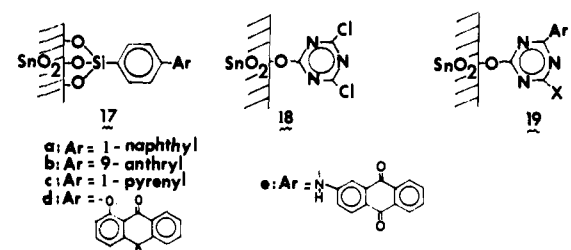
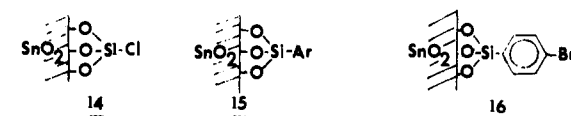
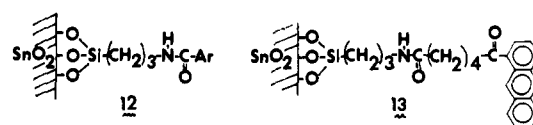
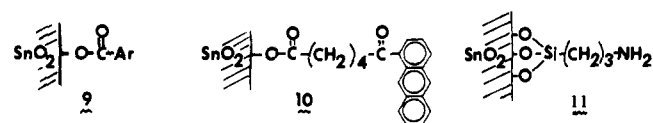
By cyclic voltammetry (reduction of **2a** at Pt in anhydrous CH₃CN), a reversible one-electron wave was observed at -1.95 eV, while a second nearly irreversible wave was found at -2.55 eV (vs. SCE). Although the radical anion appeared to be stable on a cyclic voltammetric scale (5 s), preparative electrochemical reduction of **2a** (1 faraday) in acetonitrile led to a complex mixture of products. Among these were anthracene and a compound tentatively identified as **4**, which was obtained independently by the Clemmensen reduction of **2a**. **4** presumably arises via initial reduction of ketone **2a** to an alcohol, analogues of which have been reduced electrochemically.¹¹

1-Naphthyltrichlorosilane¹² (**5**) was prepared by the attack of 1-naphthylmagnesium bromide on tetrachlorosilane. Cyclic voltammetry of **5** at Pt in anhydrous DMF revealed two reversible reduction waves at -0.48 and -2.55 eV (vs. SCE). The solvolysis product of **5**, **6**,¹³ gave a single, reversible cathodic wave at -2.52 eV (vs. SCE). **5** is much more photosensitive than **6**. After photolysis of a THF (10^{-2} M) solution of **6** with low-pressure mercury lamps (254 nm) for 30 min, some traces of polymer and naphthalene could be detected but **6** could be recovered largely ($<80\%$) unchanged (conditions under which **5** is virtually completely destroyed). Similar results were obtained upon sensitized irradiation (pyrene) where nearly quantitative recovery of **6** was achieved after 35-min irradiation at ~ 350 nm.

Nucleophilic attack on cyanuric chloride by the potassium salts of 1-hydroxyanthraquinone or 2-aminoanthraquinone gave **7** and **8**, respectively. Complex photochemistry of moderate efficiency ensued upon either direct or sensitized (acetone) photolysis of **7**. Cyclic voltammetry of **7** revealed quasi-reversible reduction waves at -0.63 and -1.27 eV (vs. SCE) in THF.



Covalent Modification of SnO₂ Electrodes. The appropriate arene derivatives were attached to antimony-doped tin oxide coated NESA glasses (PPG Industries). The modification of these pretreated, polycrystalline surfaces to give electrodes of type 9–19 was attempted (Ar = aryl).



Esterification (to form **9** or **10**) was attempted by exposing the pretreated glass-coated electrodes to the acid chlorides of **2a** or 9-anthrylcarboxylic acid (**20**), to the parent acids in the presence of dicyclohexylcarbodiimide (DCC), or to the mixed anhydrides formed from these acids and trifluoroacetic anhydride. Silanation (to form electrodes **11**–**17**) was achieved by treating the activated electrodes with appropriate trialkoxy- or trichlorosilanes either in the gas phase¹⁴ (by suspending an SnO₂ plate in the vapors above a refluxing solution of the silane) or in solution (by stirring a THF solution of the silane at room temperature overnight in a flask containing the glass plates).^{6,15,16} Specifically, **11** was obtained by treatment of the polycrystalline plates with 3-aminopropyltriethoxysilane. **13** was obtained by treating a modified plate **11** with **2b** in the presence of DCC, an approach attempted for the parallel formation of **12b** from **11** and 9-anthrylcarboxylic acid. **14** was

Table I. Characteristics of Some Modified Electrodes

	E_{pc} eV vs. SCE ^c	λ_{em} , ^a nm \pm 3	ESCA ^b	onset of photocurrent ^c V_{onset} eV \pm 0.1 vs. SCE
9	-2.0, -2.6	455 (weak)	C, O, Sn	-0.40
10	-2.0, -2.5	460 (weak)	C, O, Sn	-0.30
11^d			C, O, N, Si	-0.80 ^d
11			C, O, N, Si	-0.35
12	-2.0, -2.6	455	C, O, N, Si	-0.30
13	-2.0, -2.5	465	C, O, N, Si	-0.40
15a	-2.5	350-400 ^e	C, O, Si	-0.35
15b	-2.0, -2.5	465	C, O, Si	-0.50
15c	-2.1, -2.6	400, 478 (weak)	C, O, Si	-0.48
17	-1.9 (weak)	468 (weak)	C, O, Si	-0.53
19d	-0.9, -1.4	575, 605 (weak)	C, O, N	-0.60
19e	-1.2, -1.6	480, 590 (weak)	C, O, N	-0.63
21 (unmodified SnO₂)		390 (very weak)	Sn, O	-0.40

