

Photoconductivity in crystalline phthalocyanines

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Abstract. The wavelength, temperature, time and intensity dependence of photocurrent of metal-free phthalocyanine (H_2Pc) and copper phthalocyanine ($CuPc$) single crystals were investigated. The thermal activation energies in the dark are 0.5 and 0.6 eV for H_2Pc and $CuPc$ respectively and the corresponding photo-thermal activation energies are 0.3 and 0.2 eV. An energy level scheme for single crystals of H_2Pc and $CuPc$ is proposed which consists of two trapping levels and five narrow optically active valence bands. In H_2Pc ($CuPc$), one trapping level at 0.5 eV (0.6 eV) above the valence band edge to which the charge carriers are thermally excited in the dark; and the other trapping level is at 0.3 eV (0.2 eV) below the conduction band edge where all the optical transitions terminate. In H_2Pc ($CuPc$), the forbidden gap is 1.44 eV (1.34 eV) wide; the five valence bands are at the band edge, and 0.09 (0.22), 0.42 (0.63), 0.69 (0.90), 1.32 (2.17) eV below the band edge.

Keywords. Organic semiconductor; photoconductivity.

1. Introduction

Phthalocyanines (Pc's) are semiconductors (Inokuchi 1989) that exhibit significant photoconductivity. The most common polymorphic forms of Pc's are designated α -form and β -form (Moser and Thomas 1963; Gutmann and Lyons 1981; Simon and Andre 1985). The α -form occurs as polycrystalline films formed by sublimation onto cold substrates, in vacuum, while the β -form, which is the subject of this study, occurs when single crystals are produced by vacuum sublimation at a temperature around 460°C. The crystals are needle-shaped, typically 2 to 3 cm long, 0.03 cm wide and 0.013 cm thick.

2. Experimental

Crystals were grown from 99.9% pure phthalocyanine by slow sublimation in vacuum at 460°C, and prepared for measurement by applying silver conducting paint electrodes across the short dimension, separated by between 1 and 2 mm.

The experimental arrangements were as shown in figure 1. Light from a 100 watt quartz-halogen lamp was incident on the sample through a monochromator (Instruments SA, H20 800VIR). The sample, kept enclosed inside a quartz cylindrical tube connected to a vacuum system, was electrically connected in series with a DC power supply and an electrometer (Keithley 614). A potential of 500 V was applied across the electrodes. For the temperature dependence of photoconductivity measurements a heater-coil arrangement and a thermocouple (Constantin-Copper) were used. The readings were registered using a X-Y plotter (YEW 3022 A4).

In H_2Pc the photoconductivity spectrum over the range 1.00 to 3.50 eV exhibits one large maximum at 1.56 eV with a width at half maximum of 0.17 eV, and a broader large maximum at 2.46 eV with about half the amplitude of the first peak and

a half-width of 0.41 eV. There are three additional smaller peaks, at 1.14, 1.23 and 1.83 eV (figure 2). In CuPc, the two major peaks appear to have coalesced into a broad feature lying between around 1.59 eV and 2.75 eV with maxima at 1.77 and 2.04 eV (figure 3). The three smaller peaks appear at 1.14, 1.36 and 3.31 eV.

