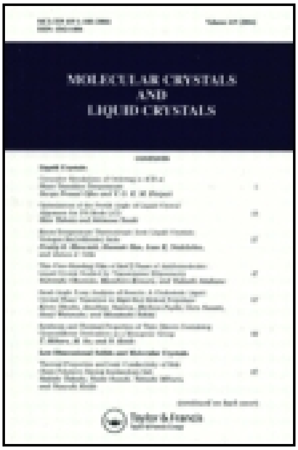

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Electrical Conduction in Uranyl Phthalocyanine

P. L. Kronick [a], J. E. Bloor [a] & M. M. Labes [a]
[a] Chemistry Division, The Franklin Institute Research Laboratories, Philadelphia, Pa., 19103

To cite this article: P. L. Kronick, J. E. Bloor & M. M. Labes (1966): Electrical Conduction in Uranyl Phthalocyanine, Molecular Crystals, 1:1, 113-123

To link to this article: http://dx.doi.org/10.1080/15421406608083264

Molecular Crystals. 1966. Vol. 1, p.113–123

Printed in Great Britain

Electrical Conduction in Uranyl Phthalocyanine

P. L. KRONICK, J. E. BLOOR, and M. M. LABES
Chemistry Division, The Franklin Institute Research Laboratories,
Philadelphia Pa. 19103

Received August 8, 1965

Abstract—Uranyl phthalocyanine in its electrical properties might be expected to be quite different from phthalocyanine complexes with transition metals. The major peak of its absorption spectrum is in the near infrared and the compound shows a strong photocurrent response in this region. In the dark, it is one of the most conductive of the phthalocyanines, but its activation energy is 0.87 eV, about the same as metal-free phthalocyanine. Single crystals exhibit a photoconductive gain about 1000-fold greater than the sublimed films, probably because of more efficient carrier transport through the more perfect crystal lattice.

Introduction

Absorption spectra and/or photoconduction action spectra have been reported for phthalocyanine substituted with various metal ions, including hydrogen, copper, nickel, cobalt, platinum, manganese, zinc, iron and uranyl, in the center of the ring.[1–10] Typically, these materials exhibit strong absorption bands in the visible-red part of the spectrum, accompanied by photoconduction maxima. In several cases, very weak absorption bands are also observed in the solids in the near infrared,[2, 3] accompanied by strong photoconduction response in this spectral region.[4, 5]

Two exceptions to the above generalization are phthalocyanine complexes with Mn(II) and uranyl ions, both of which have strong absorption bands in the near infrared.[6, 8] The uranyl complex is unique in that the visible-red absorption band (0.62 μ) is much weaker ($\epsilon \sim 1000$ M^{-1} cm^{-1}) than any other phthalocyanine. The Mn(II)Pc complex shows the usual strong absorption band in this region[8] but the photoresponse maxima have been reported to correspond more closely with the absorption at 1.35 μ.[7]

No electrical measurements have been reported for the uranyl complex. Its electronic states, possibly involving 5f electrons of the actinide atom, might extend to higher energies and greater distances from the molecular centers, leading to different electrical behavior from the more commonly investigated phthalocyanine complexes of the transition metal elements. For example, the striking difference between the mobility of charge carriers in metal-free (~ 0.4 cm^2/V sec)[11] and copper (> 30 cm^2/V sec)[12, 13] phthalocyanines has been discussed in terms of the role of the central metal atom in influencing orbital overlap between parallel molecules in the crystal, and it has been suggested that insertion of other metal ions which have greater overlap than copper would further increase the mobility.[14] Also the unusual absorption spectrum of uranyl phthalocyanine,[6, 7] featuring strong bands in the near infrared, might make the material an infrared-sensitive photoconductor. An electrical study of this material is reported in the light of these possibilities.