^a Fluorescence emission maximum, excitation monochromator blazed at 385 nm. Fluorescence measurements were conducted at maximum sensitivity in the Spex fluorimeter. ^b In all cases, the Sn(3d 5/2) peak decreased in intensity by at least a factor of 3. The atoms listed appeared or increased in intensity by at least a factor of 2. The transitions monitored (low-resolution spectrum) include C(1s), N(1s), O(2s), Si(2p), and Sn(3d 5/2). ^c In CH₃CN, TBAP = 0.1 M. Irradiation: Pyrex-filtered 200-W high pressure mercury arc. ^d Solution-phase silanation procedure. ^e Whether this fluorescence is from attached naphthalene or SnO₂ is unclear.

synthesized by bathing the pretreated SnO₂ plates in the vapors above refluxing tetrachlorosilane. The resulting modified electrode was treated with an anhydrous solution of aryllithium at room temperature to give **15**. Alternately, **15** could be synthesized by bathing a pretreated SnO₂ plate in a dilute solution of **5** overnight. Identical electrodes (**15a**) were obtained by either method. **16** and **17** were obtained in parallel fashion by treatment of the cleaned SnO₂ plates successively with *p*-bromophenyltrichlorosilane and with aryllithium.

A covalent triazine linkage agent (cyanuric chloride) coupled the tin oxide surface with alcohols or amines. For example, **19** was obtained from the previously described modified electrode **18**¹⁷ by treatment with alkali metal salts of functionalized arenes. Non-covalently-attached arenes were removed from the modified electrodes by Soxhlet extraction of the plates with water, ethanol, benzene, and/or tetrahydrofuran.

The surface coverage for each electrode was evaluated by ESCA, by fluorescence spectroscopy, and/or by cyclic voltammetry (Table I). In the ESCA determination of surface coverage, a comparison of the C(1s)/Sn(3d 5/2) ratios for the esterified surfaces, the Si(2p)/Sn(3d 5/2) ratios for the gas-phase silanized surfaces, and the N(1s)/Sn(3d 5/2) ratio for triazine-linked surfaces was consistent with greater than single monolayer coverage in **11-19** but with only partial coverage (5-15%) in **9** and **10**. The expected reduction peak was completely absent in a cyclic voltammetric scan of plates of the type **9** in CH₃CN. A very weak, very broad reduction peak, present in **10**, was accompanied by a very weak fluorescence, in sharp contrast to the more easily observed emission and the cyclic voltammetric reversible reduction observed when a pretreated plate was dipped into a 10⁻² M solution of **2a** in THF and allowed to dry at 100 °C (Figure 1).

Electrodes **12**, **13**, **15**, **17**, and **19** all exhibited the expected oxidation and reduction peaks expected for substantial coverage. A typical cyclic voltammogram for electrodes with Sn-O-Si-Ar (**15a**) and the cyanuric chloride linkages (**19d**) are shown in Figures 2 and 3, respectively. The properties of these modified electrodes were also examined by measuring the potential required for the onset of photocurrent in the absence of electroactive species (Table I).

Discussion

Electrochemistry of Arene Derivatives. The substitution of keto ester, trialkoxysilane, or cyanuric chloride derivatives appeared to have little effect on the reduction potential of the

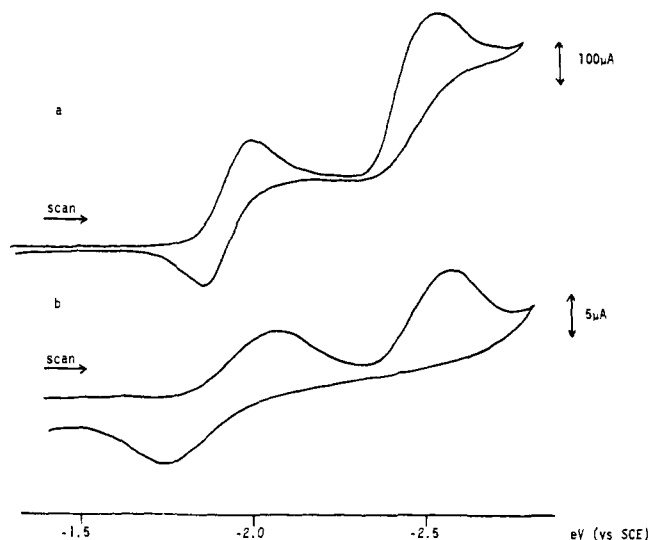


Figure 1. Cyclic voltammograms of anthryl keto ester derivatives: (a) **2a**, CH₃CN, 0.1 M TBAP, Pt, room temperature; (b) **10**, CH₃CN, 0.1 M TBAP, room temperature. Reference: standard calomel electrode (SCE). Scan rate: 500 mV/s.

substituted arene or the stability of the radical anion so produced. As is shown in Table II and in Figures 1-3, a comparison of the observed cyclic voltammograms for several arenes and their appropriate derivatives shows nearly identical electrochemical behavior. When these derivatives are chemically attached to a tin oxide semiconductor, the reductive waves become broadened and their reversibility diminishes. These effects derive from the reduced rate of electron transfer at the semiconductor compared with those observed at metallic electrodes. Similar behavior has been observed by Murray¹⁸ in the reduction of attached molecules. We assume, therefore, that the electrochemical behavior of attached arenes may often be predicted from that observed in the parent, unsubstituted arene.