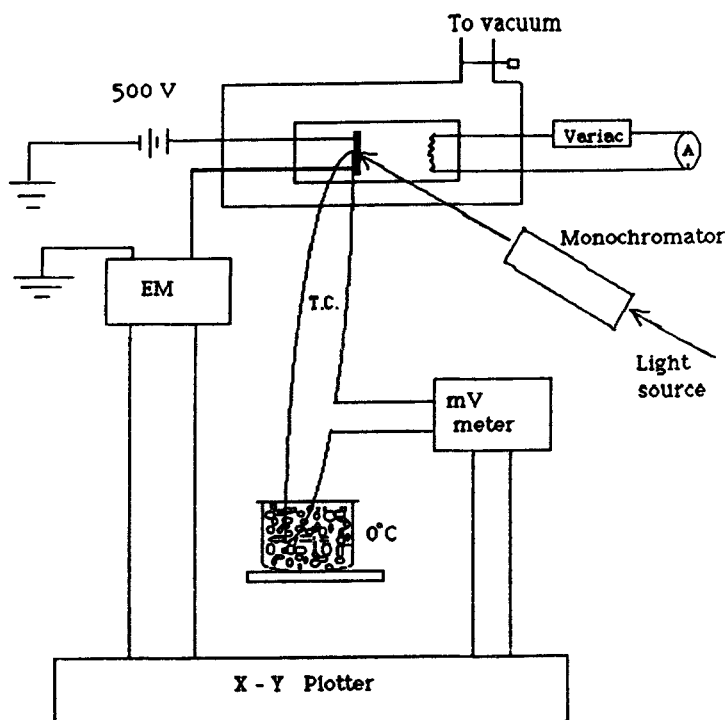


Figure 1. Apparatus for photoconductivity measurement.

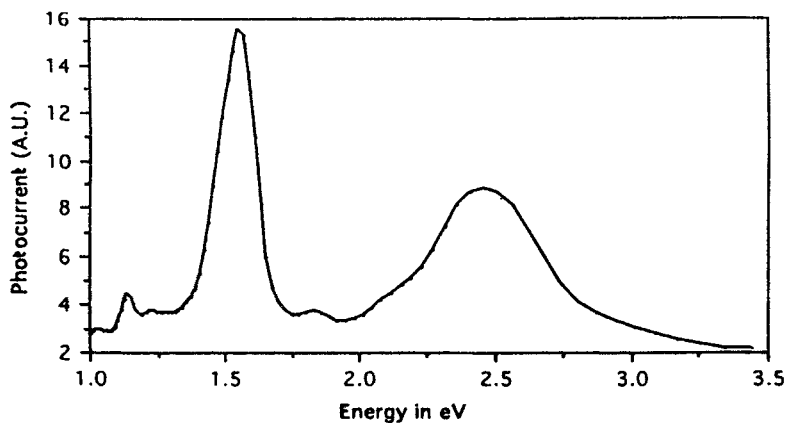


Figure 2. Photoconductivity spectrum of H₂Pc crystal.

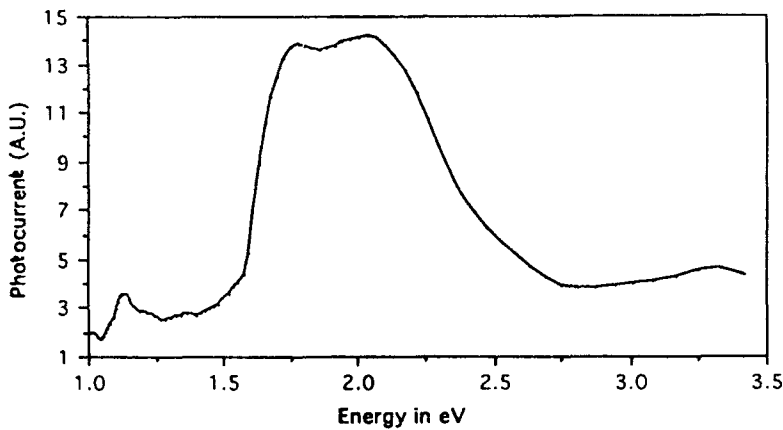


Figure 3. Photoconductivity spectrum of CuPc crystal.

The photocurrent is dependent on the square root of the intensity in both modifications:

$$I_{\text{ph}} = (\text{const}) L_{\text{int}}^{0.5} \quad (1)$$

Over the temperature range 100–300 K, the photoconductivity follows the relation

$$\sigma = \sigma_0 e^{-E_t/kT} + C, \quad (2)$$

where T is the temperature, E_t the activation energy, and C represents dark current plus leakage current. Under excitation at wavelengths corresponding to the major peaks the activation energy, E_t , is 0.3 eV for H_2Pc (figure 4) and 0.2 eV for CuPc. In the dark, over a similar temperature range, the thermal activation energy for H_2Pc is 0.5 eV, and for CuPc it is 0.6 eV.

