the phosphate oxygens interacting (at pH 7) strongly with the three symmetrically disposed ammonium ions. A determination of the binding of benzyl phosphate to **1** in the presence of inorganic phosphate gave a $K_{\rm diss}$ value identical with that obtained in its absence, indicating that, within the errors of such an indirect determination, inorganic phosphate itself does not bind ($K_{\rm diss} > 200$ mM) to **1**.[10]

In this model system, highly specific recognition of complex molecules depends on independent recognition sites, one hydrophobic and the other electrostatic, providing a model for multiple recognition sites common in biological systems.[11] We anticipate that variations in the structure of the hydrophobic moiety of the guest molecule will cause predictable variations in the equilibrium position of the guest within the cyclodextrin cavity, leading to a change in the observed $K_{\rm diss}$. Direct study of the precise geometry of the interactions in the observed complexes (e.g., by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy or X-ray crystallography) should clarify the energetic relationships between these hydrophobic and electrostatic recognition sites and the effects of such binding on the geometry and reactivity of the bound guest molecule.

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(3) Potentiometric titrations were done at 30 ± 0.02 °C, *I* 0.10 (KCl). The method of Sayce (Sayce, I. G. *Talanta* **1968**, *15*, 1397) was used to derive the individual pK_a values. This method minimizes the deviation of the actual base titer from that calculated on the basis of the pK_a values. For the triammonio-α-cyclodextrin **1**, the mean deviation was 0.14%; for the monoammonio-α-cyclodextrin, **2**, the mean deviation was 0.9%. For **1**, the successive pK_a values differ by 4.0-fold and 5.9-fold (compared with the statistical minimum of 3-fold).

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(7) The indirect method (Broser, W.; Lautsch, W. *Z. Naturforsch.* **1953**, *86*, 711) enables the spectral determination of the $K_{\rm diss}$ of any nonchromophoric guest molecule and host, where the binding of a chromophoric guest species has been previously determined. The binding of 2,4-dinitrophenol to both **1** and **2** was studied by the method of Hildebrand, J. A.; Benesi, H. A. *J. Am. Chem. Soc.* **1949**, *71*, 2703 (see also Rossotti, F. J. C.; Rossotti, H. "The Determination of Stability Constants"; McGraw Hill: New York, 1961; pp 270–277), which established that the complexes were strictly 1:1. Since this method, while qualitatively reliable, can lead to (usually small) systematic errors (Bergeron, R. J.; Roberts, W. P. *Anal. Biochem.* **1978**, *90*, 844) and in order to obtain dissociation constants and extinction coefficients under the exact conditions to be used in the indirect determinations, the binding of 2,4-dinitrophenol was restudied, using a nonlinear least-squares fit to an unsimplified expression (see, for example: Bergeron, R. J.; Channing, M. A.; Gibeily, G. J., Pillor, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 5146). In the indirect determination of the binding of benzyl alcohol or benzyl phosphate, the nonchromophoric guest was added to solutions of 2,4-dinitrophenol and the cyclodextrin host. Changes in the spectrum are used to calculate a value for the unknown $K_{\rm diss}$. Each $K_{\rm diss}$ reported was determined at several widely separated wavelengths, each using values obtained at several concentrations of the nonchromophoric guest. The value reported is the average from this matrix of experiments, along with the standard deviations.

(8) The $K_{\rm diss}$ values determined for benzyl phosphate and **1** at pH **7** were dependent on the concentration of benzyl phosphate added. This phenomenon has been noted before in a similar competitive inhibition study of the binding of thiocyanate anion to α-cyclodextrin: Rohrbach, R. P.; Rodriguez, L. J.; Eyring, E. M.; Wojcik, J. F. *J. Phys. Chem.* **1977**, *81*, 944. Those authors attributed the variation to a breakdown in the assumption that the binding of the thiocyanate completely expelled the reporting chromophore. This appears to be the case for benzyl phosphate and **1** reported here. At each of several wavelengths, plots of the calculated $K_{\rm diss}$ vs. the concentration of benzyl phosphate (seven concentrations, spanning an order of magnitude) were extrapolated to zero concentration, and the values obtained at the several wavelengths were averaged to give the $K_{\rm diss}$ shown in Table I. In no other case was any systematic variation of $K_{\rm diss}$ with concentration observed. Using models of the complex, there is ample room for some interaction of 2,4-dinitrophenol with the secondary end of the cyclodextrin, although the chromophore cannot penetrate significantly into the cavity without expelling the benzyl phosphate. The binding of 4-*tert*-butylbenzyl phosphate to **1** at pH 7 ($K_{\rm diss} = 16$ μM) shows no such variation with concentration. In models, the *tert*-butyl group should prevent the formation of the proposed ternary complex. (The ternary complex may be present to some extent with benzyl alcohol or with the weaker benzyl phosphate complexes, but it would be undetectable using the indirect method since small variations in the observed absorbance do not greatly affect the calculated $K_{\rm diss}$ for such weak complexes.)

