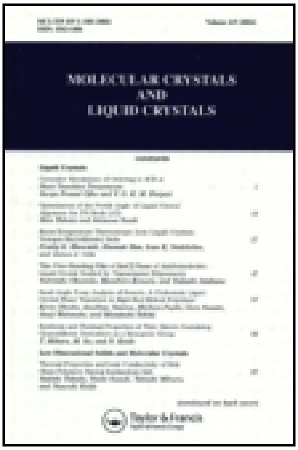

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Soluble Phthalocyanines: Photoconductivity

S. Pochekaylov [a b] , S. Nešpůrek [a b] , J. Rakušan [c] & M. Karásková [c]

[a] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

[b] Faculty of Chemistry, Brno University of Technology, Brno, Czech Repulic

[c] Research Institute for Organic Syntheses, Pardubice-Rybitví, Czech Republic

Version of record first published: 22 Sep 2010

To cite this article: S. Pochekaylov, S. Nešpůrek, J. Rakušan & M. Karásková (2007): Soluble Phthalocyanines: Photoconductivity, Molecular Crystals and Liquid Crystals, 468:1, 23/[375]-31/[383]

To link to this article: http://dx.doi.org/10.1080/15421400701229404

Mol. Cryst. Liq. Cryst., Vol. 468, pp. 23/[375]–31/[383], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701229404

Soluble Phthalocyanines: Photoconductivity

S. Pochekaylov
S. Nešpůrek
Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic and Faculty of Chemistry, Brno University of Technology, Brno, Czech Repulic

J. Rakušan
M. Karásková
Research Institute for Organic Syntheses, Pardubice-Rybitví, Czech Republic

New soluble Zn phthalocyanine substituted by 3-diethylamino-1-propylsulphonamide groups, as potential material for photodetectors is presented. Optical absorption spectrum consists of two strong Q and Soret bands with maxima at 680 and 338 nm, respectively. HOMO and LUMO energies of thin film were determined by electrochemical method to be approximately 5.8 and 4.1 eV, respectively. The material under study is strongly photoconductive; the photoconductivity spectrum is symbatic with optical absorption. Current-voltage characteristics show ohmic behavior at low electric fields ($F < 10^6\,V\,m^{-1}$); a strong hole injection from electrode was observed at higher fields.

Keywords: absorption; current-voltage characteristic; electronic structure; photodetector; sulphonamide-substituted phthalocyanine

INTRODUCTION

Phthalocyanines (Pc, Fig. 1) are stable molecular semiconductors suitable for many electronic applications, like photodetectors, gas sensors, transistors, solar cells, non-linear optical media, etc. [1]. There are many information in literature concerning the photoconductivity and photovoltaic properties. The best sensitivity was found for metal-free

The financial support by grant No. FT-TA/036 from Ministry of Industry and Trade of the Czech Republic is gratefully appreciated.

Address correspondence to S. Pochekaylov. E-mail: sergey@imcm.cas.cz

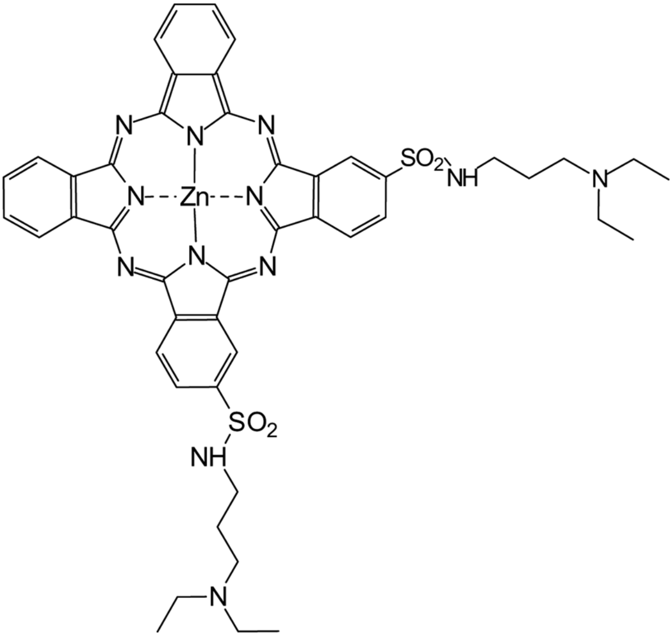

FIGURE 1 Structural formula of phthalocyanine molecule under study. Positions of the substituents are not exactly known.

