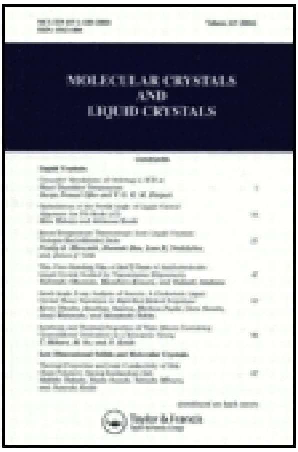

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Photoconductivity of Bridged Polymeric Phthalocyanine

Hans Meier [a] [b] , Wolfgang Albrecht [a] [b] & Michael Hanack [a] [b]
[a] Staatliches Forschungsinstitut für Geochemie, AuBenstelle des Bayerischen Geologischen Landesamtes, D-8600, Bamberg, F.R.G.
[b] Institut für Organische Chemie der Universität Tübingen, D-7400, Tübingen, F.R.G.

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PHOTOCONDUCTIVITY OF BRIDGED POLYMERIC PHTHALOCYANINES

HANS MEIER and WOLFGANG ALBRECHT
Staatliches Forschungsinstitut für Geochemie, Außenstelle des Bayerischen Geologischen Landesamtes,
D-8600 Bamberg, F.R.G.

MICHAEL HANACK
Institut für Organische Chemie der Universität
Tübingen, D-7400 Tübingen, F.R.G.

Abstract: Photoelectric properties of one-dimensional bridged polymeric phthalocyanines, $[PcML]_n$, have been measured. Experiments in surface-type photocells show that photocurrents depend on temperature, intensity, voltage and wavelength. Action spectra of photoconductivity are characterized by definite peaks in the visible and near-infrared region. Moreover, it has been noted that by specific combinations of macrocycles, Pc, bridging ligands, L, and central metal atoms, M, photoconductive gain and spectral response can be tailored.

Keywords: Polymeric phthalocyanines. Photoconductivity. Onsager mechanism. Effect of chemical structure.

INTRODUCTION

In the field of conducting polymers there is increasing interest in polymeric phthalocyanines. On the one hand, by producing sheet-like structures of phthalocyanine rings[1], conducting polymers with high stability in air and remarkable electrocatalytic activity have been obtained[2-3]. On the other hand, by polymerization via bridging ligands to linear chains phthalocyanines with conductivies up to several orders of magnitude greater than the conductivies of monomers have been synthesized[4-7].

In addition, phthalocyanines belonging to these classes of polymeric materials exhibit photoconductivity without external doping[8-12]. Thus the well-known photoelectric properties of monomeric phthalocyanines, which have been studied for application in xerographic photoreceptors, diode laser printers, vidicon television pick-up tubes and photoelectrochemical devices[13-15] may be incorporated in polymeric structures.

Therefore, systematic experiments on the photoelectric behaviour of polyphthalocyanines with different structures have been started. In this paper results are summarized on the photoconductivity of bridged polymeric phthalocyaninatometal compounds.

EXPERIMENTAL

Methods

The photoelectric properties of bridged polymeric phthalocyanines have been measured as polycristalline samples without any binder or dopant on identical conditions in surface-type cells employing copper/zinc contacts with electrode distances of 0.2 mm[8].

Materials

Two classes of bridged polymeric phthalocyanines, $[PcML]_n$, consisting of different combinations of macrocycles, Pc, bridging ligands, L, and central metal atoms, M, have been studied:

(1) Polymeric germanium phthalocyanines in which phthalocyanines as macrocyclic units are rigidly held in a face-to-face configuration by strong covalent linkages with oxygen or sulfur as bridging ligands (Type I). These compounds were prepared as described elsewhere[4].

(2) Axially stacked macrocyclic transition metal complexes with phthalocyanine as macrocycle, Fe, Co, Ru, Cr and Mn as central metal atoms, and linear, π-electron containing molecules as bridging bidentate ligands, e.g. pyrazine (pyz), 4,4'-bipyridine (bpy), 1,4-diisocyanobenzene (dib), s-tetrazine (tz) or cyanide (CN^-), which were synthesized as previously described[4-7] (Type II).

