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## *The Photoconductivity of Cobalt Phthalocyanine Thin Films*

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### Introduction

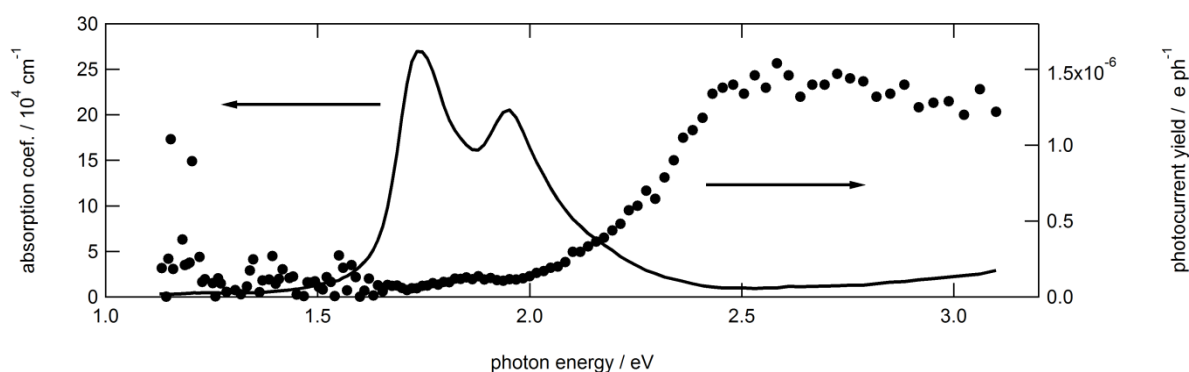
The phthalocyanine ligand can complex with a wide variety of central metal ions. Many of the open shell metal-phthalocyanine complexes, such as cobalt phthalocyanine (CoPc), exhibit interesting spin properties. As far as the solid state photo-electrical properties of the first row transition metal phthalocyanine complexes are concerned the electron configuration of the central metal ion does not generally appear to have a much influence. There is rarely any mixing between the current-carrying electronic states and the atomic orbitals of the central metal. The metal ion may, however, indirectly alter the electrical properties of the material via steric effects which change the packing structure, and hence the intermolecular orbital overlaps. CoPc may therefore be considered a “generic” phthalocyanine complex, and we examine the photoconductivity in the context of exploring the typical behavior of this class of organic semiconductor.

Our aim is to address one of the fundamental difficulties in discussing electrical measurements on organic thin films: the difficulty in assigning the observed properties to intrinsic or extrinsic effects. Organic films have amorphous and/or polycrystalline structure, with a high defect density and a large number of grain boundaries. The chemical purity is also relatively low. Extrinsic effects (acceptor, donor, and trap sites) would normally be expected to dominate the measured electrical properties, so the challenge is instead to observe and identify *intrinsic* (trap free) behavior. We do this by carefully purifying the starting materials and by using *in situ* measurement techniques under an ultrahigh vacuum environment.

### Experimental

CoPc (Aldrich) was sublimed three times under 30 Pa N<sub>2</sub> gas flow before use. Single crystal sapphire [0001] substrates (Shinkosha) were first annealed at 1000 °C in air to expose atomically flat terraces, over which 30 nm titanium electrodes spaced 0.1 mm apart were vacuum deposited through a metal mask. Once placed inside the measurement chamber, the substrates were degassed at 250 °C under UHV before use. Leakage currents (dark or photoconductance) were below 10 fA at 10<sup>5</sup> V m<sup>-1</sup>. Films were prepared by thermal deposition from a resistively heated crucible. The substrate temperature was kept at 125 °C, and the deposition rate was held constant at 1.5 ± 0.5 nm min<sup>-1</sup>. After deposition, the film was annealed at 200 °C for 12 h. Photocurrent action spectra were evaluated for wavelengths from

400 nm – 1180 nm, using a Bunkokeiki SM-25 monochromatic light source and a Keithley 6487 picoammeter-sourcemeter. The incident photon flux was  $10^{19}$  photons  $m^{-2}$  and the applied bias was  $10^5$  V  $m^{-1}$ . Measurements were obtained at a repetition rate of approximately 0.1 Hz, with dark current subtraction performed for each data point. The optical absorbance was measured *ex situ* on a reference 10 nm CoPc film, prepared identically to the measurement sample but without the metal electrodes.



**Figure 1.** Photocurrent yield for a 50 nm thick CoPc film, and the reference absorption spectrum.

## Results and Discussion

If the absorbance of the film can be determined, photocurrent action spectra may be expressed as “photocurrent yield” having units of electrons per *absorbed* photon. It can be shown that the photocurrent yield is directly proportional to the internal quantum yield[1], and is therefore the most useful photocurrent-derived quantity for the discussion of the mechanistic pathways involved in the photo-generation of charge carriers. By way of example, typical of the results, the action spectrum of a 50 nm CoPc film is shown in **Figure 1**. The photocurrent yield increases at photon energies above 2 eV immediately following the first singlet absorption excitation “Q-band” - indeed overlapping the higher-order vibrational excitations. Following the work of Geacintov [2] and Silinsh [3] on linear acenes we attribute this rise to an increase in the intrinsic photo-generation yield at photon energies near the transport gap.

## References

- [1] A. Rose, Concepts in Photoconductivity and Allied Problems, Interscience, New York, (1963) 168.
- [2] N. Geacintov, M. Pope, J. Chem. Phys, 50 (1969) 814.
- [3] E.A. Silinsh, V.A. Kolesnikov, I.J. Muzikante, D.R. Balode, Phys. Status Solidi B, 113 (1982) 379.