

contaminated presumably by cocrystallization of an iron(III) material as shown by EPR spectroscopy, indicated the presence of a THF molecule bonded to iron as second axial ligand.

Hence, **3** is an iron(IV)-oxo-"picket-fence" porphyrin complex and **4** is the picket-fence porphyrin analogue of [Fe(=O)(1-MeIm)(TPP)] reported by Balch et al.²²

The mechanism of formation of **3** is still unclear. A reactive monoperoxy carbonate intermediate forms presumably when carbon dioxide reacts with the peroxy-iron(III) derivative **2**, but such an intermediate could not be detected. Moreover, the overall stoichiometry of the carbon dioxide reaction with **2** has, so far, not been established.

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(28) Crystallization of **3** at $-40\text{ }^\circ\text{C}$ yielded small crystals, all contaminated by an iron(III) bromo picket-fence porphyrin, presumably by cocrystallization of two almost identical molecular entities. X-ray studies²⁹ at $-100\text{ }^\circ\text{C}$ indicated that these crystals belonged to the monoclinic system with $a = 18.661(8)\text{ \AA}$, $b = 19.030(8)\text{ \AA}$, $c = 18.245(7)\text{ \AA}$, $\beta = 90.99(2)^\circ$, space group $C2/c$, $Z = 4$. Preliminary results obtained by anisotropic refinements of all non-hydrogen atoms (present R_1 value = 0.075) indicated the presence of an iron "picket-fence" porphyrin with a THF molecule bonded to the metal on the nonprotected side of the ring. Approximately 85% of the electron density located inside the molecular cavity of the porphyrin could correspond to an oxygen atom with an Fe-O distance of 1.604(19) \AA , the remaining 15% of the density corresponds probably to a bromide ion with Fe-Br = 2.355(8) \AA . The other distances found are $\overline{\text{Fe-Np}} = 2.005(8)$, $\text{Fe-O(THF)} = 2.269(10)$ and $\text{Fe-C}_1 = 0.13\text{ \AA}$. These Fe=O and Fe-Np distances are identical with those derived by preliminary EXAFS studies at $-100\text{ }^\circ\text{C}$ of several iron(IV)-oxo-porphyrin derivatives.³⁰

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The Au/GaPc-Cl/Ferri,ferrocyanide/GaPc-Cl/Pt Photoelectrochemical Cell

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A photochemical cell consisting of a thin film photoconductor (PC) backed by a conductive metal substrate (M) and in contact with an electrolyte solution (R,Ox) (M/PC/R,Ox) develops an open-circuit photopotential which is limited in magnitude by the difference in Fermi potential (work function) of M and the Fermi potential of an electron in the redox couple (represented by the $E^{\circ'}$).¹⁻³ Analogous behavior is observed in solid-state photo-voltaics (using SiH_x or organic thin films) where the electrolyte is replaced by a metal counter electrode.^{4,5} We have taken advantage of this fact to construct a photoelectrochemical cell

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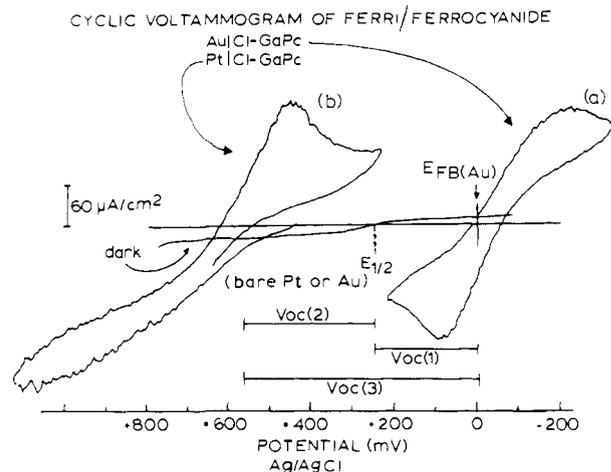


Figure 1. Cyclic voltammograms (scan rate = 50 mV/s, potentials measured relative to Ag/AgCl) for (a) Au/GaPc-Cl and (b) Pt/GaPc-Cl in the dark and in the light in contact with a 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$, 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.4 M KHPthalate, pH = 4 solution.

