Covalently-Linked Cyclooctatetraenyl Dianions as Sensitizers in Photoelectrochemical Cells

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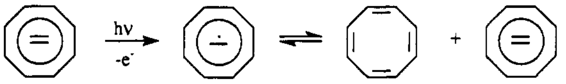
Many efforts to employ organic molecules as sensitizers[1] to induce a photoelectrochemical response in large band gap semiconductor electrodes have been thwarted by either the proposed sensitizers' lack of strong absorption in the visible region or by their relatively high oxidation potentials. Accordingly, the metal oxide–sensitizer systems which so far have been reported to enjoy the highest efficiency have typically involved metal complexes[2] or metalloporphyrins[3] either covalently bound or strongly physisorbed to large area semiconductor dispersions. Several years ago we showed that these limitations could be at least partially overcome by employing the cyclooctatetraenyl dianion **1** either as an adsorbate[4] or as a covalently bound sensitizer[5] at the surface of a titanium dioxide or tin oxide electrode. Upon photoexcitation, **1** is known to eject an electron,[6] producing a radical anion whose disproportionation equilibrium is highly dependent on both solvent and associated cation.[4,7] Because this disproportionation is governed by the rate of the conformational change occurring as the planar radical anion is converted to the tub-shaped neutral, this reaction, eq 1, provides a means for avoiding both the energy-dissipative electron recapture at the surface of the irradiated electrode and the numerous chemical side reactions which often characterize singly oxidized organic intermediates. As a result, **1** proved to be a reasonably effective sensitizer for producing a photogalvanic response in an electrochemical cell.[4,5]



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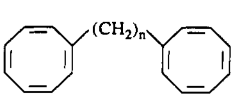
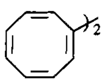
(1)

In order to explore whether this photoresponse, i.e., the critical disproportionation, might be improved by constraining two such sensitizer units to a single molecule, we have examined the electroreduction of a series of covalently bridged bis(cyclooctatetraenyls) **2–4**[8] to determine whether this hydrocarbon link would pemit significant perturbation of their electrochemical behavior. We then compare the utility of their dianions with those of **1**, bis(cyclooctatetrenyl) **5**,[9] and perfluorotetrakiscyclobutacyclooctatetraene **6**[10] as sensitizers in photoelectrochemical cells.



2: n = 1
3: n = 2
4: n = 3



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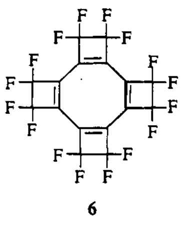

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Table I. Reduction Peak Potentials[a] for Several Derivatized Cyclooctatetraenes

compd	E_p (V vs SCE)	solvent
1	−1.62, −1.82[12a]	DMF
	−1.62, −1.86[this study]	DMF
2	−1.62 (2e), −2.05, −2.45	DMF
	−1.73, −1.86, −2.12 (2e)	HMPA
3	−1.66 (2e), −1.78, −1.86	DMF
	−1.72, −1.85, −2.07 (2e)	HMPA
4	−1.68 (2e), −1.82, −1.88	DMF
	−1.88 (2e), −2.08 (2e)	HMPA
5	−1.66 (2e), −2.32, −2.56[9]	DMF
	−1.68 (2e), −2.40, −2.60[this study]	DMF
6	+0.79, +0.14[10]	DMF

[a] Measured as cyclic voltammetric peak maxima for 0.01 M solutions in dry degassed DMF or HMPA (1 mM) containing 0.1 M tetrabutylammonium perchlorate as inert electrolyte. At room temperature under argon; scan rate 100 mV/s.

Table II. Relative Sensitization Efficiencies for the Production of Anodic Photocurrent[a] in an Indium Tin Oxide Electrochemical Cell Induced by Visible Excitation of Several Substituted Cyclooctatetraenyl Dianions

precursor to the sensitizer dianion	anodic photocurrent (±0.2 μA/cm²)	relative sensitization efficiency
1	2.62	1.00
2	2.78	1.06
3	2.84	1.08
4	2.75	1.05
5	3.02	1.16
6	2.30	0.88

[a] Measured under argon at constant light flux from a water-filtered 300-W tungsten lamp in a previously described photoelectrochemical cell.[5] Sensitizer was generated by exhaustive chemical or electrochemical reduction of the 0.002 M COT derivative (0.004 M for **1** and **6**) in rigorously dried THF containing 0.1 M tetrabutylammonium perchlorate. Reported values are an average of three separate determinations.

The bis(cyclooctatetraenyl)alkanes **2–4** were prepared by coupling cyclooctatetrenylmagnesium bromide with the corresponding α,ω-dibromoalkane.[11] The cyclic voltammogram of **2** in dry, degassed dimethylformamide containing tetrabutylammonium perchlorate as inert electrolyte was virtually identical to that reported previously for the parent bis(cyclooctatetrene) **5**.[9] This observation indicates appreciable electronic interaction between the two rings, as is consistent as well with our previous report of

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strong electronic coupling evidenced by the electron spin resonance spectrum of **2**.[11] In contrast, the cyclic voltammograms of **3** and **4** were very similar to that of cyclooctatetraene **1**,[12] indicative of the presence of predominantly electronically isolated rings, differing only in that the second wave was slightly split. The observed reduction potentials for these substrates are summarized in Table I.

