

UNIVERSITY OF  
CALIFORNIA

*Radiation  
Laboratory*

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

UNIVERSITY OF CALIFORNIA

Radiation Laboratory  
Berkeley, California

Contract No. W-7405-eng-58

THE PHOTOVOLTAIC EFFECT AND PHOTOCONDUCTIVITY IN  
LAMINATED ORGANIC SYSTEMS

David Kearns and Melvin Calvin

September 1958

THE PHOTOVOLTAIC EFFECT AND PHOTOCONDUCTIVITY IN  
LAMINATED ORGANIC SYSTEMS\*

David Kearns and Melvin Calvin

Department of Chemistry and Radiation Laboratory  
University of California, Berkeley, California

September 1958

---

\*The work described in this paper was sponsored by the U.S. Atomic Energy Commission.

---

As a result of a wide variety of studies on photosynthesis in living plants and plant fragments, together with the development of photosensitive, photo-voltaic junctions in inorganic crystals<sup>1</sup> and the discovery and exploration of semiconduction in organic molecular substances<sup>2, 3, 4, 5, 6, 7</sup> a suggestion has been made<sup>8, 9, 10, 11, 12, 13</sup> that the primary quantum conversion process in

- 
1. D.M. Chapin, C.S. Fuller and G.L. Pearson, Bell Lab. Record, 33, 241 (1955).
  2. D.D. Eley, G.D. Parfitt, M.J. Perry and D.H. Taysum, Trans. Faraday Soc. 49, 79 (1953); D.D. Eley and G.D. Parfitt, Trans. Faraday Soc. 51, 1529 (1955).
  3. H. Mette and H. Pick, Z. Physik, 134, 566 (1953).
  4. H. Akamatu, H. Inokuchi and Y. Matsunaga, Bull. Chem. Soc. Japan, 29, 213 (1956).
  5. For a recent survey see Felmayer and Way, J. Electrochem. Soc. 105, 141 (1958).
  6. A.S. Vartanyan, J. Chem. Phys. U.S.S.R., 20, 1065 (1946) Zhur. Fiz. Khim., 24, 1361 (1950).

- 
7. D. C. Northrop and G. Simpson, Proc Phys. Soc. (London) B67, 892 (1954).
  8. D. F. Bradley and M. Calvin, Proc. Nat. Acad. Sci. 41, 563 (1955).
  9. E. Katz in Photosynthesis in Plants, Iowa State College Press, Ames, Iowa (1949), 291.
  10. G. Tollin, P. B. Sogo and M. Calvin, Ann. N. Y. Acad. Sci., in press (1958).
  11. W. Arnold and H. K. Sherwood, Proc. Nat. Acad. Sci. 43, 105 (1957).
  12. M. Calvin, in Brookhaven National Laboratory Symposium on "Photochemical Apparatus: Its Structure and Function," June 1958.
  13. W. Arnold and H. Macley, in Brookhaven National Laboratory Symposium on "Photochemical Apparatus: Its Structure and Function," June 1958.

---

photosynthetic tissues involves the creation and separation of charge to opposite sides of an asymmetrically-constructed lamina, followed by the trapping of both the electrons and the holes which then lead to their respective chemical processes, namely, reduction of carbon dioxide and oxidation of the water to oxygen. This has led us to study model systems<sup>1</sup> as semiconductors with a view to creating an organic photovoltaic junction.<sup>14</sup>

We have found that magnesium phthalocyanine (MgPh) discs coated with a thin film of air-oxidized tetramethyl p-phenylenediamine (TM $\phi$ D) are organic systems which do show the photovoltaic effect. The maximum voltage as yet developed by one of these discs was 200 mv. The rise and ~~delay~~ is instrument-limited ( $\sim 1$  sec). The maximum power output was only  $3 \times 10^{-12}$  watts. The power output appears to be limited by an internal cell resistance of  $10^8$  ohms and by the maximum radiant energy incident on the junction.

Discs 1.5 cm in diameter and 0.1 cm thick were formed by pressing powdered MgPh in a die. These discs were then made photovoltaic when coated with a film of air-oxidized TM $\phi$ D by evaporation of an acetone solution of the amine. The coated sides of the discs were pressed in contact with a conducting glass electrode by a stainless steel piston applied to the back of the disc. This formed the photovoltaic cell which was placed in a vacuum chamber along with suitable electrical

---

14. D. Kearns and M. Calvin, unpublished results from this laboratory.

leads in insulation. During measurements a mechanical pressure of  $9 \text{ kg/cm}^2$  held the disc against the glass and a gas pressure of  $10^{-4}$  mm Hg was maintained. The junction was illuminated by passing light from a 500-watt projection lamp through a window in the chamber and through the conducting glass electrode. A recording vibrating reed electrometer was used to measure the photovoltage, photoconductivity and resistance of the cells. Action spectra for the photovoltaic effect and the photoconductivity were obtained by use of a Bausch and Lomb monochromator.

