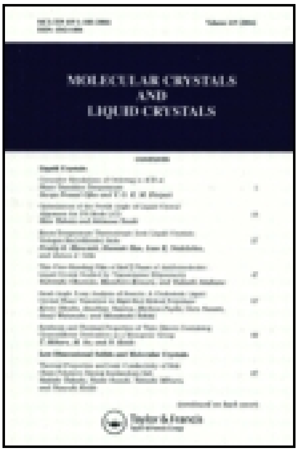

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Correlations between Photoconductivity and Molecular Structure of Bridged Polymeric Phthalocyanines

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CORRELATIONS BETWEEN PHOTOCONDUCTIVITY AND MOLECULAR STRUCTURE OF BRIDGED POLYMERIC PHTHALOCYANINES

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Abstract Experiments on the effect of chemical structure to photoconductivity have been carried out on one-dimensional bridged polymeric phthalocyanines $[PcML]_n$. It is shown that by specific combinations of macrocycles, Pc, bridging ligands, L, and central metal atoms, M, photoconductive gain and spectral response to specific wavelength regions can be tailored.

Keywords: Photoelectric properties of organic compounds (polymers, dyes, CT-complexes): photoconductivity and structure, polymeric phthalocyamines

INTRODUCTION

It has recently been demonstrated that polymeric phthalocyanines formed by polymerization of squareplanar phthalocyanine rings to linear chains exhibit photoelectric properties without any additive[1–2]. This observation suggests that for applications, e.g., as components in photovoltaic cells[3–4], organic photoconductors with relatively low bulk resistance may become available. However, no experimental results are known to us showing correlations of different combinations of macrocycles, bridging ligands and central metal atoms to the photoelectric properties of this type of one-dimensional conductor. Therefore, studies seem necessary to obtain an insight into the effect of chemical structure to photoconductivity of bridged polymeric phthalocyaninatometal compounds $[PcML]_n$.

In this report the first results of studies on photoconductivity of phthalocyanines, $[PcML]_n$, consisting of different combinations of macrocycles, Pc, bridging ligands, L, and central metal atoms, M, are given.

EXPERIMENTAL

Methods

The photoelectric properties of bridged polymeric phthalocyanines have been measured without any additive in surface-type cells employing copper/zinc contacts with electrode distances of 0.2 mm. The samples were measured at pressures of 10^{-5} - 10^{-6} Torr in the temperature range 190 - 300 K by using a continuous-flow cryostat. Dark- and photocurrents were registered with a Keithley 480 picoammeter in combination with a fast recorder. The light source consisted of a 1000-W xenon lamp, focused by quartz lenses onto the photoelectric cell. Monochromatic light in the spectral range 350 - 1900 nm was obtained with bandpass filters with bandwidths of 50 nm. Light intensities were varied with neutral density filters.

Materials

Two classes of bridged polymeric phthalocyanines (see Figure 1) have been examined:

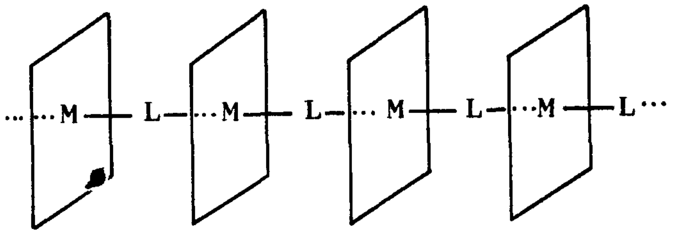

FIGURE 1 Scheme of the structure of axially bridged polymeric phthalocyanines. M = metal, L = bridging ligand.

(1) Polymeric germanium phthalocyanines in which cyclic units are joined by strong covalent linkages with oxygen or sulfur as bridging ligands (Type I). These compounds were prepared as described[5-6].

(2) Axially stacked macrocyclic transition metal complexes bridged by bidentate π-electron containing ligands, e.g. pyrazine (pyz), 4,4'-bipyridine (bpy), 1,4-diisocyanobenzene (dib), tetrazine (tz), cyanide (CN^-), which were synthesized as previously described[7-11] (Type II).