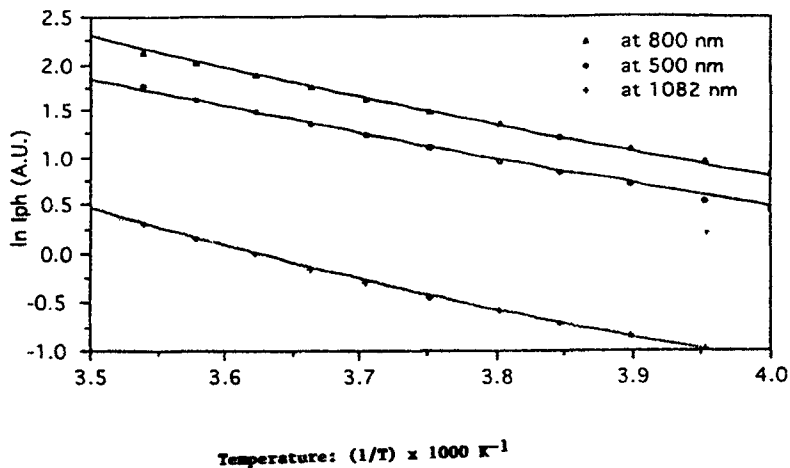


Figure 4. $\ln I_{\text{ph}}$ vs $(1/T)$ of H_2Pc crystal.

The time dependences of the photoconductivity at the onset and removal of excitation are exponential with long time constants. A representative plot of the time dependence of photocurrent, I_t , in H_2Pc illuminated at 800 nm is shown in figure 5a. The rising portion corresponds to the relation

$$I_t = I_0(1 - e^{-t/\tau_r}), \quad (3)$$

where t is the time and τ_r is a characteristic time constant. The resulting value of τ_r is 1.55 sec (figure 5b).

The decaying portion corresponds to the relation

$$I_t = I_0(e^{-t/\tau_1} + e^{-t/\tau_2}). \quad (4)$$

The shorter time constant, τ_1 , is 1.33 sec. The longer time constant, τ_2 , is 11.4 sec (figure 5c). Simultaneous illumination of the crystal with IR light ($\lambda > 1100$ nm) results in an approximate doubling of the photocurrent and no change in the rise time but a 30% reduction in the decay time.

3. Discussion

We consider first the steady-state characteristic.

With regard to the intensity dependence, it has been suggested (see, e.g. Bube 1960, Rose 1963, Böer 1990) that carrier traffic among multiple trapping levels with the associated shift in the "quasi-Fermi levels" does, under these conditions, yield, in the steady state as found here, a dependence on intensity of the form $n_i = (g_0/C)^{1/2}$.

The thermal activation energy in the dark is 0.5 eV for H_2Pc and 0.6 eV for $CuPc$. Under constant illumination it is, respectively, 0.3 and 0.2 eV independent of the exciting wavelength. This behaviour suggests that the effective phototransitions lead to a common terminal state which becomes the source of the thermally excited carriers. On this basis and considering the p-type behaviour of both modifications, the following energy level schemes (figures 6 and 7) emerge.

In H_2Pc there are two electron trapping levels, one 0.5 eV (F) above the valence band edge and a second 0.3 eV (G) below the conduction band edge. Level F serves as a trap for electrons thermally excited in the dark. The common thermal activation for equilibrium photoconductivity at all excitation wavelengths corresponds to a common trapping level 0.3 eV below the conduction band. Electrons trapped into these levels subsequently are either thermally excited into the conduction band, recombine with holes in the valence bands, or are trapped in a trapping level at a lower energy. With the lowest energy valence band at 1.14 eV (E) below the common trapping centre, the two trapping levels are separated by 0.64 eV (G–F) and the entire forbidden gap is 1.44 eV (E–H) wide. The five narrow valence bands are therefore located at the band edge (E) and at 0.09 eV (D), 0.42 eV (C), 0.69 eV (B), and 1.32 eV (A) below the band edge (see figure 6).