Experimental

The sample of uranyl phthalocyanine (UO_2Pc) used in this work was prepared by the method of Bloor *et al.*[8] Crystals were grown by entrainment sublimation at 390° in a flow of nitrogen of about 50 ml per hour at 7 torr pressure, and collected over a period of three or four days. They were very small prisms, a few tenths of a millimeter in their largest dimensions. In the cooler, distal, part of the sublimation tube, an amorphous green film formed on the walls. A film with a similar absorption spectrum could be obtained by sublimation in high vacuum onto a cool plate.

Photoconduction studies were carried out on an amorphous green film about 100 microns thick, sublimed onto silver electrodes painted on a glass plate in a form similar to that described by Calvin.[9]

Regularly shaped uranyl phthalocyanine crystals were selected and mounted in the two configurations described by Kronick and Labes[15] using micromanipulative techniques. To avoid contamination, no cement was applied to the crystals except at the electrodes.

Adhesion to fine copper wires through silver paint was relied upon to fix them. Because of the size of the crystals no guard ring could be applied, so reliable bulk conduction measurements could not be performed.

Measurements on the crystals were carried out in an evacuable cell at 10^{-3} torr oxygen (obtained by pumping out the air-filled cells without prior purging), 10^{-3} torr nitrogen (obtained by repeatedly evacuating the cell and refilling with nitrogen), and under one atmosphere of hydrogen. No variation in the dark or photoconduction of the crystals resulted from these changes in atmosphere. Measurements on the amorphous film were carried out in 10^{-3} torr nitrogen.

The light source was a tungsten-iodine lamp combined with a Bausch and Lomb Model 33-86 grating monochromator. High-order and scattered light was removed with glass filters. Electrical data were obtained by means of a simple d.c. circuit comprising a Keithley Model 240 power supply and a Keithley Model 610A electrometer with zero suppression when necessary. The photoresponse was only a few tenths of a percent of the dark current in the film, but 30% of that in the crystal, for which no zero suppression was required. The applied field was between 1000 and 2000 V cm^{-1}, in which range the dark current was linear with applied field.

Steady-state photoconduction measurements are best carried out on samples which are illuminated throughout their bulk. Unfortunately, spectral response measurements under such conditions are impossible in these opaque crystals, in which the volume uniformly illuminated in the absorption band is less than 10^{-4} cm thick, almost within the estimated skin depth for surface states.[16] Weakly absorbed light does not excite photocurrent efficiently. Thus, production of carriers occurs mostly near the surface of these crystals, permitting two experimental approaches if the wavelength of exciting light is to be varied: bulk-conduction measurements in which carriers are photogenerated at an electrode and injected into the bulk by the electric field; and surface-conduction measurements, in which carriers are uniformly produced in a thin superficial layer between electrodes attached to a sample surface. To minimize reduction of photoconductive gain due to the strong carrier trapping generally found in phthalocyanine crystals, shown by pulse measurements, the surface configuration was used for the present study. It will be seen, however, that bulk conduction, when it is an efficient process, can be observed and even dominate in a surface-cell arrangement.

Results

UO_2Pc can appear in either of two solid forms. Sublimed at high temperature or recrystallized from solution under certain conditions,[8] blue-black lustrous crystals appear. Collected from vapor at low temperature the solid is bright green, the same color as the solution, and appears to be amorphous. The specularly reflected light from the back side of a glass plate on which the green film is deposited appears blue.

In Fig. 1 is the spectrum of UO_2Pc dissolved in 1,3,5-trichlorobenzene. The same spectrum in solution is obtained whether the starting solid solute is the blue form or the green form. It is quite different from that of other phthalocyanine derivatives, showing only moderate absorption ($\epsilon = 1000\ M^{-1}\ cm^{-1}$) at 0.56 and 0.615 μ and strong absorptions at 0.8 and 0.9 μ and at 0.35 to 0.42 μ.