(9) Benzyl phosphate was added as its bis(cyclohexylammonium) salt. Cyclohexylamine does not bind to the cyclodextrin derivatives at pH 5.5 or **7**. However, at pH 9.5 the $K_{\rm diss}$ for cyclohexylammonium and **1** is ~50 mM. At pH 9.5, additions of the benzyl phosphate salt to the solution of **1** and 2,4-dinitrophenol caused some spectral change, which could be ascribed to the binding of cyclohexylamine (or cyclohexylammonium ion). Residual absorbance changes placed a lower limit of 100 mM on the binding of benzyl phosphate at this pH.

(10) The addition of inorganic phosphate caused no spectral changes in the indirect determination, indicating only that, if inorganic phosphate binds, it does so in a way that does not expel the reporting chromophore. This would not appear to exclude interaction with the ammonium groups. However, the failure of added inorganic phosphate to alter the $K_{\rm diss}$ for benzyl phosphate does establish that the inorganic phosphate does not interact strongly with the ammonium groups, since such an interaction would be expected to alter benzyl phosphate binding.

(11) There have been two recent reports of the associative properties of charged cyclodextrin derivatives: (a) Tabushi, I.; Shimizu, N.; Sugimoto, T.; Shiozuka, M.; Yamamura, K. *J. Am. Chem. Soc.* **1977**, *99*, 7100. (b) Matsui, Y.; Okimoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3030. The reported effects of the electrostatic interaction on dissociation constants was small. In the former, a monoanion guest interacting with a dicationic (metal complex) cyclodextrin host gave a $K_{\rm diss}$ 23 times smaller than with a neutral host. In the latter, a monocation host and monoanionic guest showed a $K_{\rm diss}$ lowering of only 4.

Joshua Boger, Jeremy R. Knowles*
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

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7.3% Efficient Thin-Film, Polycrystalline n-GaAs Semiconductor Liquid Junction Solar Cell

Sir:

In a series of recent papers, we reported that the n-GaAs|0.8 M K_2Se-0.1 M K_2Se_2-1 M KOH|C cell shows good stability and higher efficiency than other photoelectrochemical cells.[1] Further, the solar to electrical conversion efficiency of this cell can be increased to 12% by chemisorbing a layer of ruthenium ions[2] which also substantially reduces the surface recombination velocity, not only at n-GaAs-electrolyte interfaces, but also at the n-GaAs-oxide (air) interface.[3] Most importantly, if the ruthenium ions are allowed to diffuse into boundaries of n-GaAs grains, recombination in these is substantially reduced.[4] After such diffusion, the efficiency of a semiconductor-liquid junction solar cell made with a thin-film, polycrystalline chemically vapor deposited layer of n-GaAs on carbon increases by a factor of 4.[4] We proposed that this improvement derived from the fact that a strongly chemisorbed ion reacting with a surface will split a surface state to levels from which it is no longer accessible by tunneling to majority carriers. This region is, in n-type semiconductors, below the edge of the conduction band and, in p-type semiconductors, above the edge of the valence band. By our model, the chemisorption of ruthenium ions causes in n-GaAs the splitting of initially present surface states located below the edge of the conduction band both to states above this edge and to states too deep in the band gap to be accessible by tunneling.[2,5]

Ideally, by elimination of grain boundary effects, it would be possible to approach single-crystal efficiency provided that the mobility remains high and an optimal, uniform doping level is maintained throughout the grains. We now report that such a situation is approached in thin-film, chemically vapor deposited n-GaAs, following exposure to a Ru(III) solution.

