CHEMISTRY LETTERS, pp. 99-102, 1975. Published by the Chemical Society of Japan

PHOTOINJECTION OF ELECTRONS AND HOLES INTO p-TERPHENYL FROM METALLIC CONTACTS

Masahiro KOTANI and Shigeru OHNO
Faculty of Science, Gakushuin University
Mejiro, Toshima-ku, Tokyo 171

The photoconduction excitation spectrum was measured in the energy range of 1.0-6 eV for p-terphenyl single crystals. The photoconduction by photons $h\nu < 2.4$ eV was attributed to the injection of excited holes from the gold electrode. The ionization energy of p-terphenyl was estimated to be 6.0 eV.

The luminescent properties of p-terphenyl have been extensively investigated, mainly because of its short fluorescence lifetime which has stimulated its use as the scintillation counter. The investigation of the photoconductive phenomena are, however, rather scarce. One can only find a measurement of the activation energy by Kommandeur et al.1) and a rather indirect estimation of the carrier mobility from an analysis of the space-charge-limited-current by Mark and Helfrich.2) Kryszewski et al. have also reported the photoconductive properties of p-terphenyl.3)

We have been interested in the photoinjection of carriers from metallic contacts which has been first demonstrated with organic crystals by Williams and Dresner,4) and have tried to extend the method to p-terphenyl in order to check the validity of the proposed model.

p-Terphenyl was purified by recrystallization and zone-refining. Thin platelet crystals were grown from 1,2-dichloroethane solutions. Thickness of the crystals ranged from 10 to 50 μm. The light from a 1 kW Xenon lamp was focused onto crystals after monochromatized with a combination of interference filters and suitable cut-off filters. The intensity of the incident light was measured by a thermopile and phototransisters. Crystals were cemented with epoxy resin on Pyrex plates in a similar manner as described by Williams and Dresner. The aqueous solution of NaCl (0.1 M) was employed as the transparent electrode, as it dose not inject carriers to an appreciable extent. Metal electrodes were formed by vacuum sublimation. During the vacuum sublimation the water behind the crystal acted as the heat sink, preventing the sublimation of the specimen. The electrode area was 1×10^{-2} cm^2. The observed dark currents were of the order of $10^{-12} \sim 10^{-13}$ A. Photocurrents of $10^{-8} \sim 10^{-14}$ A were observed. Currents were measured by a Takeda-Riken TR-8651 electrometer, which enabled the subtraction of the dark currents.

The excitation spectra for photoconduction were measured in the energy range from 0.7 to 6 eV. When single crystals of p-terphenyl were sandwitched between aqueous electrodes, they exhibited a structured photoconduction spectra mainly lying in the wavelength range shorter than 350 nm (Fig. 1). They exhibited no observable photoconduction below the photon energy of 2.2 eV. When the positive electrode was replaced by an evaporated gold film, the excitation spectrum extended to as low as 1.0 eV, as shown in Fig. 2. Also shown in the figure is the photoconduction with reversed applied voltage, which is essentially identical with the spectrum observed in the water/p-terphenyl/water system. The shape of the excitation spectra for the hole injection changed little when the applied voltage from 30 to 300 V, although the photocurrents increased with applied voltage. Photocurrents in the long wavelength region were also observed with silver and copper electrodes. The threshold energies for the photoconduction are listed in Table 1.

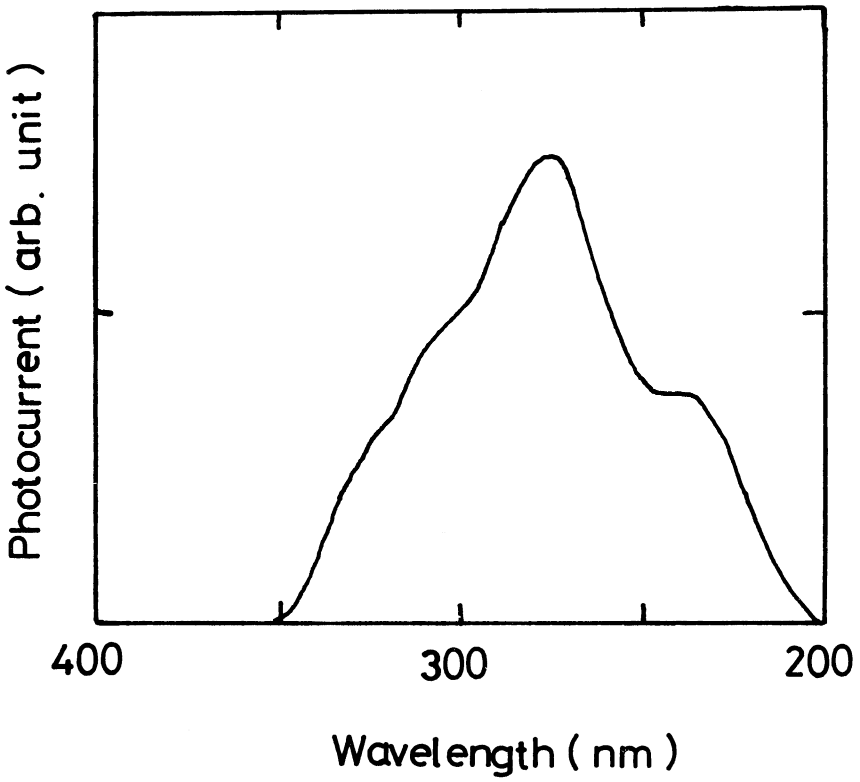

Fig. 1. Photoconduction Excitation Spectrum of p-Terphenyl.