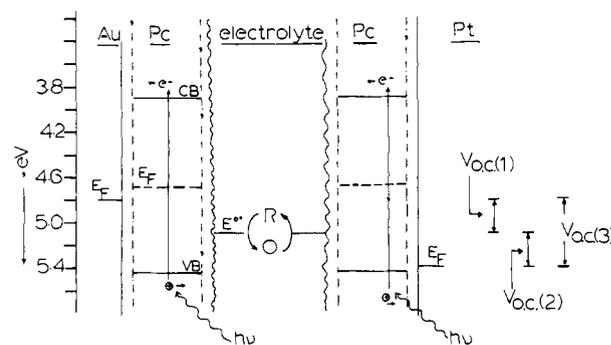


Figure 2. Band diagram for the Au/GaPc-Cl/ferri,ferrocyanide/GaPc-Cl/Pt photovoltaic cell at the flatband condition. $V_{OC}(1)$, $V_{OC}(2)$, and $V_{OC}(3)$ are as seen in Figure 1.

based upon vacuum-deposited (chlorogallium phthalocyanine, GaPc-Cl) thin films in contact with two metals of different work function (a Au/GaPc-Cl anode and a Pt/GaPc-Cl cathode) and a redox electrolyte which acts as the contacting phase (and electron shuttle) between the photoanode and photocathode. The details of photoconductor preparation on optically transparent metal substrates and the photoelectrochemical characterization are as described previously.²

Chlorogallium phthalocyanine (GaPc-Cl) films of 0.7-1.0 μm thickness on thin (300 \AA) gold films on a polymer substrate produce sizable positive and negative photopotentials in contact with aqueous redox couples.^{2,3} The current-voltage curves under illumination of the Au/GaPc-Cl/R,Ox system are displaced to the potential of zero net current flow as dictated by the apparent flatband potential (E_{FB}) for the Au/GaPc-Cl/R,Ox system (see Figure 1a for the ferri, ferrocyanide redox couple). A linear correlation between these potential shifts ($V_{OC}(1)$ in Figure 1) and the $E^{\circ'}$ of the redox couple, for values of $E^{\circ'}$ from -0.6 to $+0.9\text{ V}$ (vs. Ag/AgCl), is observed.² The effective Fermi energy of these GaPc-Cl films before contact with metal or electrolyte is at least 0.7 V above the valence band edge.³ Other phthalocyanine films have exhibited a more p-type character.^{6,7}

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GaPc-Cl films of ca. 1.0 μm thickness were vacuum deposited on optically transparent platinum substrates and placed in contact with the same aqueous ferri/ferrocyanide redox couple. Upon illumination (Figure 1b), the entire current-voltage curve is displaced *positively* from the true $E^{\circ'}$ to the E_{FB} of the Pt/GaPc-Cl system, by an amount $V_{\infty}(2) \approx +0.30$ V. The difference in the E_{FB} of the Au/GaPc-Cl and Pt/GaPc-Cl system is due to the difference in the *effective* work functions of the two metal substrates.⁸ Tabulated values of the work function for clean Pt surfaces range from 5.65 to 5.75 eV (below the energy of an electron in vacuum) while those for Au are typically near 4.8 eV.⁹ The predicted work function difference of 0.8 V or greater is not quite realized in the photoelectrochemical cells where $|V_{\infty}(1)| + |V_{\infty}(2)| = V_{\infty}(3) \leq 0.65$ V. The first molecular layers of GaPc-Cl deposited from vacuum may be expected to lower the effective work function to the observed value as would other hydrocarbon constituents of the Pt-MPOTE surface.⁹

The Pt/GaPc-Cl films fabricated so far tend to have a higher porosity to solution reactants compared to the typical Au/GaPc-Cl films (as evidenced by the larger dark currents observed), which leads to some lowering of photopotential because of short-circuiting of the photoelectrochemical process at the exposed metal sites.¹⁰ In photoelectrochemical cells using unstirred solutions, we have found that the dark current process is inhibited relative to that at photoactive sites. Reasonable photopotentials and photocurrents are still observed on films where the dark currents are up to 50% of those seen on the bare metals.¹⁰