[2], Zn [3,4] and TiO [5,6] phthalocyanines and the cells containing TiO_2 nanostructures [7]. Both photo- and dark conductivity can be improved by doping the material with electron acceptors. The highest solar cell quantum efficiency, ca. 2%, was reached for Zn phthalocyanine doped by fullerene C_{60} [8]. Phthalocyanines take a big interest because of their exceptive thermal and chemical stability; they are environmentally friendly and non-toxic. However, they are mostly not soluble in either water or organic solvents. To prepare thin films it is necessary to use a complicated and expensive vacuum evaporation technique. Some substituted phthalocyanines are soluble, thus, one can use simple cold technologies for film preparation, as spin-coating, drop-casting, ink-jet printing, etc. One can find also in literature some information about the photoconductivity for substituted phthalocyanines [9,10]. The sulphonated phthalocyanines were studied intensively, however, the power quantum efficiency was quite low ($<1\%$) [11]. Photoconductivity of sulphonamide-substituted phthalocyanines was studied in solutions [2], but there is no information concerning the photosensitivity in the solid phase. Some results concerning

the photosensitivity in thin films of Zn sulphonamide-substituted phthalocyanine are presented in this work.

EXPERIMENTAL

Material

3-diethylamino-1-propylsulphonamide Zn-phthalocyanine (ZnPcSu) was synthesized from the commercially available non-substituted ZnPc by the chlorsulphonation and the following condensation of the product with 3-aminopropyl-N,N′-diethylamine. As a result the mixture of 1- and 2-sulphonamide-substituted phthalocyanine was obtained. This material was extracted from the reaction mixture and used for the experiment after a recrystallization.

Thin Films

Thin films from ZnPcSu were prepared by spin-coating of chloroform, water or dimethylformamide solutions. Thickness of the films varied from 50 to 200 nm depending on the concentrations of the solutions. Samples for photoelectrical measurements were prepared in the surface (interdigital Au electrode system, electrode distance 50 μm) or in the sandwich configuration. In the case of the sandwich sample the structures glass|FTO|PEDOT-PSS|ZnPcSu|Al were used. The fluorine doped tin oxide (FTO) used as the bottom electrode, was cleaned by isopropanol vapors. PEDOT-PSS film was used to modify the work function of FTO. The film was prepared by mixing 3,4-ethyldioxythiophene (EDOT) and iron p-toluensulphonate, the resulting film thickness was 20–50 nm. After PEDOT and phthalocyanine deposition the samples were kept 7 hours in vacuum of 1 Pa at 150°C. Then, the Al electrode was vacuum evaporated.

Absorption spectra were measured using the UV-VIS-NIR Perkin-Elmer Lambda 950 spectrophotometer. The electrical characterization of the samples was performed using the Keithley 6617 A electrometer/high resistance meter. The ORIEL halogen lamp and the HAMAMATSU lightningcure LC6 xenon lamp with the monochromator ORIEL CornerStone were used for sample illumination.

RESULTS AND DISCUSSION

Absorption Spectra and Electronic Structure

Typical absorption spectrum of ZnPcSu thin film and solution are shown in Figure 2. There are two main characteristic bands: the Soret

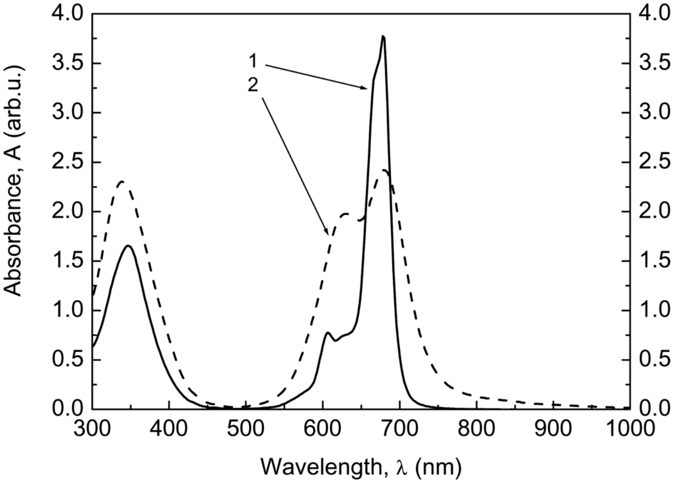

FIGURE 2 The absorption spectra of Zn 3-diethylamino-1-propylsulphonamide phthalocyanine in solution (1) and in thin film (2).