The ionization energy of p-terphenyl crystal, I_c, calculated as

$$I_c = \phi_M + \phi_h ,$$

where ϕ_M is the work function of the electrode metal and ϕ_h is the threshold photon energy for the photoconduction, yields the mean value of 6.0 eV with three different electrode metals. This value is in fairly good agreement with that obtained by Hino, 6.1 eV, through the external photoemission measurement.$^{5)}$ The agreement support our interpretation that the long wavelength photoconduction is ascribed to the photoinjection of holes into p-terphenyl.

On evaporation of sodium or calcium onto the surface the crystal exhibited deep blue color, indicating the presence of (p-terphenyl)$^-$ ion. Photoconduction response extending to long wavelengths was observed when the evaporated metals were negatively biased, indicating the electron injection to occur. The threshold energies are also listed in Table 1.

If the metal-insulator interaction is purely electrostatic, the electron affinity of the crystal, A_c, is estimated as,

$$A_c = \phi_M - \phi_e ,$$

where ϕ_e is the threshold energy for the electron injection. Calculated electron affinity amounts to 1.5∼1.8 eV. A rough estimation of the electron affinity is also possible from the relation,

$$\frac{I_c + A_c}{2} = 4.15 \text{ eV} ,^{6,7)}$$

which, adopting 5.96 eV as I_c , yields 2.3 eV for A_c of p-terphenyl.

Table 1. Threshold energy for photoinjection into p-terphenyl and ionization energy (eV)

Metal	ϕ_M	ϕ_h	ϕ_e	I_c
Au	4.97	1.00		5.97
Ag	4.68	1.28		5.96
Cu	4.40	1.54		5.94
Ca	3.21		1.73	
Na	2.30		0.9	

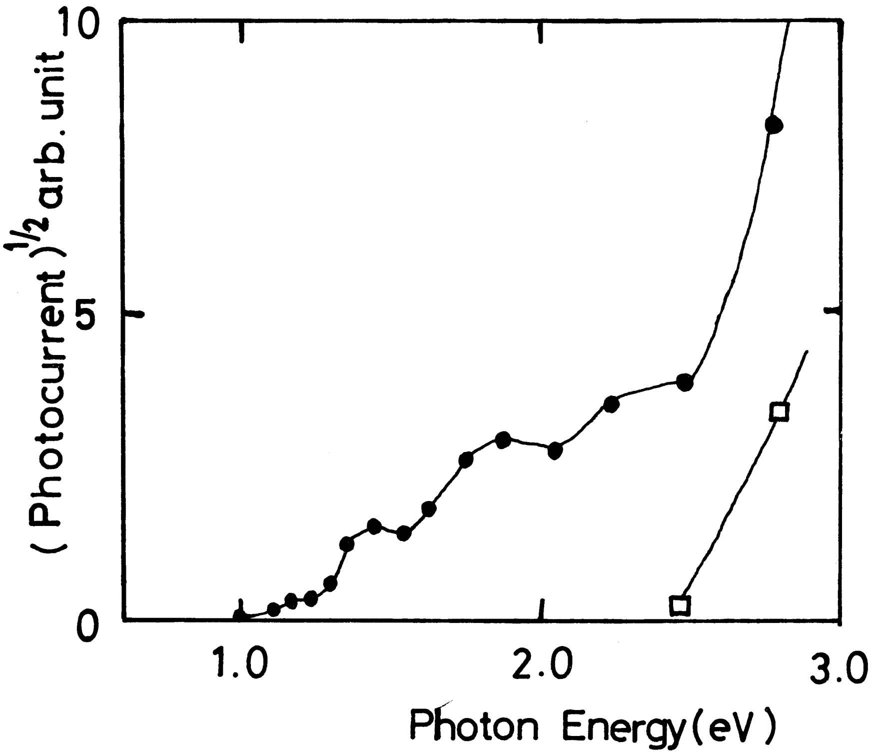

Fig. 2. Photoconduction Spectrum for Au/p-terphenyl/H_2O. Applied Voltage;300V

REFERENCES

1)J.Kommandeur, G.J.Korinek, and W.G.Schneider, Can. J. Chem., 35,998 (1957).
2)P.Mark and W.Helfrich, J.Appl.Phys., 33, 205 (1962).
3)M.Kryszewski, S.Sapieha, and A.Szymanski, Acta Phys. Pol., 33,529 (1968).
4)R.Williams and J.Dresner, J.Chem.Phys., 46, 2133 (1967).
5)S.Hino, private communication.
6)R.S.Becker and E.Chen, J.Chem.Phys., 45, 2403 (1966).
7)M.Kotani and H.Akamatu, Bull.Chem.Soc.Jap., 43,30 (1970).

(Received October 30, 1974)