Chemical Stability of Model Arenes. Anthryl keto ester **2a** (a crude model for electrodes **9**, **10**, **12**, and **13**) can be reversibly reduced on an electrochemical time scale. Although preparative electrolysis does lead to reduction products, the cyclic voltammetry results suggest that the radical anions of these derivatives are stable on a CV time scale. The observed photoreactions for this model compound only include inefficient

Table II. Comparison of the Electrochemistry of Some Arene Derivatives

compd	E_{pc}	conditions	ref
	-2.50 (rev)	DMF, 0.1 M TBAP, Pt	19
6	-2.5 (rev)	DMF, 0.1 M TBAP, Pt	
15a	-2.5 (rev)	DMF, 0.1 M TBAP	
	-1.90 (rev)	DMF, 0.1 M TBAP, Pt	19
2a	-1.95 (rev)	CH ₃ CN, 0.1 M TBAP, Pt	
10	-2.55 (irrev)		
13	-2.0 (q-rev)	CH ₃ CN, 0.1 M TBAP	
	-2.5 (irrev)		
15b	-2.0 (irrev)	CH ₃ CN, 0.1 M TBAP	
	-2.0 (rev)	CH ₃ CN, 0.1 M TBAP	
	-2.5 (irrev)		
	-1.55 (irrev)	DMF, 0.1 M TBAP, Pt	
	-0.71 (vs. Ag/AgCl)	DMF, 0.1 M TEA1, Pt	20
	-1.31 (in DMF)		
7	-0.21 (vs. Ag/AgCl)	70% EtOH, 0.1 M TBAP, Pt	21
	-0.63 (rev)		
	-1.27 (rev)		
19d	-1.63 (irrev)	THF, 0.1 M TBAP, Pt	
	-0.9 (q-rev)		
	-1.4 (q-rev)		
	-1.8 (irrev)	CH ₃ CN, 0.1 M TBAP	

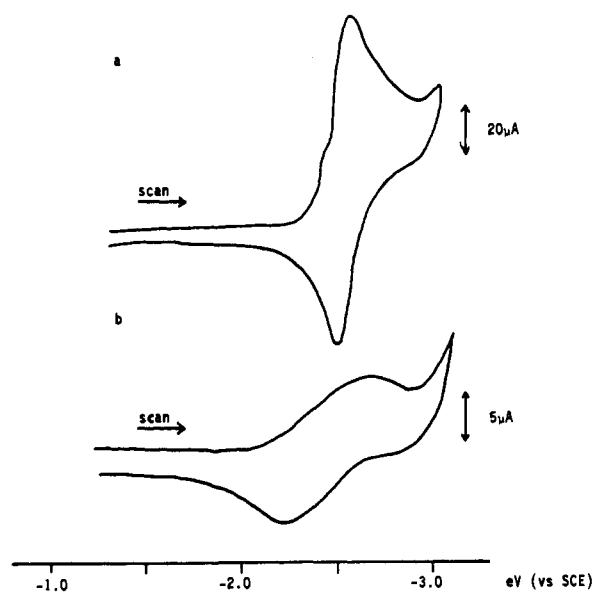


Figure 2. Cyclic voltammograms of naphthyltrialkoxysilane derivatives: (a) **6**, DMF, 0.1 M TBAP, Pt, room temperature; (b) **15a**, DMF, 0.1 M TBAP, room temperature. Reference: SCE. Scan rate: 500 mV/s.

photodimerization from the singlet excited state. Since even this inefficient reaction could not be sensitized, the triplet should persist long enough to allow for participation in the photogalvanic mode.

Similarly, the reversibility of the reduction of **5** or **6** by cyclic voltammetry and the lack of reactivity upon triplet sensitization suggest that the electrodes **15** and **17**, which **5** and **6** model, may participate in photogalvanic cells without appreciable diverting side reactions. That **7** undergoes only quasi-reversible reduction and fairly efficient photodecomposition suggests that long-term stability may be a problem for electrodes **19**.

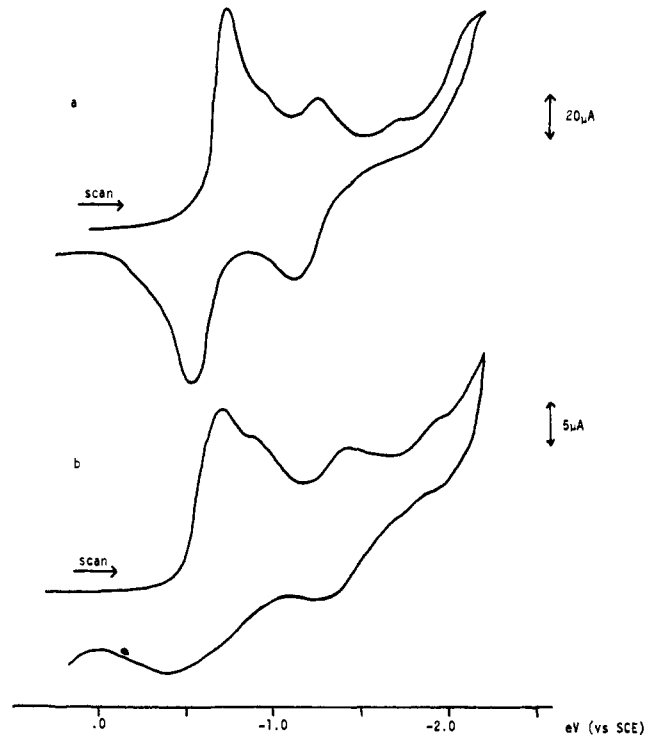


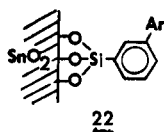
Figure 3. Cyclic voltammograms of aryltriazine derivatives. (a) **7**, THF, 0.1 M TBAP, Pt, room temperature; (b) **19d**, THF, 0.1 M TBAP, room temperature. Reference: SCE. Scan rate: 500 mV/s.