In all cases the MgPh layer was at a positive potential with respect to the oxidized TM $\phi$ D layer, indicating electron transfer from the MgPh to the TM $\phi$ D. Several junctions were made with MgPh and TM $\phi$ D where precautions were taken to prevent air oxidation of the amine. These junctions produced little or no detectable photovoltage, indicating that the oxidized TM $\phi$ D is required. Space-charge effects were present only when there was a visible amount of white un-oxidized TM $\phi$ D on the coated MgPh discs. The MgPh alone exhibited no photovoltaic effect. The oxidized TM $\phi$ D alone gave a very small photovoltaic effect, appearing slightly negative with respect to the stannic oxide layer of the conducting glass. The action spectra of the photovoltaic effect and the photoconductivity of a representative cell are shown in Fig. 1.

The action spectrum, although resembling that of the absorption of solid magnesium phthalocyanine, does not coincide with it. This is to be expected since the action spectrum should be that of the junction layer rather than of the magnesium phthalocyanine itself and perhaps has more in common with Wurster's blue than with the phthalocyanine derivative.

A completely different system has also been investigated in a preliminary way. A matrix of coronene was coated with a thin layer of o-chloranil as an electron acceptor. In this case the internal resistance of the cell was extremely high ( $10^{11}$  ohms) but a photovoltaic effect was easily measured in which the coronene was positive and the chloranil layer was negative. These and other systems involving matrices of much better conductivity and both electron donor and electron acceptor layers are being investigated in greater detail.

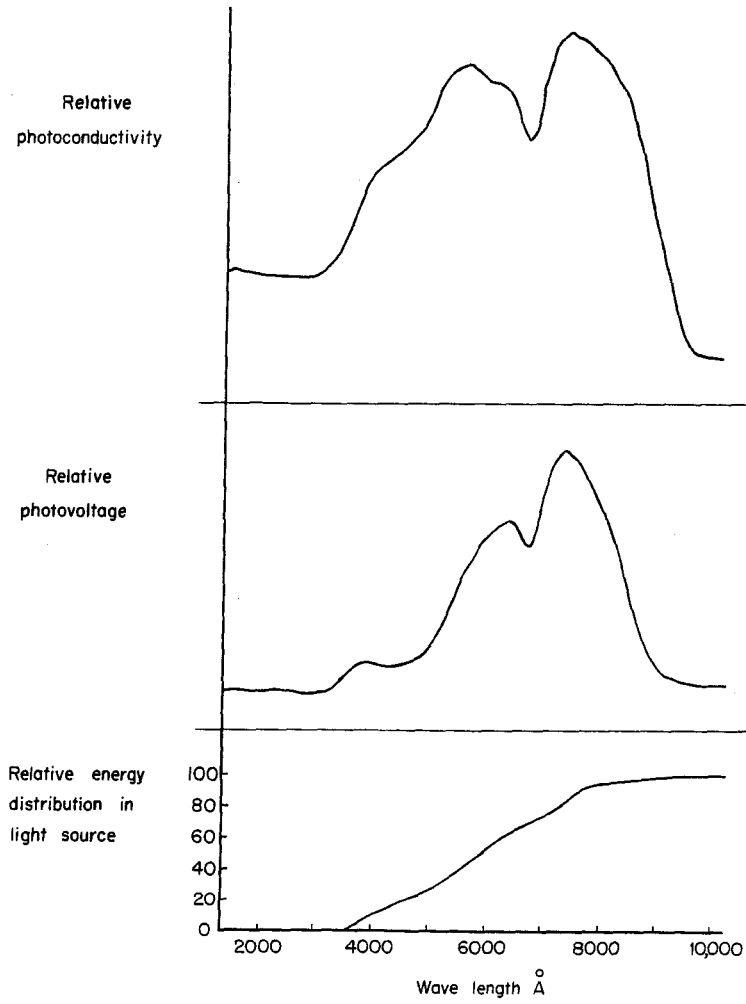


Figure 1. PHOTOCONDUCTIVITY AND PHOTOVOLTAIC EFFECT AT Mg PHTHALOCYANINE-OXIDIZED TM<sub>2</sub>D JUNCTION