RESULTS AND DISCUSSION

Photoconductivity of type I

Polymers obtained by stacking macrocycles via covalent linkage show the following photoelectric properties:

The photoconductive spectra of sulfo- and oxo-bridged phthalocyanines exhibit peaks in the near-infrared region at about 1100 - 1200 nm as shown in Figure 2.

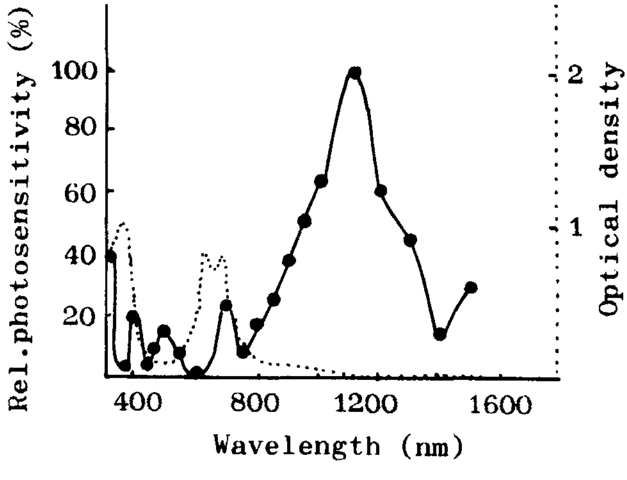

FIGURE 2 Photoconductive spectrum of $[PcGeO]_n$.

The photoconductive gain, G, increases with decreasing size of the bridging ligand because of decreasing ring-ring separation. The photoconductive gain, G, defined as the number of charge carriers passing through the sample per absorbed photon, according to the equation

$$G = \frac{I_{ph}/e}{I_A V} \tag{1}$$

gives, e.g., at 2500 V cm^{-1} (λ = 1100 nm) G $\simeq 4 \times 10^{-7}$ in $[PcGeS]_n$ and G $\simeq 1 \times 10^{-6}$ in $[PcGeO]_n$ (I_{ph} is the photocurrent, I_A the number of photons per cubic centimeter absorbed per second and V the volume of the sample).

There is no change of the near-infrared photosensitivity of oxo-bridged phthalocyanines by introducing bulky substituents into the macrocycle. However, the photoconductive gain, G, decreases by about one order of magnitude and dark conductivity, σ_D, decreases by several orders of magnitude as demonstrated in Table I.

TABLE I Influence of steric effects in $[R_4PcGeO]_n$.

Compound	G (E = 2500 V/cm)	σ_D (S/cm)
$[PcGeO]_n$	1×10^{-6}	2×10^{-11}
$[(t\text{-}Bu)_4PcGeO]_n$	7×10^{-8}	2×10^{-14}
$[(Me_3Si)_4PcGeO]_n$	2×10^{-8}	4×10^{-14}

The results 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 because maingroup (closed shell) phthalocyanines show no electronic bands other than the Q band and the Soret band.

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[12-13]. In this context, it is remarkable that charge pair separation is due to the Onsager mechanism[14-15]. In agreement with the equation

$$I_{ph}/E = (e\mu\tau I_A V/L)\eta_o \exp(-r_c/r_o)(1 + er_c E/2kT) \qquad (2)$$

where η_o is the primary quantum yield for initial charge pair generation, r_o the initial charge separation distance, r_c the critical Onsager distance, ϵ the dielectric constant, ϵ_o the electric permittivity of free space, μ the mobility, and τ the carrier lifetime, a plot of I_{ph}/E versus the field strength, E, gives a linear dependence as shown in Figure 3.

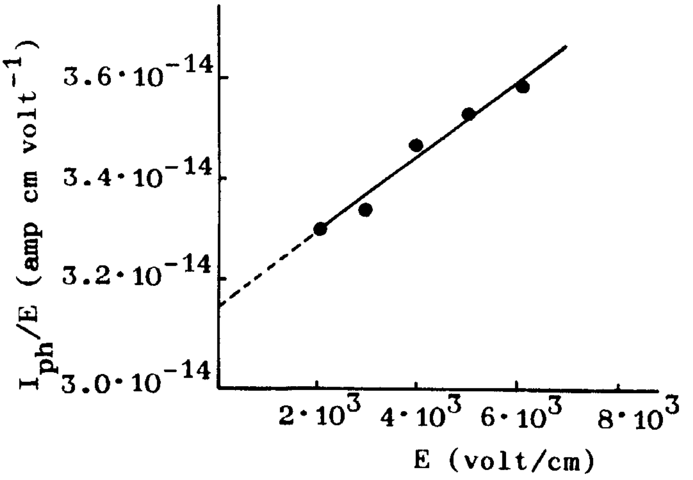

FIGURE 3 Plot of I_{ph}/E vs E for $[(Me_3Si)_4PcGeO]_n$. 1200 nm. 303 K. S/I = 2.5 x 10^{-5}.