Covalent Modification of Tin Oxide Electrodes. Esterification³⁻⁵ (for **9** and **10**), silanation^{6,13,14} (for **11-17**), and triazine coupling^{15,16} (for **18** and **19**) were employed as methods for covalent attachment of substrates with potential photo- or electroactivity. Although the first method has been shown to be effective in attaching rhodamine **B** directly to a semicon-

ductor surface to give modified electrodes with improved photoelectrochemical properties,^{4,5} esterification has proved, in our hands, a less effective method for attachment of carboxylic acid derivatives than silanation/amidation. Although our failure to achieve high coverages of the tin oxide surface with **20** can be attributed to steric hindrance by the 1- and 8-peri hydrogens, this acid having required rigorous conditions for solution-phase esterification,²² the incomplete coverage of the tin oxide surface by the sterically more accessible carboxylic acid **2b** is more troublesome. The success of surface esterification may depend subtly on the presence of other functional groups in the molecule to be attached. For example, while rhodamine B can be effectively attached by esterification, fluorescein, a close structural analogue, resists this type of covalent attachment.²³

Furthermore, esterified surfaces are apparently easily solvolyzed since the amount of covalently attached material was much lower if water or ethanol were used as solvent in the Soxhlet extraction of extraneous arene than if benzene or THF were so employed. The stability of the esterified electrodes was also much less than that of the silanized modification, possibly because of hydrolysis during photogalvanic operation. Sufficient esterification was apparently achieved nonetheless to make observable small effects on the photostability of electrodes **9** and **10** in photogalvanic operation with RhB/HQ²⁴ and esterification may well be the technique of choice for the attachment of certain special substrates.

In contrast, silanation has proved to be an effective, versatile method for the covalent attachment of arenes. The synthesis of **11**, which has been described previously by several other groups,^{14,15} presumably proceeds by nucleophilic attack by the oxide or hydroxy surface groups present after pretreatment of the semiconductor on the trihalo- or trialkoxysilane. One, two, or three O-Si linkages, indistinguishable by our analytical techniques,²⁵ may therefore join the carbon chain to the semiconductor. The conversion of **14** to **15** by treatment of aryllithium could proceed by nucleophilic substitution (if the number of O-Si bonds is one or two) or by coupling by a silyl radical. The attachment of aryllithiums to **16** may occur by conventional aromatic nucleophilic substitution. Our analytical procedure would not distinguish **17** from the isomeric **22** which



might be also expected if a benzyne mechanism for the arylation occurs.

We have found, however, that the technique employed for the initial silylation step can profoundly affect the properties of a modified electrode in a photogalvanic cell. In our hands, silanation achieved in the gas phase by the Haller method¹⁴ gives reproducible, evenly distributed coverage while that achieved in even dilute solution gives partially polymerized silane surfaces. The uniformity in the surface coverage of the gas-phase silanized electrodes could be demonstrated by ESCA or by visual inspection of the transparent electrodes. The inhomogeneity of coverage in the solution-phase silanized electrodes could easily be seen as thickened, opaque areas on the electrode surface. This surface polymerization also affects redox reactions occurring on the modified electrode. For example, the hydroquinone-benzoquinone redox couple is quasi-reversible on unmodified SnO₂ or on gas-phase-prepared **11** but is nearly completely irreversible on **11** prepared in solution. Analogous results are observed at electrodes **12-14**. Solution-phase polymerization in the silanation process was less significant when aryl silylating reagents were used. Thus, **15a** prepared via gas-phase-synthesized **14** or via solution-

phase silylation with **5** gave electrodes with nearly identical ESCA spectra.

The synthesis of **18** and the attachment of amines are unprecedented,^{16,26} although **19c** and **19d** are newly prepared. As in analogous cases, effective coverage was indicated by all analytical techniques. The triazine linking agent is apparently less susceptible to surface polymerization than are the silylating reagents. This allows effective monolayer coverage to be achieved with conventional solution phase attachment methods.

Spectroscopy of Covalently Attached Molecules. The optical properties of attached molecules differ somewhat from those observed from solution-phase solute molecules. Covalently attached keto anthracene **13**, for example, exhibits its long-wavelength absorption band at 392 nm while **2a**'s long wavelength maximum occurs at 385 nm. Similarly, the fluorescence emission maxima of **13** and **2a** differ by 10 nm. Nonetheless, the approximate position of the antibonding orbitals populated by excitation or electron transfer will be independent of the state of attachment unless the attachment process leads to new aggregation (excimer, etc.) or ground-state complexation phenomena. In **15c**, for example, where strong redox waves attributable to pyrene can be observed, the fluorescence spectrum shows two broad peaks: one near the position expected for monomer emission (395 nm) and a weaker second band at 478 nm consistent with excimer emission. This latter shows that the covalently attached pyrene differs in geometry from adsorbed pyrene²⁷ and that intramolecular interactions between attached molecules may be expected. Since orientation effects in redox reactions of electroactive species at covalently modified electrode surfaces have been noted,²⁸ this altered bonding geometry may also contribute to the differences in photoelectroactivity at covalently attached and physically adsorbed surfaces.²⁴

The effect of covalent attachment on excited-state lifetime is unknown. While fluorescence quenching by metal ions is well documented,²⁹ enhanced excited-state lifetimes in molecules adsorbed on polar solids are also known. For example, for pyrene adsorbed on porous glass a nearly 100-fold increase in triplet lifetime in the adsorbed state was observed.³⁰

Although the solution-phase fluorescence lifetimes of model compounds can be easily measured by picosecond laser spectroscopy, the fluorescence signals from modified electrodes **9-19** are too weak for lifetime determination with a mode locked Nd-Yag laser coupled to a Hamamatsu streak camera.^{31,36}

