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Photoconductivity of iodine-doped single crystals of phthalocyanine

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Abstract. Single crystals of metal-free phthalocyanine (H_2Pc) and of copper phthalocyanine (CuPc) were grown in the presence of iodine vapour. The presence of iodine enhances the spectral dependence of photoconductivity of H_2Pc in the visible region but of CuPc in the near-IR region. The dark current is decreased but the photocurrent is increased by one order of magnitude in iodine-doped H_2Pc but in the case of iodine-doped CuPc both currents are increased by nearly three orders of magnitude. Introduction of iodine results in about one order of magnitude decrease in response time for both modifications. Thus the introduction of iodine into Pc crystals decreases the energy barrier for conduction and increases the drift mobility of charge carriers thereby enhancing the conductivity of the material.

Keywords. Photoconductivity; doping; organic semiconductor.

1. Introduction

Study of doped semiconductors has proven useful in the area of electronic technology today. Some organic materials which have a structure of conjugated single/double bond chain possess photoconductivity (Inokuchi 1989). Doping of photoconductors by suitable dopants has been shown to increase the conductivity of materials (Schramm *et al* 1980; Hoffman *et al* 1983; Barbaszweski *et al* 1986; Zabkowska-Waclawek *et al* 1987; Orihashi *et al* 1988; Harikumar *et al* 1989) by several orders of magnitude (Waclawek *et al* 1987). The doping is, in general, done by diffusion, i.e. exposing the crystals to iodine vapour for a few hours. But in this investigation single crystals of metal-free phthalocyanine (H_2Pc) and copper phthalocyanine (CuPc) were grown in the presence of iodine vapour.

2. Experimental

In a Pyrex tube 20 cm long and 3·5 cm in diameter fitted with a side arm, phthalocyanine powder (about 5 g) was placed. A few iodine crystals were placed in the side arm. The Pyrex tube was then evacuated. Because of the high vapour pressure of iodine the pressure could not be brought below about 40 millitorr but with the use of a liquid nitrogen trap to lower the iodine vapour pressure, the pressure was brought down to a few millitorr before sealing off the tube. The main tube was inserted into a temperature-controlled oven leaving the side arm outside the oven near room temperature. Crystal growth was then allowed to proceed. For iodine-doped metal-free phthalocyanine (HPcI) single crystal growth the temperature at the point where Pc powder was placed was maintained at 460°C, whereas the iodine-doped copper phthalocyanine (CuPcI) single crystals started growing only when the temperature was raised to 500°C. The crystals appeared in the form of clusters of hundreds of whiskers with dimensions of about 15 mm × 0·3 mm × 0·13 mm. The colour of the crystals was dark red. The crystals were tested for the presence of free iodine by rinsing them with trichloroethylene. In no case was the characteristic purple colour of free iodine observed. Further the doped crystals were heated up to 100°C and it was established, from the study of the photoconductivity spectra, that the iodine was stable in the doped crystals.

For the study of the spectral behaviour of the photoconductivity, the samples were mounted on a glass substrate. Electrode contacts, spaced 1 to 2 mm along the crystal growth axis (*b* axis), were attached to the crystals using silver paint and thin copper wires. The sample thus prepared was connected in series with an electrometer (Keithley 614) and a DC power supply. A potential of 500 V DC was applied across the sample. The photoconductivity was measured as a function of wavelength by use of a monochromator. In the case of undoped H_2Pc the photoconductivity spectrum exhibits maxima at about 1·14, 1·23, 1·56, 1·83 and 2·46 eV (figure 1a). The spectrum of iodine-doped crystal (HPcI) retains the same maxima as in the undoped material. There is, however, an additional broad maximum at about 2·1 eV (figure 1b). In the case of CuPc undoped crystal the photoconductivity spectrum exhibits maxima at about 1·14, 1·36, 1·77, 2·04 and 3·31 eV (figure 2a). But the photoconductivity spectrum of CuPcI differs markedly from that of the undoped form. The major response is shifted entrirely toward the red end of the spectrum (figure 2b) with maxima at about 1·05, 1·19, 1·26, 1·49 and 2·44 eV.

Comparison of the doped-during-growth crystals with the undoped crystals reveals that the dark current in the unsubstituted modification is decreased by one order of

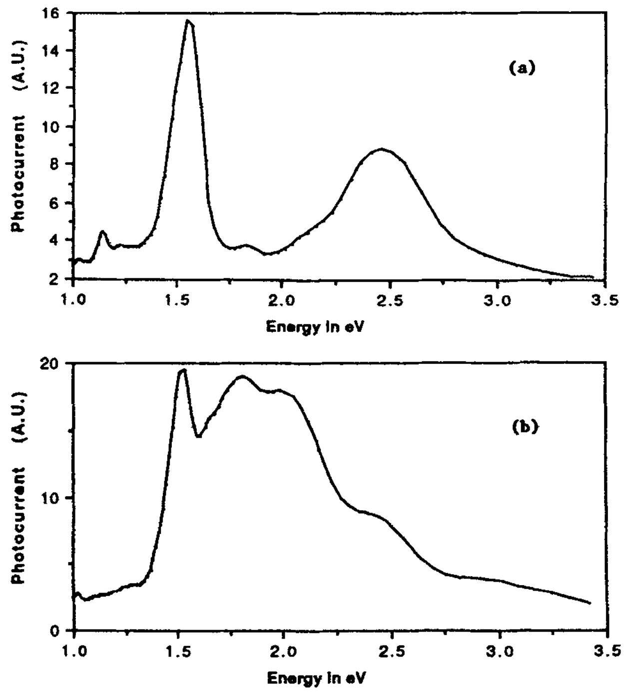

Figure 1. Spectral dependence of photoconductivity of (a) single crystal of H_2Pc and (b) iodine-doped single crystal of H_2Pc.