or B-band with maximum at 338 nm and the Q-band with maximum at 680 nm. The first band is related to the $d - \pi^*$ electronic transitions, the second are to $\pi - \pi^*$ electronic transitions of carbon atoms [12]. There are also vibrational and dimeric bands visible in the spectrum of phthalocyanine solution in chloroform at 608 and 626 nm, respectively. The spectrum of thin film is broader and it is shifted to longer wavelengths. The band gap energy $E_g = 1.72\,\text{eV}$ was determined from the $(h\nu \times \alpha)^2$ vs. $h\nu$ dependence, where $\alpha$is the absorption coefficient and $h\nu$ is the photon energy. From electrochemical measurements the oxidation potential was found to be $E_{ox} = -5.3\,\text{V}$. This value is usually higher than real HOMO value on 0.3–0.5 eV level [13]. It was impossible to measure E_{red} directly because of low film stability. Using the value of E_g position of LUMO level was estimated as $-4.1 - -3.9\,\text{eV}$. The activation energy of the dark current was measured in the temperature interval 15–80°C; the value 0.77 eV was found. This value is in good agreement with the energy gap.

Photoconductivity

The current-voltage characteristics of the samples with interdigital electrode system are presented in the Figure 3. Sulphonamide-substituted phthalocyanine shows quite low dark conductivity. At low

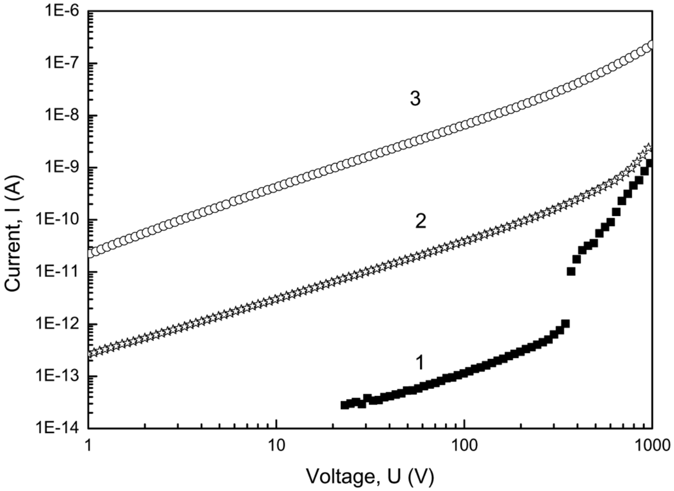

FIGURE 3 The current-voltage characteristics of Zn 3-diethylamino-1-propylsulphonamide phthalocyanine in the dark (full squares), in the light of wavelength 340 nm, illuminance $\varphi = 22.5\,\mathrm{W/m^2}$ (empty circles) and in the light of wavelength 675 nm, illuminance $\varphi = 1.8\,\mathrm{W/m^2}$ (empty stars).

electric fields the current shows ohmic character. At higher electric fields a superlinearity was observed, which could be ascribed to charge carrier injection from the electrode. Under illumination by monochromatic light ($\lambda = 340\,\mathrm{nm}$), the sample showed quite high photoconductivity, the current was four orders of magnitude higher than the dark current (cf. curve 3 vs. curve 1 in Fig. 3, photon flux $\varphi = 22.5\,\mathrm{W/m^2}$).

The diode and photovoltaic characteristics were studied on sandwich samples. The samples showed a weak diode behavior, the values of forward and reverse currents were almost the same (Fig. 4). The shift of the minimum of the dark characteristic with illumination was caused by the formation of open-circuit voltage V_{oc}. As it follows from Figure 5, the short circuit current $I_{sc} = 1.4 \times 10^{-9}\,\mathrm{A}$, the open circuit voltage $U_{oc} = 0.635\,\mathrm{V}$. The fill factor was $FF = 0.01$, power quantum efficiency $\eta = 0.0006\%$. The dependence of the photocurrent on wavelength of light was symbatic with the absorption spectrum (Fig. 6).

The photocurrent kinetics showed the stable current level both in dark and under illumination. The increase of the current was 1.5 orders of magnitude at the illumination level $\varphi = 1.8\,\mathrm{W/m^2}$,