Physical Properties of the Semiconductor in Modified Electrodes. The valence and conduction bands of semiconductor material can be determined by differential capacitance measurements³² or by potential for onset of photocurrent and by wavelength dependence for initiation of photovoltaic effects at the semiconductor.³³ When the conduction band position is measured by the latter technique, our surface modifications apparently cause some minor alteration in the position of the conduction band edge (Table 1); i.e., the interface energetics seem to be somewhat changed by derivatization. Our modifications may indicate a lower doping level at the semiconductor surface, however.^{6,34}

Conclusions

Covalent attachment of arene derivatives to tin oxide semiconductor surfaces can be achieved directly (by esterification or silanation) or indirectly by employing a linking agent (3-aminopropyltriethoxysilane, tetrachlorosilane, or cyanuric chloride). The reduction potential of the attached arenes is largely unaltered by the attachment, although cyclic voltammetric waves attributable to the attached arenes are significantly broadened. This result implies that such modified electrodes may function as effective mediators of electron

transfer from appropriate solution donors. The absorption maximum of covalently attached molecules is slightly shifted compared with dissolved model compounds.

Experimental Section

Materials. Benzene was heated overnight under reflux over lithium aluminum hydride and was deaerated by two freeze-pump-thaw cycles. Methanol and ethanol were distilled from concentrated H₂SO₄ and stored over molecular sieves. THF was distilled from sodium benzophenone ketyl. Acetonitrile was purified by repeated vacuum distillation from phosphorus pentoxide.

Analytical Instrumentation. Ultraviolet and visible spectra were obtained on a Cary 14 spectrophotometer. Mass spectra were obtained on a Du Pont 21-471 spectrometer. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Perkin-Elmer R-12 or a Varian A-60 instrument. Gas-liquid chromatography (GLC) was conducted on a Varian 920 gas chromatograph. Infrared (IR) spectra were recorded on a Beckman Acculab-7 or an IR-5A instrument. Corrected front-face fluorescence spectra were measured on a Spex Fluorolog spectrofluorometer. Phosphorescence spectra were obtained on a previously described phosphorimeter.³⁵ Fluorescence lifetimes were measured on a mode locked neodymium-Yag laser coupled with a Hamamatsu streak camera.³⁶ Electrochemical experiments were conducted with a PAR Model 173 potentiostat, a Model 179 digital coulometer equipped with positive feedback for *iR* compensation, a Model 175 universal programmer, and a Houston Instrument X-Y recorder. ESCA measurements were made with a Physical Electronics Model 548 electron spectrometer with a magnesium or aluminum K α source.

General Procedure for Cyclic Voltammetry (CV). Cyclic voltammetric measurements were obtained in a vacuum-tight three-compartment electrochemical cell with either a silver wire quasi-reference electrode or a standard calomel electrode/agar bridge isolated from the test solution by a fine porosity frit. The potential of the quasi-reference was determined following each series of experiments by adding benzoquinone and observing its known redox potentials. The working electrode for cyclic voltammetry was a platinum disk with an area of 0.05 cm² or a tin oxide pretreated plate (see below). A platinum wire was used as the counter electrode. For preparative reduction, a platinum foil electrode (1 × 1 cm) was used as the working electrode. Metal electrodes were polished before each use with 0.5- μ alumina polishing powder. Semiconductor plates were washed with distilled water and heated overnight under vacuum before use. Electrolytes were dried by heating overnight (100 °C, 1 × 10⁻³ mm) under high vacuum in the evacuated electrochemical cell. A background CV was taken of the solvent-electrolyte system before each experiment to ensure the absence of residual oxygen and electroactive trace contaminant.

Synthesis and Properties of Derivatizing Agents. 2a. Adipic acid monomethyl ester (16 g, 100 mmol) was added to a solution of 20 mL of thionyl chloride in 200 mL of dry benzene. The resulting solution was heated at 40 °C under N₂ for 4 h. The excess thionyl chloride was removed under vacuum and the residue was taken up in 200 mL of freshly distilled *sym*-dichloroethylene. Anthracene (30 g, 168 mmol) and anhydrous aluminum chloride (20 g) were added and the resulting suspension was stirred at 0 °C for 2 h and then at room temperature for 3 h. The mixture was poured onto ice and the neutral fraction was extracted with toluene. The solvent was removed under vacuum and the residue was chromatographed on alumina (Skelly B/ether eluent). The major fraction (**1a**, 60%) was a yellow solid, mp 64 °C (recrystallized from Skelly B/ether). A small amount (5%) of **2b** (see below) could also be detected. **2a** could be hydrolyzed nearly quantitatively to **2b** by heating under reflux in a 1:1:1 mixture of toluene-methanol-2 N NaOH for 4 h. On neutralization the acidic fraction gave a yellow powder (**2b**), mp 150–152 °C (recrystallized from CH₂Cl₂). **2c** was prepared by stirring a mixture of **2b** with a twofold excess of SOCl₂ for 3 h at 30–40 °C. After the excess SOCl₂ was distilled off under vacuum, the crude product was used directly. **2a**: ¹H NMR (CCl₄) δ 1.7 (m, 4 H), 2.3 (t, *J* = 7 Hz, 2 H), 2.9 (t, *J* = 7 Hz, 2 H), 3.6 (s, 3 H), 7.15–8.15 (m, 7 H), 8.3 (s, 1 H), 9.3 (s, 1 H); IR (CCl₄) 3.3, 3.45, 5.75, 5.95, 6.55, 7.0, 8.4, 11.4 μ ; λ_{\max} 385 nm (ϵ 6100), 365 (60 000), 255 (96 500), 240 (35 000); mass spectrum *m/e* 143, 177, 205, 243, 289, 320 (M⁺). Emission: see text. Anal. (C₂₁H₂₀O₃) C, H.