For comparison in Fig. 1 the absorption spectrum of a thin film sublimed onto a glass plate is also shown. The same bands are again evident, shifted slightly to the red, so that they now appear at 0.98 μ, 0.625 μ and 0.435 μ instead of 0.914 μ, 0.615 μ and 0.42 μ. Assuming that the bands do not change much in intensity in going from the solution to the solid state and that the solid state has a molar concentration of 2 M, then 90% of the light between 0.625 μ and 0.52 μ is absorbed in a layer from 2 to 5 μ thick in the solid. To a depth of a few tenths of a micron one can consider the solid to be uniformly illuminated.

Tiny, well-formed crystals of UO_2Pc appear blue both on their surfaces and in their interiors when broken. At first glance, they might appear to be a second crystalline form of this compound (polymorphism in phthalocyanines is well known).[17] When examined under a high-power microscope however, polarizing transparent regions with straight extinction can be found about 2 μ thick, transmitting green light. The morphology of these regions appears continuous with the adjacent blue-reflecting regions. When these crystals are ground with potassium bromide and pressed into a transparent pellet, the main absorption band in the near infrared appears at 0.94 μ, accompanied by less intense bands in the visible at 0.615 μ, 0.56 μ and 0.425 μ. Thus the solid in potassium bromide is almost identical to that in solution (Fig. 1). This spectrum is consistent with the observation that when the blue microcrystalline powder is gently crushed, for example between two glass plates, it turns green. Thus the blue color of the crystal is either due to a changed absorption spectrum characteristic of the crystalline form which is completely destroyed when the crystals are subjected to mild shearing forces (but not when larger

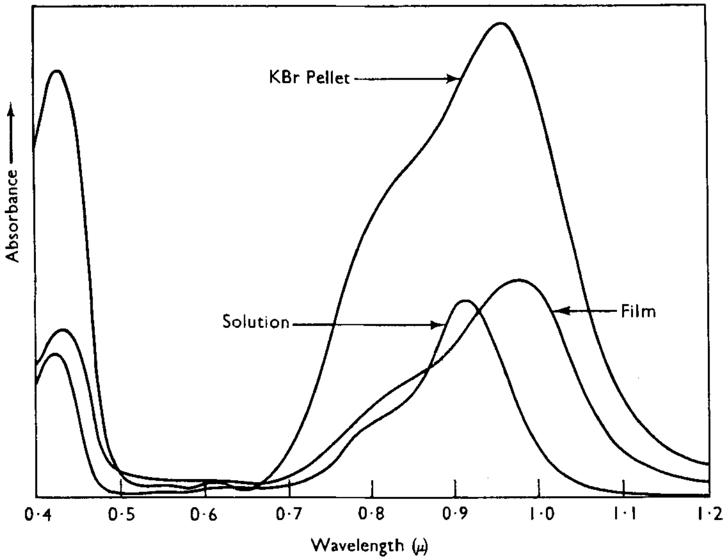

Figure 1. Absorption spectrum of uranyl phthalocyanine.
(A) 1,3,5-trichlorobenzene solution;
(B) Green sublimate on a glass plate;
(C) Blue crystals in a potassium bromide pellet.

crystals are broken), or, more likely, the absorption spectra of the amorphous powder and the crystalline powder are identical. The differences in color might be due to variations in reflection properties of the surfaces in different states of subdivision.