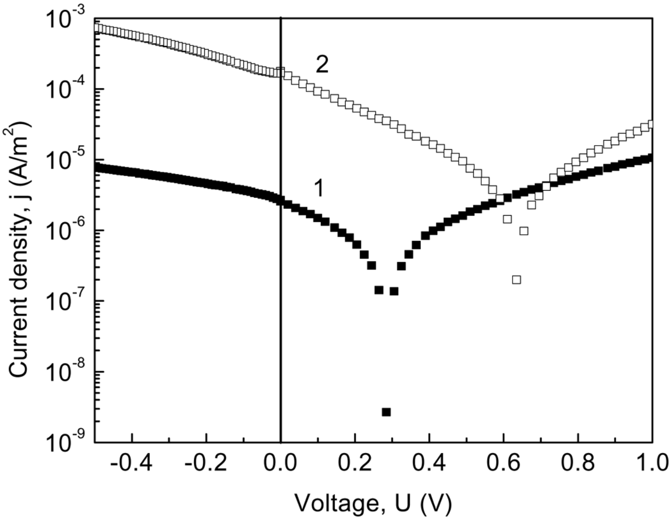

FIGURE 4 The current-voltage characteristic of sandwich sample with Zn 3-diethylamino-1-propylsulphonamide phthalocyanine. 1 – in dark (full points); 2 – under illumination by monochromatic light with wavelength 675 nm, irradiance $\varphi = 1.77\,\mathrm{W/m^2}$ (open points).

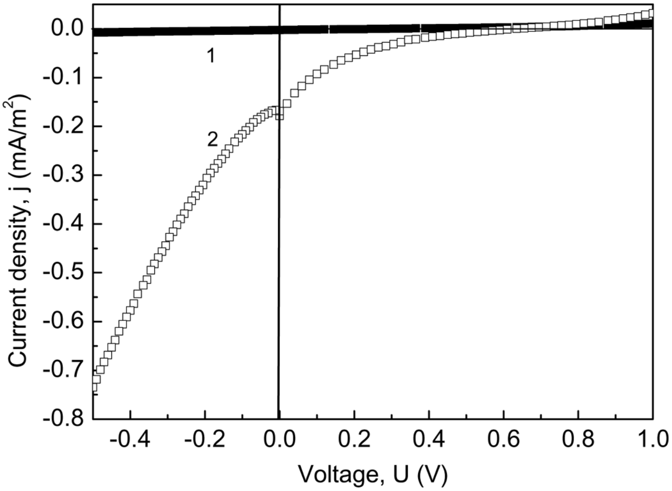

FIGURE 5 The current-voltage characteristic of sandwich sample from Zn 3-diethylamino-1-propylsulphonamide phthalocyanine. 1 – in dark; 2 – under illumination by monochromatic light with wavelength 675 nm, irradiance $\varphi = 1.8\,\mathrm{W/m^2}$.

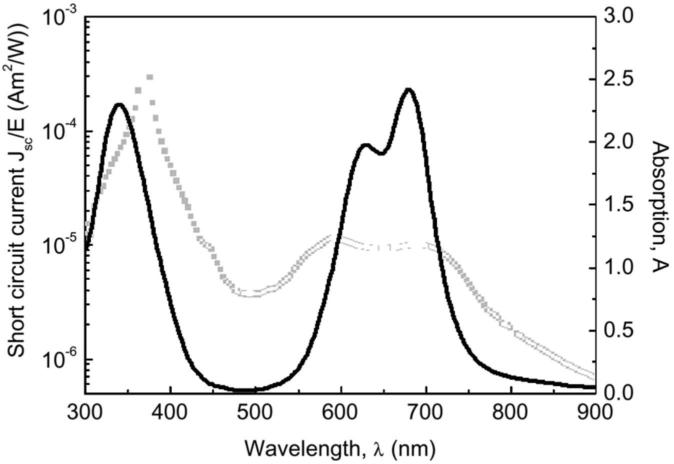

FIGURE 6 Current vs. wavelength dependence for sandwich sample of Zn 3-diethylamino-1-propylsulphonamide phthalocyanine.

$\lambda = 675\,\text{nm}$ (see Fig. 7). The slope of the dependence of the short-circuit current on photon flux was about 0.5 (Fig. 8). It supports the existence of the strong charge carrier hopping.

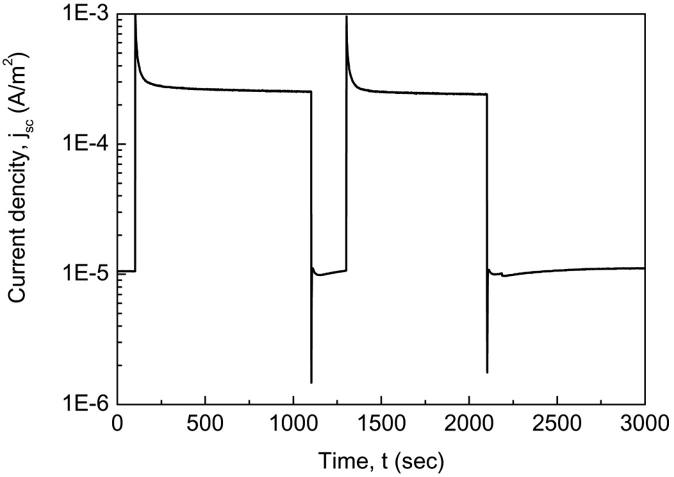

FIGURE 7 The kinetic of photocurrent when switching from dark condition to the illumination by light with wavelength 675 nm.

