

***In situ* photoconductivity action spectra of phthalocyanine thin films**

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Photon-induced charge carrier generation in molecular semiconductor materials is understood to proceed by either extrinsic or intrinsic mechanisms, the former being common, the latter only being observed in rare instances, in unusually pure samples where, in addition, exciton dissociation processes leading to charge injection at the electrode interface could be sufficiently suppressed^{1,2}. Intrinsic photocurrent is an important property because the onset is strongly correlated to the (transport) energy gap of the material. Unfortunately, however, it has not been generally possible to observe intrinsic photocurrent in vacuum deposited molecular thin films, presumably owing to the higher concentrations of traps and defects in typical samples.

We have recently developed *in situ* methods for measuring the electrical properties of molecular thin films³, and here report the photoconductivity action spectra for some representative phthalocyanine (Pc) compounds, CoPc and PbPc, deposited on single crystal sapphire substrates. The electrodes are vacuum deposited metals, Al or Ti. As shown in **Figure 1**, the photocurrent yield for a CoPc film, expressed as electrons per absorbed photon, was observed to increase above the first singlet exciton absorption bands – behavior characteristic of intrinsic photogeneration in organic semiconductors.

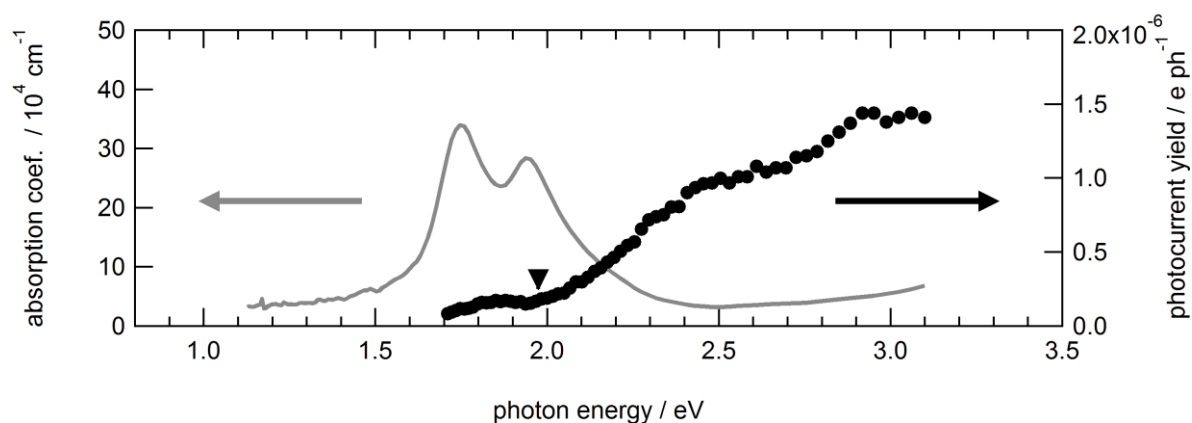


Figure 1. The *in situ* photoconductivity action spectrum recorded at 50 °C for an annealed 40 nm thick CoPc film, compared with the absorption spectrum, recorded *simultaneously*. Enhanced photocurrent yield is observed at photon energies above an onset value of about 2 eV (▼).

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[2] S. Barth, H. Bässler, H. Rost, H.H. Hörhold, *Phys. Rev. B* **56**, 3844 (1997).

[3] R. Murdey and N. Sato, *J. Chem. Phys.* **134**, 234702 (2011).