The anode used was n-GaAs/n^+-GaAs/W/graphite.[6,7] A 24-μm thick layer of n-GaAs was deposited on a 2-3-μm tungsten-on-POCO graphite substrate by the reaction by hydrogen chloride, gallium, and arsine at 775 °C. The grains were of 1-20-μm diameter, with an average linear dimension of 9 μm. Figure 1 shows a scanning electron micrograph of the grains. The samples, of ~0.5 × 0.3 cm size, were mounted as

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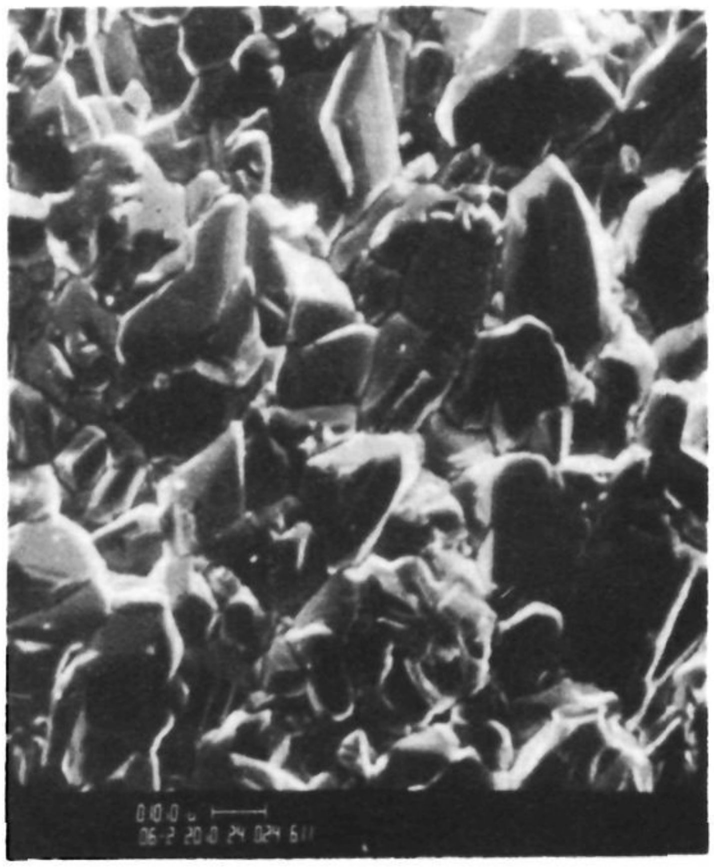

Figure 1. Scanning electron micrograph of the chemically vapor deposited n-GaAs film on tungsten coated graphite.