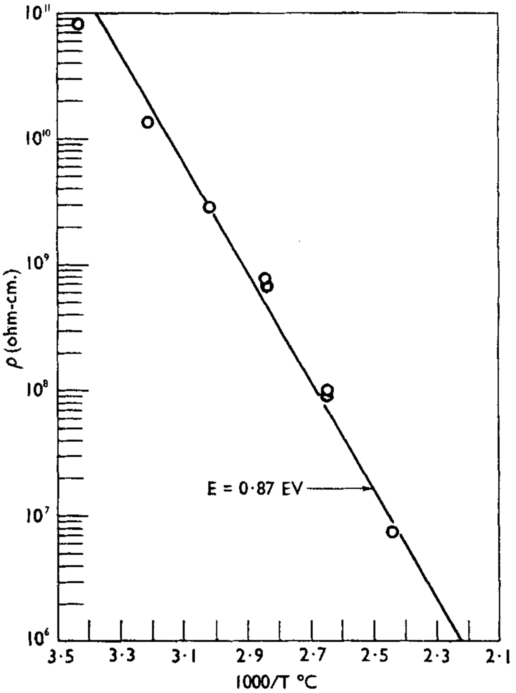

Figure 2. Dark conduction (ρ) in a uranyl phthalocyanine crystal. The slope of the line corresponds to E equal to 0.87 eV from the expression $\rho/\rho_0 = \exp(E/kT)$.

UO_2Pc in the dark is one of the more conductive of the phthalocyanines, with a resistivity of 3×10^{10} Ω-cm determined at room temperature on two blue single crystals (Fig. 2). Because of the very small size of the crystals no guard ring could be used, so it is impossible to distinguish between bulk and surface conduction in this sample. The values of resistivity in Fig. 2, however, are reproducible to an order of magnitude from one crystal to another although the crystallographic directions were varied from sample to sample. Also the values did not vary when the measurements were performed either in high vacuum, oxygen, or hydrogen. This insensitivity to the presence of oxidizing or reducing vapors is to be contrasted with that reported for copper phthalocyanine, for which the photoresponse increased[16] and the dark conduction decreased[13] when hydrogen was introduced. It may be that surface states are less important in the case of uranyl phthalocyanine than they are for the copper derivative. While the low value of resistivity might be taken as confirmation of the hypothesis about the role of 5f electrons, the activation energy of 0.87 is as high as reported for H_2Pc.[1] The crystals obtained in the present study were too small for the mobility to be determined by either Hall or pulse measurements. Further attempts are being made in this regard.

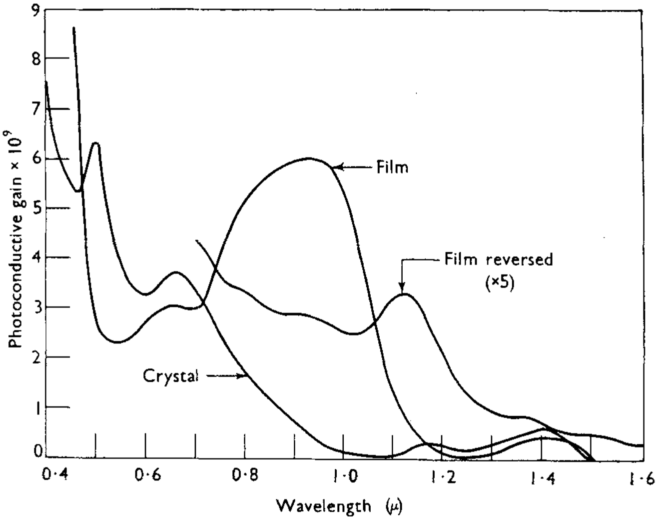

Figure 3. Photoconduction action spectra of uranyl phthalocyanine samples. Response curve for the reversed film has been multiplied 5 × .

Photoconduction was observed in the solid in both the green and blue forms. The photoconductive action spectrum of the green form is shown in Fig. 3. An outstanding deviation from the absorption spectrum appears at 1.42 μ where a photocurrent response peak is observed. No absorption in this region was observed; if a band exists here, its intensity must be less than 200 M^{-1} cm^{-1}. Weak bands in this infrared region have been reported for nickel-, Co-, Mn(II)- and H_2Pc.[2,3] In these materials again the absorption spectra do not exactly follow the photoconduction response spectra, although photocurrent maxima are also claimed in this IR region for Mn(II)Pc.[7]