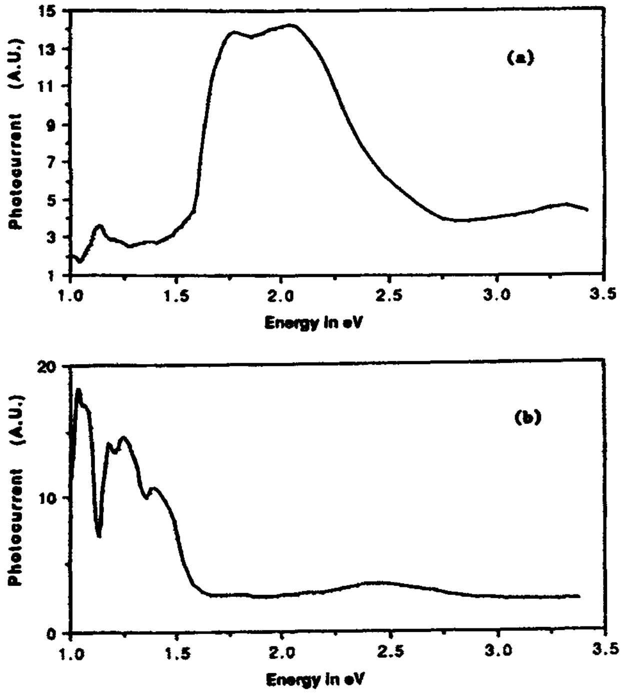

Figure 2. Spectral dependence of photoconductivity of (a) single crystal of CuPc and (b) iodine-doped single crystal of CuPc.

Table 1. Comparison of iodine-doped crystals with undoped crystals.

	H_2Pc	HPcI	CuPc	CuPcI
Dark current (amp)	$4{\cdot}45 \times 10^{-11}$	$3{\cdot}15 \times 10^{-12}$	$1{\cdot}82 \times 10^{-13}$	$1{\cdot}13 \times 10^{-10}$
Photocurrent (amp)	$1{\cdot}86 \times 10^{-9}$	$1{\cdot}12 \times 10^{-8}$	$2{\cdot}53 \times 10^{-12}$	$2{\cdot}76 \times 10^{-9}$
Rise time (sec)	1·37	0·10	1·97	0·28
Decay time (sec)	2·20	0·09	2·68	0·18

magnitude upon doping while in CuPcI it is increased by nearly three orders of magnitude upon doping as shown in table 1. The discrepancy in the case of the copper-substituted Pc may be due to the leakage current in the circuit. For the purpose of measuring the photocurrent, light from a quartz–halogen lamp (through the monochromator at zero order) was incident on the sample and the corresponding current in the circuit noted using an electrometer (Keithley 614). The photocurrent at similar conditions of incident intensity is greater in HPcI than in H_2Pc by one order of magnitude and it is three orders of magnitude greater in CuPcI than in CuPc (Grigoryan *et al* 1984; Waclawek *et al* 1987) as shown in table 1. All the samples investigated—both undoped and iodine-doped—exhibited pronounced photoconductivity along the *b*-axis, while no photoconductive response was observed perpendicular to this direction.

The illumination was modulated by means of a standard camera leaf shutter capable of opening and shutting within 0·01 sec or faster. From the current measuring circuit the output of the electrometer was led to a strip chart recorder ($t_r = 0{\cdot}1$ sec; maximum chart speed 30 cm/min). Light from the source was incident on the crystal through the monochromator set at zero order and fitted with the camera shutter. The measurements were carried out at room temperature. The procedure was first to illuminate the sample for a few seconds and then close the shutter while recording the decay of the photocurrent. After the current reached its minimum value, the shutter was opened and the steady-state current was allowed to rise till it attained a constant value once more. The rise and decay times were measured between 10% and 90% points using an oscilloscope (Hitachi V-222). In the iodine-doped crystals the response time were lower by one order of magnitude for both modifications (table 1).

3. Discussion

The introduction of iodine into a Pc results in a new material where the dopant iodine is stable since heating of the iodine-doped material up to 100°C does not alter the characteristics of the doped crystal. In the case of HPcI, the introduction of iodine seems to populate all the energy levels between 1·56 and 1·83 eV and also those between 1·83 and 2·4 eV (figures 1a and 1b). The level corresponding to the energy level at 1·83 eV which is seen in the undoped H_2Pc is still seen in the iodine-doped crystal. Due to the population increase in this level also, the photocurrent seen at 1·83 eV in the doped crystal is higher than that seen for the undoped crystal. In the case of CuPcI, the material becomes photoactive in the near-infrared range of the spectrum on doping with iodine, in lieu of its activity between 1·6 to 2·5 eV in the undoped crystal (figures 2a and 2b). The valence band in the CuPcI crystal is therefore continuous for energies higher than about 1·6 eV. The increase of photocurrent in iodine-doped crystal indicates that the iodine makes the crystal more photosensitive. Since the Pc's are p-type material and iodine is an electron acceptor, introduction of iodine probably enhances the mobility of holes acting as a trap for electrons. The shorter rise and decay times in the iodine-doped crystals probably indicate that the drift mobility of charge carriers is greater since the lifetime of charge carriers in the traps is shorter. Based on this experimental evidence we could conclude that the introduction of iodine into Pc crystals decreases the energy barrier for conduction and increases the drift mobility of charge carriers thereby enhancing the conductivity of the material.

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