Complete reduction of **1**–**6** could be achieved either by treatment with a 4-fold excess of either sodium or potassium metal in tetrahydrofuran or, more conveniently, by coulometrically monitored electrochemical reduction at a potential approximately 150 mV cathodic of the most negative reductive wave observed by cyclic voltammetry. A solution of each of the fully reduced substrates in dry, degassed DMF was then transferred to the previously described electrochemical cell.[5] Upon irradiation of the di- or tetraanion by a IR-filtered tungsten lamp ($\lambda > 400$ nm) of a thin, but opaque, layer (ca. 5-mm thick) of solution interspersed between a clean[13] indium tin oxide electrode and a Pyrex optical flat, an anodic photocurrent was observed. The magnitude of the observed photocurrent sensitized by **1**–**6** under constant light flux, obtained by correcting the observed current for the respective dark response, is listed in Table II.

The quantum efficiency for photocurrent sensitization (ca. 10^{-2}%) is significantly lower for this series than has been reported recently by Grätzel and co-workers for sensitization by several Ru(bpy)$_3$ derivatives.[2a] The similarity of the photocurrents observed in **1**–**6** implies a comparable mechanism for photocurrent production throughout the series, probably in each case involving photoinduced electron injection from an anionic excited state into the indium tin oxide conduction band.[5] Apparently the electronic interaction between rings in **2** and **5** causes only a modest perturbation in the sensitization efficiency. Since parallel conformational variance and ion pairing effects control the electrochemical behavior of the hydrocarbons **1**–**5**, the absence of dramatic differences in their photosensitization efficiency is perhaps reasonable, with the observable current probably being governed instead by the availability of surface carrier traps at the metal oxide–electrolyte interface. Perhaps more surprising is the apparent similarity between the observed sensitization efficiency of these hydrocarbons and that of the tetrakisperfluorocyclobutano-fused derivative **6**, where the neutral hydrocarbon, the singly reduced radical anion, and the dianion are all planar.[10] In **6**, however, all three oxidation levels are stable, making the disproportionation equilibrium position of lesser consequence than the physical character of the electrode surface.

Experimental Section

Bis(cyclooctatetraenyl)methane (**2**) and bis(cyclooctatetraenyl)ethane (**3**), prepared as previously described,[11] were purified by chromatography on silica gel (hexane). **2** (12% yield) as a pale yellow liquid: mass spectrum (m/e) 220.45 (P$^+$). **3** (36%) as a pale yellow viscous oil: mass spectrum (m/e) 234.20 (P$^+$).

Bis(cyclooctatetraenyl)propane (4). A solution of cyclooctatetraenylbromide[14] (2.1 g, 11 mmol) in 4 mL of dry THF was added dropwise to a stirred mixture of magnesium turnings (25 mmol) in 25 mL of dry THF at rt under N$_2$. As the reaction began, the solution was cooled with an ice bath as the addition continued over ca. 1.5 h. The resulting mixture was stirred at 0 °C for 2 h before being allowed to warm to rt, after which stirring continued for an additional 2 h. A 0.2-mL aliquot was removed from the mixture and was titrated with an HCl standard, showing 94% conversion of bromide. While being rigorously stirred while immersed in an ice bath, the remaining solution was treated by dropwise addition over 20 min with 1,3-dibromopropane (1.33 g, 6.6 mmol) in 30 mL of THF. The addition being complete, 0.34 mL of freshly prepared Li$_2$CuCl$_4$ in THF was added by syringe. The resulting mixture was stirred at 0 °C for 3 h and then at rt for an additional 18 h. Saturated NH$_4$Cl was then added, and the mixture was cooled to 0 °C. The organic layer was separated, washed with saturated NaHCO$_3$, dried over MgSO$_4$, filtered, and concentrated. Upon chromatographic purification on silica gel (hexane), **4** was isolated as a viscous yellow oil in 8% yield: ^{1}H NMR (CDCl$_3$) 1.57 (pentet), 2.09 (t, 4 H), 5.77 (m, 14 H); ^{13}C NMR (CDCl$_3$) 27.1, 37.0, 131.9 (overlapping peaks), 144.2; mass spectrum (m/e) 248.00 (P$^+$).

Electrochemical Measurements. Cyclic voltammetric measurements were conducted as 0.01 M solutions in dry DMF containing 0.1 M tetrabutylammonium perchlorate in a standard two-compartment cell with a Pt wire working electrode, a Pt disk counter electrode, and a silver wire quasi-reference electrode. The reported potentials are referenced with respect to the reported value for **1**[12] or **5**.[9] The cell potential was controlled with a Princeton Applied Research electrochemical system comprising a Model 173 potentiostat, a Model 175 universal programmer, and a Model 179 digital coulometer, with traces recorded on a Houston Instruments 2000 x/y recorder.

Photocurrent measurements were made under an argon blanket as previously described, in a cell identical to that employed earlier,[5] on a Fluka microammeter. Quantum efficiencies were crudely estimated by taking a ratio of the observed photocurrent to the incident light flux, measured by a power meter at the surface of the photoelectrochemical cell.

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Excellent Regiochemical Control in the Hydroformylation of α,β-Unsaturated Esters Catalyzed by Zwitterionic Rhodium Complexes and 1,4-Bis(diphenylphosphino)butane

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One of the most thoroughly investigated reactions in homogeneous catalysis is the hydroformylation of olefins. Recently, one of us[1] found that the zwitterionic rhodium complex **1** is an excellent catalyst for this process, with high regioselectivity observed for the branched (eq 1) or linear (eq 2) aldehyde depending on the nature of the reactant. However, poor regiochemical control was found during attempts to apply the reaction to α,β-unsaturated esters such as methyl acrylate and methyl methacrylate.

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