The glass slide carrying the silver electrodes and green film was reversed, so that the exciting light was incident on the back of the specimen, on the face away from the electrodes. Since the film was at least 100 microns thick, no light in the main absorption band reached the surface carrying the electrodes. The photocurrent response multiplied 5 times is shown in Fig. 3. It resembles the behavior of a similar film of H_2Pc.[9] In the region of weak absorption the sample is illuminated in the bulk and at the surface no matter which side the light is coming from. The electrode contacts are much more weakly illuminated in the reversed film, however, because of light scattering from the rough back surface. The optical density of the sample is about 1 in the non-absorbing region. That the photocurrent peak at 1.42 μ, observed in front illumination, is missing in the curve for the reversed film suggests that this peak is an electrode effect.

When the wavelength is decreased toward the absorption peak, the absorption depth drops, the photocurrent response for the reversed sample falling below that for the directly illuminated sample. At these shorter wavelengths more and more carriers are being formed in a surface layer and fewer in the bulk. At 1.12 μ the photocurrent in the reversed sample begins to decrease, owing to the fact that charge transport in the electrodeless surface layer is much less efficient than in the front surface layer.

The strong increase in photocurrent as the light becomes more and more strongly absorbed in the front-illuminated sample indicates that photocurrent response of the film is greater when the carriers are generated at the surface than when they are generated in the bulk. If lifetimes and mobilities are not much greater at the surface, then photons absorbed close to the surface must be more efficient in producing carriers than those absorbed in the bulk. Thus, while the results on the reversed film indicate that there are some bulk-generated carriers, the most efficient carrier-generating process occurs at the surface. Photoconduction in the green film is then not an intrinsic process. This behavior is similar to that in aromatic hydrocarbons such as anthracene, in which carrier production by a single-exciton process occurs only near the surface of the crystal: bulk generation in anthracene requires either higher energy excitation above the first singlet exciton absorption[18] or a two-exciton process.[19]

Figure 3 also shows that the photocurrent response of the blue crystal does not follow the absorption spectrum, resembling more closely the response for the reversed green film. The photoresponse spectrum is clearly not that expected for a blue surface-conducting material, since its minimum response to visible light occurs at 0.6 μ, which for surface-generated carriers would occur in a material transmitting mostly orange light. A strong photocurrent maximum centered at 0.9 μ, which is the most prominent feature in the response curve for the green film, is almost entirely missing in the curve for the crystal. Instead, the photoresponse of the crystal begins to rise as the wavelength of the exciting light approaches the absorption maximum from the low-energy side, reaching a maximum at 1.18 μ. Below this wavelength most of the illuminating energy is absorbed in a film about 5×10^{-5} cm thick. A small photocurrent is seen in these crystals in the light-absorbing region, increasing only slowly with increasing exciting energy at wavelengths below 1.1 μ but increasing more sharply as the absorption intensity begins to decrease, below 0.98 μ. The response peak of the crystal at 0.66 μ does not correspond to the absorption peak at 0.625 μ (Fig. 1); the minimum at 0.60 μ more nearly does. Analogously, the response maximum at 0.50 μ need not correspond to an absorption maximum at that wavelength but could result from a balance among the efficiencies of carrier generation at the surface and in the bulk and the lifetimes of the carriers in the two regions.

Thus in the crystal the photoresponse *diminishes* as the exciting wavelength approaches the center of absorption bands. At a wavelength of 1.2 μ, 99% of the light is absorbed in the crystal beyond the skin depth of 5×10^{-5} cm, across which depth the optical density is 0.1. As the wavelength decreases below 1.2 μ, more and more of the light is absorbed in this surface layer. At the same time the photocurrent decreases in the crystal, indicating that greater photocurrents may be obtained from the bulk than from the surface. Further, the photocurrents corrected for illumination intensity in Fig. 3 for the crystal and the front-illuminated sublimed film, are of the same order of magnitude. These data, however, represent total photocurrent gains for the respective samples. The illuminated area of the film is about 1000 times greater than that of the crystal, so that the photocurrent sensitivity of the crystal per unit illuminated area is actually a thousand times greater than of the film.