RESULTS AND DISCUSSION

Photoelectric properties

Analogous to polymeric phthalocyanines with sheet-like structures, e.g., polyCuPc[8], the conductivity of $[PcML]_n$ increases rapidly (i.e. within 1 s) on irradiation with visible light. In discussing the photoelectric response of $[PcML]_n$ the following relationships should be taken into account:

(1) Photocurrents increase with light intensity, I_B, yielding curves

$$I_{ph} = bI_B^{\gamma} \tag{1}$$

where b is constant and γ is an intensity parameter. The values of the intensity parameters measured in $[PcML]_n$ complexes ($0.5 < \gamma < 1.0$) can be understood if we assume photosensitive ohmic currents in the presence of exponentially distributed traps that control carrier recombination[9-10,13].

(2) Photocurrents increase with increasing voltage according to

$$I_{ph} = aU^s \tag{2}$$

where a is a constant and s is a voltage parameter. For instance, $s \simeq 1.2$ observed in $[PcCoCN]_n$ is in agreement with the ohmic character of the photocurrents[10].

(3) The temperature dependence of photoconductivity can be expressed by

$$\sigma_{ph} = \sigma_{o,ph} \exp(-\Delta E_{ph}/kT). \tag{3}$$

The pre-exponential factor $\sigma_{o,ph}$ seems to be connected with the activation energy of photoconductivity, ΔE_{ph}, according to

$$\log \sigma_{o,ph} = \alpha\Delta E_{ph} + \beta \tag{4}$$

as demonstrated, e.g., in $[PcCoCN]_n$ and $[PcGeS]_n$ (α and β are constants[9-10]).

(4) The photoconductivity can drop on varying the temperature at specific regions, e.g., at about 308 K in $[PcGeS]_n$

and around 285 K in $[PcCoCN]_n$. This anomaly may be the result of a phase change of the crystal structure which can affect, for instance, the rate of generation of carriers[9-10].

Photoconductivity and molecular structure

Type I. Polymers obtained by stacking macrocycles via covalent linkage show the following properties:

The photoconductive spectra of sulfo- and oxobridged phthalocyanines exhibit peaks in the near-infrared region at about 1100 - 1200 nm[11].

Photoelectric sensitivity increases with decreasing size of the bridging ligand because of decreasing ring-ring separation. E.g., the photoconductive gain, G, gives at 2500 V/cm (λ = 1100 nm) $G \simeq 4 \times 10^{-7}$ in $[PcGeS]_n$ and $G \simeq 1 \times 10^{-6}$ in $[PcGeO]_n$.

There is no change of the near-infrared photoelectric sensitivity of oxo-bridged phthalocyanines by introducing bulky substituents into the macrocycle[12].

Type II. Axially polymerized macrocyclic transition metal complexes containing bridging ligands which are bound either by two coordinative bonds or by one coordinative bond and one σ-bond are characterized by the following properties:

Photocurrent action spectra show peaks above all in the visible and near-infrared regions. By using bridging ligands leading to greater interplanar distances photoconductivity bands are shifted to shorter wavelengths[12].

Electronic influences of substitutents on the macrocycles and on the bridging ligands, respectively, can result in different photoelectric sensitivities[12]. E.g., $G = 1.5 \times 10^{-5}$ at 2500 V/cm in $[PcFe(pyz)]_n$ and $G = 3.2 \times 10^{-7}$ at 2500 V/cm in $[Cl_{16}PcFe(pyz)]_n$.

Photoconductivity may depend on the central metal atom. For instance, we have G = 0.07 at 2000 V/cm in $[PcCoCN]_n$, $G = 5.6 \times 10^{-6}$ in $[PcCrCN]_n$, and $G = 1.3 \times 10^{-6}$ in $[PcMnCN]_n$.

The type of the bridging ligand can influence the photoelectric response via its size as demonstrated by the photoconductive gain, G, at 2000 V/cm: $G = 4 \times 10^{-2}$ in $[PcFe(tz)]_n$, $G = 4 \times 10^{-6}$ in [PcFe(pyz)], and $G = 6 \times 10^{-7}$ in $[PcFe(bpy)]_n$.