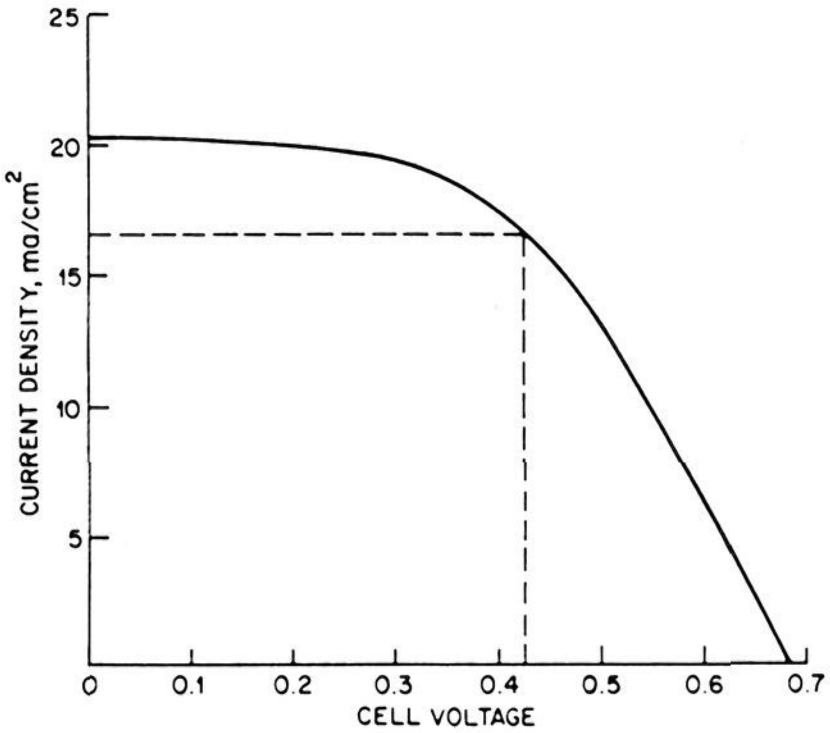

Figure 2. Current voltage characteristics of the thin-film n-GaAs|0.8 M K$_2$Se-0.1 M K$_2$Se$_2$-1 M KOH|C cell at 96.4 mW/cm^2 insolation. The maximum power point is marked with dashed lines.

earlier described[8] using a silver-filled epoxy to attach a copper wire to the graphite. A 3 M Scotchcast XR5241 resin was used to electrically insulate the back of the photoanodes from the solution. The areas of the encapsulated electrodes were measured to within ±2%.

The photoanodes were treated somewhat differently than previously.[2-5] First, they were run as part of the n-GaAs|0.8 M K$_2$Se-0.1 M K$_2$Se$_2$-1 M KOH|C cell until their output no longer increased. The electrodes were then rinsed for 20 s in flowing deionized water, etched in bromine-methanol solution at room temperature for 30 s, rinsed for 20 s in deionized water, and then dipped into 0.01 M RuCl$_3$ in 0.2 M HCl at 60 °C for 2 min to allow diffusion of the ruthenium ions into the grain boundaries. After being rinsed in deionized water for 20 s, the photoanodes were remounted in the cell. An improvement in performance was observed in the current-voltage cycles during the first 15 min, as is also common to single-crystal n-GaAs electrodes[5] and presumably chiefly due to slow chemical surface reequilibration after immersion in the selenide electrolyde.[7] The cell characteristics were determined after the output stabilized.

The measurements were done under 96.4-mW/cm^2 incident sunlight. The insolation was determined by an Eppley Model PSP radiometer, which measures the direct and scattered insolation from the entire sky. The cell was magnetically stirred. The current-voltage characteristics are shown in Figure 2.

The open circuit voltage is 0.67 V, the short circuit current density 20.3 mA/cm^2, and the fill factor 0.51. The maximum power output at 0.425 V and at 16.5 mA/cm^2 is 7.0 mW/cm^2, corresponding to a solar to electrical conversion efficiency of 7.3%. This represents 60% of the efficiency of the single-crystal n-GaAs counterpart. The cell is the most efficient thin-film GaAs cell to date, and one of the most efficient solar cells made with semiconductors of similarly small average grain size.

The importance of these and of earlier results is in the demonstration that grain-boundary diffusion of a strongly bound impurity can reduce the grain-boundary-related losses in solar cells made with thin-film polycrystalline semiconductors. This work and the effect of hydrogenation of grain boundaries of silicon[9] suggest that it is possible to approach more closely single-crystal efficiencies in thin-film polycrystalline solar cells than originally thought.

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A. Heller, B. Miller
Bell Laboratories, Murray Hill, New Jersey 07974

Shirley S. Chu, Y. T. Lee
Southern Methodist University, Dallas, Texas 75275

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Tricyclo[4.3.1.1^{3,8}]undec-3-ene (Homoadamant-3-ene). Stability of Bridgehead Olefins[1]

Sir:

The gas-phase carbene route provides access to the "anti-Bredt" bridgehead olefins, bicyclo[2.2.2]oct-1-ene (**1**),[2] tricyclo[4.3.1.1^{3,8}]undec-3-ene (homoadamant-3-ene) (**2**),[3] and adamantene (**3**).[4] However, **1**, **2**, and **3** were detected only as transient intermediates, as they suffered a retro-Diels-Alder reaction,[2] dimerizations,[2,4] and other trapping reactions[4] under the conditions employed. Modification of our method allows rapid capture at low temperature; we now report the isolation and spectroscopic characterization of homoada-

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