In the copper-substituted modification, thermal activation of the photoexcited states places the upper trapping level 0.2 eV (G) below the first conduction band. The dark activation energy places the lower trapping level at 0.6 eV (F) above the first valence band. The five optically active valence bands are at the band edge (E) and at 0.22 eV (D), 0.63 eV (C), 0.90 eV (B), and 2.17 eV (A) below the band edge (see figure 7).

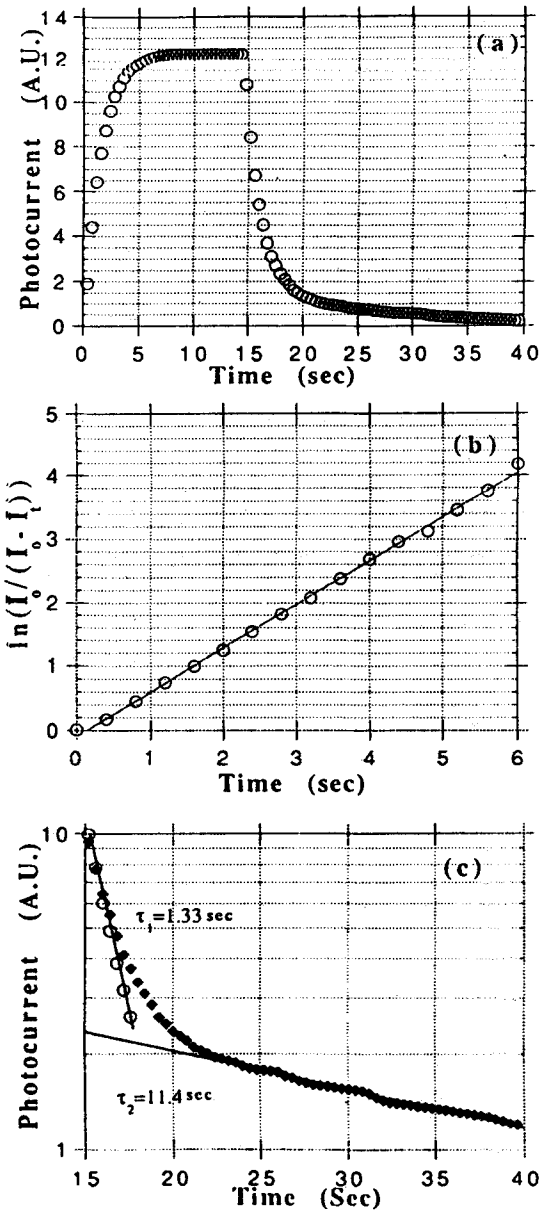


Figure 5. a. Response curve for H₂Pc crystal, b. rise of photocurrent in H₂Pc crystal ($t_r = 1.55$ sec) and c. two-step decay curve for H₂Pc crystal: the shorter time constant $t_1 = 1.33$ sec and the longer time constant $t_2 = 11.4$ sec.

Thus, according to this model, in the dark electrons are excited thermally from band E into trapping level F leaving behind free holes in band E. This would account for the observed thermal dark activation energy. Similarly, electrons optically excited into level G are raised thermally into the lowest conduction band, H, giving rise to the

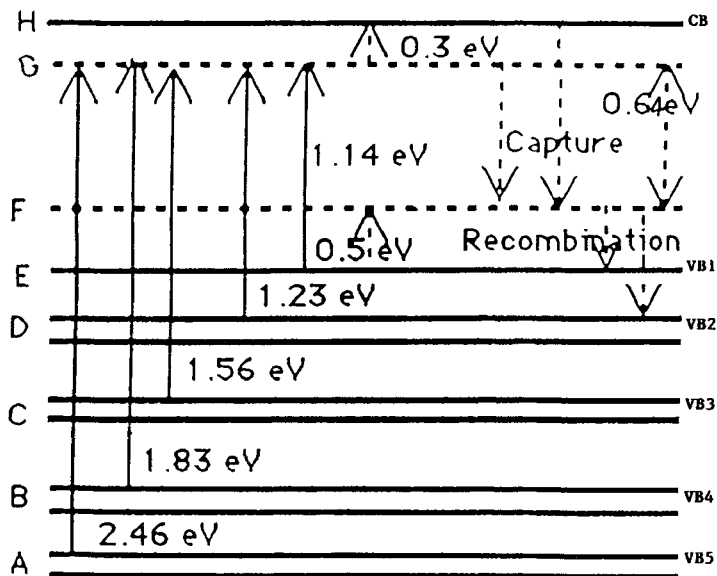


Figure 6. Energy level scheme for H_2Pc crystal.