The proposed mechanisms for generating charge carriers by light in the bulk include direct photoionization (excitation of electrons or holes into a conduction or valence band) or an indirect process involving exciton–exciton interaction. When the process is a direct one in a material with narrow bands, the thermal excitation energy should be the same as the minimum quantum energy for photoexcitation. The energy for thermal activation of carriers (from $\rho/\rho_0 = \exp(E/kT)$) in the UO_2Pc crystal (Fig. 2) is $E = 0.87$ eV, agreeing with the 0.87 eV photocurrent maximum of lowest energy, which occurs at the same place in both the evaporated film and the single crystal. The coincidence of this excitation maximum for film and crystal is to be expected at a wavelength of light of which only a negligible portion is absorbed at the surface. Exact agreement between the photoconductive excitation and the thermal activation energies need not imply a direct excitation process between the valence and conduction bands. It does, however, strongly suggest that the conduction experiments in the presence of exciting light and in the dark measure the same phenomenon in this system. The dependence of the photocurrent gain upon the sample form and upon the absorption coefficient suggests that this phenomenon is occurring in the bulk of the single crystal.

Conclusions

Irradiation in the absorption bands of UO_2Pc stimulates photocurrents, sublimed films showing strongest photocurrent response in the near infrared. In this respect the actinide-substituted phthalocyanine differs from the previously investigated transition-metal derivatives with visible-red absorption and photocurrent response maxima. Single crystals of UO_2Pc exhibit photoconductive gain about a thousand-fold greater than that found in its sublimed films. Modification of the electrical behavior in the dark, however, such as marked lowering of the activation energy for conduction was not observed.

REFERENCES

1. Linstead, R. P., *J. Chem. Soc.* 2873 (1953).
2. Fielding, P. E. and MacKay, A. G., *J. Chem. Phys.* **38**, 2777 (1963).
3. Fielding, P. E. and MacKay, A. G., *Austral. J. Chem.* **17**, 750 (1964).
4. Day, P. and Williams, R. J. P., *J. Chem. Phys.* **37**, 567 (1962).
5. Day, P. and Williams, R. J. P., *J. Chem. Phys.* **42**, 4049 (1965).
6. Engelsma, G., Yamamoto, A., Markham, E., and Calvin, M., *J. Phys. Chem.* **66**, 2517 (1962).
7. Day, P., Scregg, G., and Williams, R. J. P., *Nature*, **197**, 589 (1963).
8. Bloor, J. E., Schlabitz, J., Walden, C. C., and Demerdache, A., *Canadian J. Chem.* **42**, 2201 (1964).
9. Tollin, G., Kearns, D. R., and Calvin, M., *J. Chem. Phys.* **32**, 1013 (1960).
10. Chadderton, L. T., *J. Phys. Chem. Solids* **24**, 751 (1963).
11. Heilmeier, G. H., Warfield, G., and Harrison, S. E., *Phys. Rev. Letters* **8**, 309 (1962).
12. Delacote, G. and Schott, M., *Phys. Status Solidi* **2**, 1460 (1962).
13. Heilmeier, G. H. and Harrison, S. E., *Phys. Rev.* **132**, 2010 (1963).
14. Harrison, S. E. and Assour, J. M., *J. Chem. Phys.* **40**, 365 (1964).
15. Kronick, P. L. and Labes, M. M., *J. Chem. Phys.* **35**, 2016 (1961).
16. Heilmeier, G. H. and Zanoni, L. A., *J. Phys. Chem. Solids* **25**, 603 (1965).
17. Assour, J. M., *J. Phys. Chem.* **69**, 2295 (1965).
18. Castro, G. and Hornig, J. F., *J. Chem. Phys.* **42**, 1459 (1965).
19. Silver, M. *et al.*, *Phys. Rev. Letters* **10**, 12 (1963).