3a. 9-Anthrylmagnesium bromide³⁷ (17 g, 60 mmol) suspended in 150 mL of anhydrous Et₂O was slowly added dropwise to a cooled

(0 °C) solution of adipic acid monomethyl ester monoacid chloride (19 g, 100 mmol) in 150 mL of Et₂O. After the addition was complete, the precipitate which had formed was broken up with a spatula, and the resulting suspension was heated under reflux for 3 h. The suspension was then cooled to room temperature and poured onto ice. After neutralization with dilute H₂SO₄, the aqueous layer was extracted with ether. The residue obtained upon stripping solvent was purified by chromatography on Florisil (Skelly B eluent) giving 1.6 g (10%) of **3a**: mp 62–65 °C; ¹H NMR (CCl₄) δ 1.7–2.1 (m, 4 H), 2.3 (t, *J* = 7 Hz, 2 H), 2.9 (t, *J* = 8 Hz, 2 H), 3.78 (s, 3 H), 7.3–8.0 (m, 8 H), 8.4 (s, 1 H); IR (CCl₄) 3.3, 3.45, 3.52, 5.75, 5.90, 7.00, 7.35, 8.5, 11.4 μ ; mass spectrum *m/e* 143, 177, 205, 243 289, 320 (M⁺). Anal. (C₂₁H₂₀O₃) C, H.

Photolysis of 2a. Direct. A solution of 50 mg of **2a** in 100 mL of spectral grade cyclohexane was degassed and transferred under Ar to a sealed quartz flask. Upon irradiation for 22 h with low-pressure mercury arcs (254 nm) in a Rayonet photochemical reactor, about 50% disappearance of **2a** had occurred. Chromatography on silica gel (Skelly B/ethyl acetate) gave a nonfluorescent product mixture (mp 200–210 °C) whose mass spectrum was identical with that of **2a**. ¹H NMR revealed at least four distinct OMe singlets.

Sensitized. After photolysis for 8 h of a degassed mixture of 50 mg of **2a** in 50 mL of Et₂O containing 60 mg of benzil, pyrene, or eosin with long-wavelength UV light (phosphor-coated low-pressure mercury arcs (black light)) with λ_{\max} at 350 nm for 8 h in a Rayonet photochemical reactor, or after photolysis of 50 mg of **2a** in 10 mL of dry degassed acetone at 310 nm for 8 h, nearly quantitative recovery of **2a** could be obtained.

Cyclic Voltammetry of 2a. Cyclic voltammetric scan for **2a** in anhydrous CH₃CN containing 0.1 M tetrabutylammonium perchlorate (TBAP) revealed a reversible reduction wave on Pt at -1.95 eV (vs. SCE) and a nearly irreversible wave at -2.55 eV (vs. SCE); scan rate 100 mV/s, room temperature.

Electrochemical Reduction of 2a. One-electron preparative reduction of **2a** (75 mg, 0.3 mmol) in CH₃CN containing TBAP was conducted on Pt at -2.1 eV vs. SCE. The resulting mixture was washed with water and extracted with Skelly B. The combined organic extracts were stripped of solvent. Analysis by thin layer chromatography (silica gel/Skelly B) revealed a complex mixture. The major fractions, separated by column chromatography on silica gel (Skelly B/ethyl acetate), were shown by spectra properties to be anthracene and a compound tentatively identified as **4**, which could be prepared independently by subjecting **2a** to Clemmensen reduction conditions (5 g of Zn, 1 g of HgCl₂, 1 mL of concentrated HCl, 20 mL of H₂O, reflux 4 h). **4**: ¹H NMR (CDCl₃) 1.4–2.4 (m, 8 H), 3.1 (t, *J* = 8 Hz, 2 H), 3.7 (s, 3 H), 7.0–8.1 (m, 6 H), 8.4 (s, 1 H), 8.6 (s, 1 H); IR (CDCl₃) 1735 cm⁻¹; mass spectrum *m/e* 306 (M⁺).

1-Naphthyltrichlorosilane (5). **5** was prepared by the method of Adrianov et al.¹² white solid, mp 50 °C dec; *m/e* 162, 189, 191, 225, 227, 260 (M⁺), 262, 264. Cyclic voltammetry of distilled **5** gave waves at -0.48 and -2.55 eV (vs. SCE) (DMF, 0.1 M TBAP, Pt, room temperature).

1-Naphthyltriethoxysilane (6).¹³ To 1.5 g (6 mmol) of **5** in 3 mL of THF was added 3 mL of absolute ethanol containing 1.4 g (18 mmol) of pyridine. The mixture was stirred vigorously in a cooling bath for 2 h, as a white precipitate settled. Removal of solvent from the organic layer gave crude **6**: *m/e* 290 (M⁺); CV *E*_{pc} -2.52 eV (vs. SCE) (DMF, 0.1 M TBAP, Pt, room temperature).

Photolysis of 5 and 6. Three identical fractions of a solution (1 × 10⁻² M) of **5** or **6** in tetrahydrofuran were prepared and purged with argon for 10 min. One solution was irradiated in a quartz test tube under Ar for 30 min in a Rayonet photochemical reactor equipped with 16 low-pressure mercury lamps. The second fraction was made 0.05 M in pyrene and irradiated with phosphor-coated (350 nm) low-pressure mercury arcs in a Rayonet photochemical reactor for 35 min. The third fraction was not irradiated and served as a control for the quantitative analysis of **5** under the reaction conditions. The reactions were stripped of solvent and analyzed by low-resolution mass spectrometry and/or GLC (1/4 in. × 5 ft 15% OV-101 on 100/120 mesh Chromosorb G, 200 °C).