Figure 2 shows a schematic of the Au/GaPc-Cl/ferri,ferrocyanide/GaPc-Cl/Pt photoelectrochemical cell as we hypothesize it exists prior to contact of any of the phases. This schematic is based upon our recent electrochemical and photoelectrochemical studies of band edges and work functions, vs. the ferri,ferrocyanide redox couple solution potential.^{2,3} The relative band energies are those that are expected under strong illumination conditions, i.e., with the Au/Pc and Pt/Pc systems driven to their flatband condition. The expected open-circuit potentials for Au/Pc vs. R/Ox and Pt/Pc vs. R/Ox are shown as $V_{\infty}(1)$ and $V_{\infty}(2)$, respectively. We have found that the $E_{\text{F}}(\text{GaPc-Cl})$ can lie ca. 0.1 V positive of the $E_{\text{F}}(\text{Au})$ and 0.3 V or more positive of the $E^{\circ'}$ of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$.³ Upon contact of these phases in the dark, the Pc layer becomes charge depleted at both the Au/Pc and Pc/R,Ox interface. The *net* potential gradient in the Au/GaPc-Cl films at equilibrium, however, is such that photogenerated holes under strong illumination are still driven to the Pc/R,Ox interface. For the Pt/GaPc-Cl system, photogenerated electrons are driven to the Pc/R,Ox interface by the *net* electric field gradient within that film.

The photopotential was observed at various load currents for a Au/GaPc-Cl/ferri,ferrocyanide/GaPc-Cl/Pt electrochemical cell under ca. 100 mW/cm² polychromatic illumination (filtered to 470-900 nm) of *both* the photoelectrodes, in contact with 10⁻³ M amounts of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$. The open-circuit photovoltage was ca. +0.55 V, the short-circuit current 0.1 mA/cm², and the fill factor 0.55 for the most optimized cells. Using maximal power values, the power conversion efficiency was determined to be 0.03-0.05%. Since the cell was not optimized to minimize light losses, this efficiency may be low by a factor of 2-3. Cells with 10 mM redox electrolyte concentrations yielded higher short-circuit currents (by a factor of 3-4) but with lower fill factors (near 0.3). At higher electrolyte concentrations the i/V curves were nearly linear with a slope dictated by film resistance, thus leading to the poorer fill factors. The Pt/GaPc-Cl

films tend to exhibit lower photoconductivities than the counterpart Au/GaPc-Cl films. Even when the electrodes are produced simultaneously, such that the Pc films appear to be identical as determined by electron microscopy and spectroscopic assay,¹² the films formed on the Pt-MPOTE are more resistive and less stable than the films formed on the Au-MPOTE.

These cells demonstrate a *thin-film* photovoltaic system where the driving force for the photoelectrochemical response is provided solely by the work function difference between the two metals. The Pc films act as the charge-separating medium and the electrolyte acts as the third contacting phase, less likely to cause short-circuiting of the photoresponse than a metal contact.⁵ The resulting cell gives a photopotential response ca. 20% of the theoretical maximum dictated by the sum of the apparent bandgaps (ca. 3.0 eV) of the two GaPc-Cl/metal systems.¹¹ This technology may lend itself to additional improvements in performance through miniaturization of both the photoactive surfaces and the electrolyte layer between them.

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(12) Visible transmission spectroscopy of thin films of GaPc-Cl (≤ 500 nm) shows an absorbance band extending from ca. 500 to 850 nm with an absorptivity β of $\geq 5 \times 10^4$ cm⁻¹. Thicker films (1 μm) show similar absorbance spectra when examined by photoacoustic spectroscopy. Assay of GaPc-Cl surface coverage is made by dissolving the film in a small volume of pyridine and quantitating the resultant solution concentration from the absorbance spectrum (see ref 11).

Size and Selectivity in Zeolite Chemistry. A Remarkable Effect of Additive on the Products Produced in the Photolyses of Ketones

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Photolyses of dibenzyl ketones adsorbed on zeolites have been reported to result in decarbonylation and coupling of the resulting radicals to produce diaryl ethanes as the major products.¹ We report that the products formed in the photolysis of dibenzyl ketones on certain zeolites can be extremely sensitive both to zeolite structure and to simple sorbed additives such as water, benzene, cyclohexane, and hexane.

The zeolites² investigated were NaA, NaX, NaY, and LZ-105. Dibenzyl ketone (DBK) and *p*-methylbenzyl benzyl ketone (*p*-MeDBK) were deposited on the zeolites² from pentane solutions,³

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(3) In a typical experimental 0.4 mg of ketone in 0.2 mL of pentane was added to a vial containing 40 mg of zeolite soaked in a minimum amount of pentane. The bulk of the solvent was rapidly removed by placing the sample in a warm (50 °C) stream of flowing air. The sample was then placed into a quartz photolysis cell, equipped with a side arm, which allowed vacuum (2×10^{-4} torr) degassing.

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