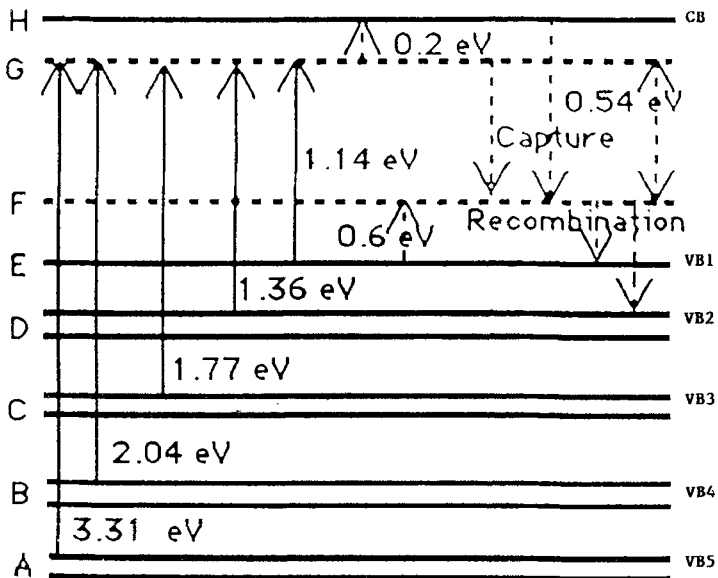


Figure 7. Energy level scheme for $CuPc$ crystal.

0.3 eV and 0.2 eV activation energy observed respectively for the optically excited states in H_2Pc and $CuPc$.

We consider next the temporal behaviour of the photocurrent (figure 5). Optical excitation raises the electrons to trapping level, G, leaving free holes in the relevant

valence band. Electrons in level G may then either be thermally excited into the conduction band, H, or captured in level F. The capture cross-section to level F both from the lowest conduction band and from level G is evidently sufficiently large to dominate. Level G continues to fill until its rate of decay to the "capture" level, F, equals the optical excitation rate. We assume, also, that electrons promoted thermally to the lowest conduction band are very quickly captured in level F (H to F). Electrons in level F are recaptured by recombining with holes in the valence band.

The two-step decay from equilibrium photocurrent after removal of illumination (figure 5c) results from the sequential electron decay G to F (shorter decay constant), followed by F to the valence bands (longer decay constant).

Infrared stimulation of photocurrent occurs because the magnitude of the photocurrent is limited by the equilibrium populations in the two trapping levels, since the electron holdup in these two levels establishes the concentration of free holes. The effect of the infrared is to excite electrons from the upper valence band into level F and from level G into H. The net effect is to increase the population of free holes in the valence bands, and simultaneously to increase the number of extra electrons in the lower conduction bands. The decrease in the decay time is a consequence of an increase in the population of photoexcited electrons in level F.

References

- Böer K W 1990 *Survey of semiconductor physics* (New York: Van Nostrand Reinhold)
Bube R H 1960 *Photoconductivity of solids* (New York: John Wiley)
Gutmann F and Lyons L E 1981 *Organic semiconductors (Part A)* (Malabar: Krieger)
Inokuchi H 1989 *Mol. Cryst. Liq. Cryst.* **171** 23
Moser F H and Thomas A L 1963 *Phthalocyanine compounds* (New York: Reinhold)
Rose A 1963 *Concepts in photoconductivity and allied problems* (New York: Interscience)
Simon J and Andre J J 1985 *Molecular semiconductors* (Berlin: Springer)