7. To a solution of cyanuric chloride (131 mg, 0.7 mmol) in 25 mL of anhydrous THF was added a solution of the potassium salt of 1-hydroxyanthraquinone (159 mg, 0.7 mmol) in 100 mL of THF. The resulting mixture was stirred for 2.5 h at room temperature under a stream of argon and then heated to reflux for an additional 2-h period. The resulting solution was stripped of solvent and the residue was

taken up in water. After removal of solvent from the organic layer, pale yellow solid, mp 270–275 °C dec, was obtained: mass spectrum *m/e* 336, 371, 373 (M⁺); IR (CHCl₃) 1690, 1540, 1420, 1330, 1310, 1290, 890, 860 cm⁻¹. Cyclic voltammetry of crude **7** (0.1 M TBAP, THF, Pt, room temperature) showed a quasi-reversible reduction wave at -0.63 and -1.27 eV (vs. SCE).

Photolysis of 7. Photolysis of a solution of 10 mg of **7** in 20 mL of THF under Ar for 2 h with low-pressure mercury arcs in a Rayonet photochemical reactor led to nearly complete disappearance of **7**. Sensitized photolysis of a solution of 10 mg of **7** in 20 mL of acetone under Ar for 2 h with phosphor-coated low-pressure mercury lamps (λ_{\max} 300 nm) also led to nearly complete disappearance of **7**. In neither photolysis was the complex product mixture analyzed.

8. To a solution of 2-aminoanthraquinone (0.30 g, 1.3 mmol) in 40 mL of anhydrous THF was added potassium *tert*-butoxide (0.15 g, 1.3 mmol). The resulting solution was stirred at room temperature for 10 min before the addition of cyanuric chloride (0.25 g, 1.4 mmol). The mixture was stirred for an additional 5 min and the solvent removed. The residue was washed with water, recrystallized from benzene, and dried under vacuum, giving a brown solid: mp >300 °C; mass spectrum *m/e* 370, 372 (M⁺); IR (CHCl₃) 3400 (Br), 1690, 1550, 1530, 1505, 1300, 1250, 1205 cm⁻¹. Crude **8** exhibited quasi-reversible reduction waves (THF, 0.1 M TBAP, Pt, room temperature) at -0.83 and 1.55 eV (vs. SCE).

Pretreatment for Unmodified Electrodes (21). A large sheet of antimony-doped SnO₂-coated glass (NESA:PPG Industries) was cut in 1/2 in. X 2 in. plates. The plates were washed with Alconox detergent, successively soaked for 15 h in Skelly B and concentrated aqueous NaOH, and extensively rinsed with doubly distilled water before overnight drying in a vacuum oven at 100 °C. All comparative measurements of relative photocurrents were obtained on electrodes cut from the same large sheet.

9. Pretreated SnO₂ plates were used as obtained above or further soaked in 1 M HCl before the final rinse and drying. The plates were suspended in a 1% solution of the derivatizing agent in dry, deaerated benzene. The solutions were suspended in an ultrasonic bath at room temperature for 30 min and/or heated to reflux under N₂ for 6 h. The electrodes so obtained were transferred to a Soxhlet extraction apparatus containing fresh portions of the reaction solvent. After the plates were extracted with refluxing solvent overnight, the electrodes were suspended successively in dry benzene, ethanol, and water for 10-min periods in an ultrasonic bath, following by repeated rinsing, to remove any non-covalently-attached arene. The electrodes so obtained were characterized by measurements of fluorescence, redox potentials, and/or ESCA (see text).

A. Esterification via Carboxylic Acid. 9-Anthracenecarboxylic acid (**20**, 110 mg, 0.5 mmol) was dissolved in 100 mL of dry benzene containing 200 mg (1 mmol) of DCC. Three pretreated electrodes were added and the resulting mixture was heated under reflux for 15 h with intermittent (10 min) vibration in an ultrasonic bath.

B. Esterification via Acid Anhydride. **20** (110 mg, 0.5 mmol) was dissolved in 100 mL of dry benzene containing 1.5 mL of trifluoroacetic anhydride. The acid dissolved after gentle warming under Ar. Three pretreated electrodes were immersed in the solution which was heated under reflux for 15 h.

C. Esterification via Acid Chloride. **20** (110 mg, 0.5 mmol) was dissolved in 25 mL of dry benzene containing 5 mL of thionyl chloride. The solution was stirred overnight at room temperature. The excess thionyl chloride was removed by vacuum distillation and the residue was taken up in fresh dry benzene. Three pretreated electrodes having been immersed, the resulting solution was heated under reflux for 15 h with intermittent (10 min) vibration in an ultrasonic bath.

10. With **1b** replacing **20**, the above procedures for esterification were employed.

11. The solution-phase preparation of **11** was conducted by the method of Murray et al.¹⁵ Vapor-phase preparation of **11** was conducted by the method of Haller.¹⁴

12 and 13. Electrodes **11** were suspended in a solution of **2b** (60 mg, 0.2 mmol) or **20** (45 mg, 0.2 mmol) in 25 mL of dry pyridine containing dicyclohexylcarbodiimide (50 mg, 0.25 mmol). The mixture was vibrated under a N₂ stream in an ultrasonic bath at 40 °C for 2 h and heated under reflux for an additional 1 h. The plates were rinsed in pyridine, ethanol, and water and evacuated overnight under high vacuum.

15. Electrodes **14**, prepared by the Haller method¹⁴ with freshly distilled tetrachlorosilane replacing 3-aminopropyltriethoxysilane,

were suspended in a solution of 1-naphthylmagnesium bromide¹² (0.4 mmol based on quantitative conversion of 1-bromonaphthalene), 9-anthryllithium³⁷ (0.4 mmol based on quantitative conversion of 9-bromoanthracene), or 1-pyrenyllithium³⁸ in 25 mL of THF from 0.4 mmol of 1-pyrenyl bromide. The mixture was vibrated under a N₂ stream in an ultrasonic bath at 100 °C for 4 h. The solution was then neutralized with saturated aqueous NH₄Cl and the resulting electrodes (**15a**) were repeatedly rinsed with ethanol before overnight evacuation under high vacuum.