Mechanism of photoconductivity

Type I. The results obtained in polymers of type I clearly indicate relationships between molecular stacking and photoconductivity: On the one hand, the small distance of the cofacial macrocycles allows a band structure to be formed by overlap of the perpendicular π-orbitals. On the other hand, exciton splitting resulting from a strong molecular interaction may be responsible for the long wavelength sensitivity. Therefore, the interaction of excitons with defect sites may be responsible for the generation of charge pairs which can undergo either geminate recombination or dissociation in an external electric field to form free carriers. In this context, it is remarkable that charge pair separation is due to the Onsager mechanism[11-13,16].

Type II. In discussing photoconductivity in polymers of type II it must be taken into account that despite a metal-metal distance of about 1200 pm in diisocyanobenzene-bridged compounds compared to 700 pm in pyrazine-bridged polymers the photoconductive gain, G, and dark conductivity were higher in $[PcM(dib)]_n$ than in $[PcM(pyz)]_n$. E.g., at 2000 V/cm: $G = 1.6 \times 10^{-3}$ in $[M_8PcFe(dib)_n]$ and $G = 4.2 \times 10^{-6}$ in $[PcFe(pyz)]_n$, and $G = 2.3 \times 10^{-5}$ in $[PcRu(dib)]_n$ and $G = 4.7 \times 10^{-8}$ in $[PcRu(pyz)]_n$. This effect may be explainable by the formation of an energy band along the central chain. Therefore, the dominant mechanism for charge-carrier generation in transition metal complexes containing bridging ligands capable of conjugation may be excitation from valence band to conduction band corresponding to a charge transfer, e.g. from the HOMO of the transition metal d-orbital to the LUMO of the bridging ligand.

CONCLUSION

In conclusion it can be stated that bridged polymeric phthalocyanines can be synthesized which show good to very good photoconducting properties. Among other things it is demonstrated that the spectral response and photoconductive gain strongly depend on specific combinations of macrocycles, central metal atoms and bridging ligands.

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REFERENCES

1. A.A. Berlin and A.I. Sherle, Inorg. Macromol. Rev., 1, 235 (1970).
2. H. Meier, Top. Curr. Chem. 61, 87 (1976).
3. H. Meier, U. Tschirwitz, E. Zimmerhackl, W. Albrecht, and G. Zeitler, J. Phys. Chem., 81, 712 (1977).
4. O. Schneider and M. Hanack, Chem.Ber. 116, 2088 (1983).
5. J. Metz and M. Hanack, J. Am. Chem. Soc. 105, 828 (1983).
6. M. Hanack, A. Lange, M. Rein, R. Behnisch, G. Renz, and A. Leverenz, Synth. Met. 29, F1 (1989).
7. M. Dreßen, M. Hanack, A. Hirsch, and R. Thies, Synth. Met. 41-43, 2609 (1991).
8. H. Meier, W. Albrecht, and E. Zimmerhackl, Polym. Bull. 13, 43 (1985).
9. H. Meier, W. Albrecht, E. Zimmerhackl, M. Hanack, and K. Fischer, J. Mol. Electronics, 1, 47 (1985).
10. H. Meier, W. Albrecht, E. Zimmerhackl, M. Hanack, and J. Metz, Synth. Met., 11, 333 (1985).
11. H. Meier, W. Albrecht, and M. Hanack, Mol. Cryst. Liq. Cryst., 194, 75 (1991).
12. H. Meier, W. Albrecht, and M. Hanack, SPIE. 1559, 89 (1991).
13. H. Meier, Organic Semiconductors (Verlag Chemie, Weinheim, 1974), pp. 435, 318.
14. H. Meier, W. Albrecht, U. Tschirwitz, N. Geheeb, and E. Zimmerhackl, Chem.-Ing. Tech. 51, 653 (1979).
15. A. Kakuta, Y. Mori, S. Takano, M. Sawada, and I. Shibuya, J. Imag. Techn., 11, 7 (1985).
16. E.A. Silinsh, V.A. Kolesnikov, I.J. Muzikante, and D.R. Balode, Phys. stat. sol., 113 (b), 379 (1982).