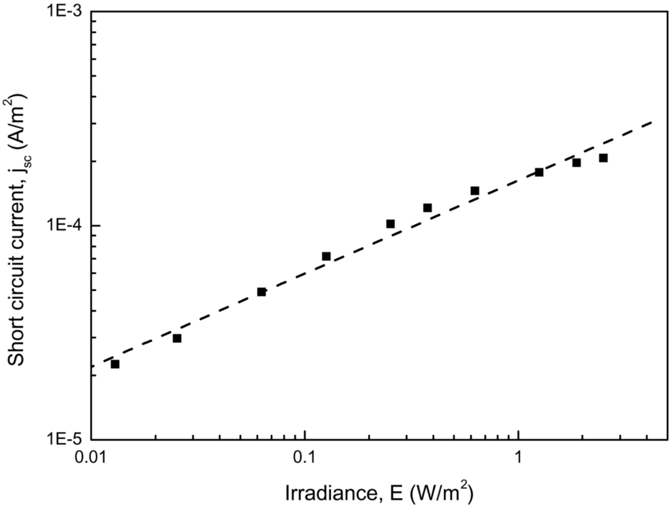

FIGURE 8 The current vs. irradiance dependence of the sulphonamide-substituted phthalocyanine. Wavelength of light is 675 nm.

CONCLUSION

3-diethylamino-1-propylsulphonamide Zn-phthalocyanine shows all typical absorption bands with maxima at 338 and 680 nm in the solid state. The material is strongly photoconductive, suitable for the construction of UV and visible light photodetectors.

REFERENCES

[1] Forrest, S. R. (2004). *Nature*, *428*, 911.
[2] Wrobel, D., Boguta, A., Wojcik, A., & Ion, R. M. (2004). *Nonlinear Optics. Quantum Optics*, *31*, 333.
[3] Koeppe, R., Sariciftci, N. S., Troshin, P. A., & Lyubovskaya, R. N. (2005). *Appl. Phys. Lett.*, *87*, 244102.
[4] Drechsel, J., Mannig, B., Gebeyehu, D., Pfeiffer, M., Leo, K., & Hoppe, H. (2004). *Organic Electronics*, *5*, 175.
[5] Tsuzuki, T., Hirota, N., Noma, N., & Shirota, Y. (1996). *Thin Solid Films*, *273*, 177.
[6] Tsuzuki, T., Shirota, Y., Rostalski, J., & Meissner, D. (2000). *Solar Energy Materials & Solar Cells*, *61*, 1.
[7] Ray, A. K., Tracey, S. M., & Hodgson, S. N. B. (2001). *Journal of Sol-Gel Science and Technology*, *22*, 15.
[8] Maennig, B., Drechsel, J., Gebeyehu, D., Simon, P., Kozlowski, F., Werner, A., Li, F., Grundmann, S., Sonntag, S., Koch, M., Leo, K., Pfeiffer, M., Hoppe, H., Meissner, D., Sariciftci, N. S., Riedel, I., Dyakonov, V., & Parisi, J. (2004). *Appl. Phys. A*, *79*, 1.

[9] Winter, G., Heckmann, H., Haisch, P., Eberhardt, W., Hanack, M., Lu1er, L., Egelhaaf, H.-J., & Oelkrug, D. (1998). *J. Am. Chem. Soc.*, *120*, 11663.

[10] Haisch, P., Winter, G., Hanack, M., Lüer, L., Egelhaaf, H.-J., Oelkrug, D. (1997). *Advanced Materials*, *9*, 316.

[11] Petritsch, K., Dittmer, J. J., Marseglia, E. A., Friend, R. H., Lux, A., Rozenberg, G. G., Moratti, S. C., & Holmes, A. B. (2000). *Solar Energy Materials & Solar Cells*, *61*, 63.

[12] Djurišić, A., Kwong, C. Y., Lau, T. W., Liu, Z. T., Kwok, H. S., Lam, L. S. M., Chan, W. K. (2003). *Appl. Optics*, *42*, 31.

[13] Liu, G., Klein, A., Thissen, A., & Jaegermann, W. (2003). *Surface Science*, *539*, 37.