Alternately, **15a** could be synthesized by vibrating a pretreated electrode in a solution of **5** in THF (10⁻² M) for 1 h and then allowing the electrode to soak overnight in the reaction mixture.

16. Pretreated SnO₂ electrodes were suspended in a solution of *p*-bromophenyltrichlorosilane (58 mg, 0.2 mmol) in 25 mL of THF. The mixture was vibrated in an ultrasonic bath under Ar for 2 h and left in contact overnight. The modified plates were rinsed with THF, ethanol, and water and evacuated overnight under high vacuum.

17. Electrodes **16** were immersed in a solution of 9-anthrylmagnesium bromide (0.2 mmol) in 25 mL of THF and heated under reflux overnight. The solution was then treated with 5 mL of saturated aqueous NH₄Cl and the electrodes were washed with THF, ethanol, and water before evacuation overnight.

19. Electrodes **18**, prepared by the method of Kuwana et al.,¹⁷ were suspended in 25 mL of THF containing the potassium salt of 1-hydroxyanthraquinone (0.2 mmol) or in 25 mL of pyridine containing 2-aminoanthraquinone. The mixture was vibrated for 2 h in an ultrasonic bath under a stream of nitrogen before overnight evacuation.

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Chemically Modified Electrodes in Dye-Sensitized Photogalvanic Cells

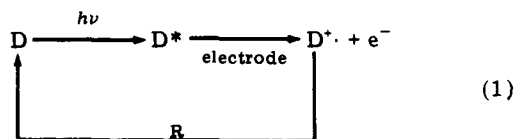
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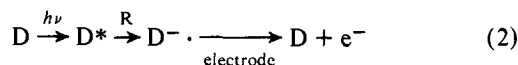
Abstract: The photocurrents observed when arene-derivatized electrodes are used as anodes in an aqueous rhodamine B-hydroquinone photogalvanic cell are consistent with electron injection into the semiconductor from either an excited state or a reduced photoproduct. The attached molecules presumably function as energy or electron relays. The derivatized electrodes are more stable in long-term operation than is the parent tin oxide electrode.

Introduction

Current understanding¹⁻⁸ of the function of dye-sensitized semiconductor photoelectrochemical cells allows for two possible modes for the production of photocurrent. In the first, a dye molecule D is excited to a state from which electron transfer to the anode occurs readily (eq 1).⁹ The oxidized dye

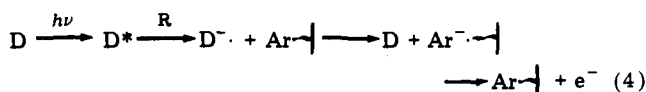
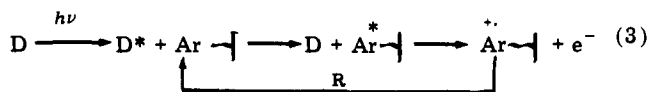


is subsequently reduced by a reductant R to regenerate the dye. In the second, an excited dye molecule accepts an electron from the reducing agent. This reduced species injects an electron, giving rise to an oxidative photocurrent.^{10,11}



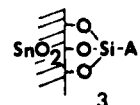
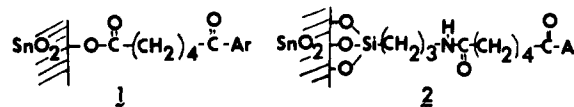
In either model, the efficiency of current production should depend significantly on several factors: (1) a long lifetime for the sensitizer excited state; (2) the chemical stability of the radical anion which functions as the electron source in the presence of supersensitizers; and/or (3) the disposition of the photo- or electroactive molecule at the semiconductor surface.

Our recent synthesis of several families of covalently modified tin oxide electrodes¹² makes available several modified surfaces in which the possibility of analogous surface-mediated energy or electron transfer can be tested. We hoped to examine whether a semiconductor electrode surface, modified by the near-monolayer attachment of an appropriate arene, could be converted to an excited state (eq 3) or a radical anion (eq 4) of the attached arene by energy or electron transfer from a dye sensitizer. The triplet energies and the reduction potentials of

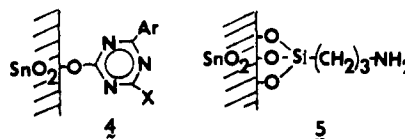


the dye and arene would be critical for operation of either mechanism.

Since the production of photocurrent at a SnO₂ electrode in the presence of rhodamine B (RhB) with hydroquinone (HQ) as supersensitizer has been previously studied, we chose RhB as a sensitizer for our modified electrodes 1-4.¹² The relevant triplet energies and the reduction potentials of these arenes are listed in Table 1.



a: Ar = 1-naphthyl
b: Ar = 9-anthryl
c: Ar = 1-pyrenyl
d: Ar = 1-hydroxyanthraquinone
e: Ar = 2-aminoanthraquinone



For efficient triplet energy transfer to an attached arene, the triplet of that arene must lie at lower energy than that of the sensitizing dye. Similarly, efficient electron transfer from a photoreduced radical anion of the dye can occur only if the reduction potential of the acceptor is less negative than that of the donor. Perusal of Table 1 demonstrates that anthracene and anthraquinone derivatives possess respectively a lower triplet energy and a less negative reduction potential than RhB. Neither naphthalene nor anthracene, both of which possess higher lying triplet states and less easily formed radical anions than RhB, should mediate photocurrent production by energy or electron transfer. Thus, triplet RhB may sensitize simple anthracene derivatives by energy transfer, while RhB^{·-} may transfer an electron exothermically to simple anthraquinone derivatives. If derivatization and attachment do not dramati-