From least squares analysis of these plots, slopes to intercept ratios from 2 x 10^{-5} to 8 x 10^{-5} cm/V for $[R_4PcGeO]_n$ are obtained. These values are in agreement with the value predicted by the Onsager model which corresponding to the equations

$$S/I = \frac{er_c}{2kT} = \frac{e^3}{8\pi\varepsilon\varepsilon_o k^2 T^2} \tag{3}$$

is 3.4 x 10^{-5} cm/V at 296 K(ε = 3.2).

Additionally, according to Eq. (3) a plot of the slope to intercept ratio, S/I, versus $1/T^2$ shows the linear dependence predicted by the Onsager mechanism.

Photoconductivity of type II

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

Photocurrent action spectra show peaks above all in the visible and near-infrared regions, as demonstrated for $[PcFe(tz)]_n$ in Figure 4.

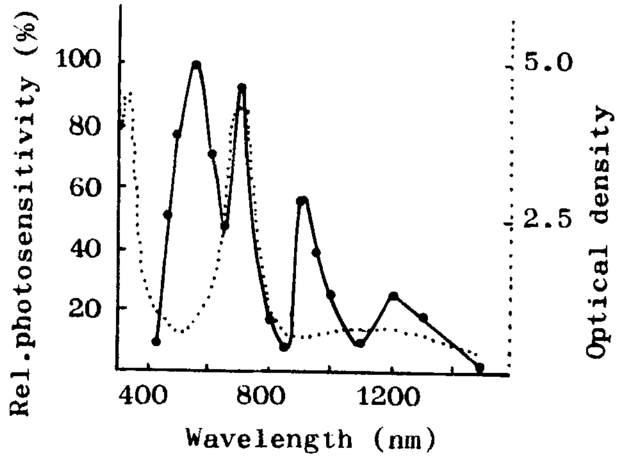

FIGURE 4 Photoconductive spectrum of $[PcFe(tz)]_n$.

By using bridging ligands leading to great interplanar distances photoconductivity bands are shifted to shorter wavelengths. For instance, photoconductivity peaks of $[Me_8PcFe(dib)]_n$ are at 460 nm (strong) and 550 nm (weak). It is conceivable that in addition to the Q band and Soret band[16] these peaks may be the result of metal-to-ligand and/or ligand-to-metal charge transfer transitions because metal-d-levels lie within the phthalocyanine HOMO-LUMO gap.

The type of the bridging ligand can influence the photoresponse via its size as demonstrated by the photoconductive gain, G, at 2000 V/cm: $G = 4 \times 10^{-2}$ in $[PcFe(tz)]_n$, $G = 1 \times 10^{-3}$ in $[Me_8PcFe(dib)]_n$, $G = 4 \times 10^{-6}$ in $[PcFe(pyz)]_n$, and $G = 6 \times 10^{-7}$ in $[PcFe(bpy)]_n$.

Electronic influences of substituents on the macrocycles and on the bridging ligands, respectively, can result in different photoelectric sensitivities. Photoconductive gain is found to be two orders of magnitude larger for $[PcFe(pyz)]_n$ ($G = 1.6 \times 10^{-5}$ at 2500 V/cm) than for $[Cl_{16}PcFe(pyz)]_n$ ($G = 3.2 \times 10^{-7}$ at 2500 V/cm). Chlorine-substitution of the ligand may also decrease the photoconductivity, e.g., $G = 1.6 \times 10^{-3}$ at 2000 V/cm in $[Me_8PcFe(dib)]_n$ and $G = 5.5 \times 10^{-4}$ at 2000 V/cm in $[Me_8PcFe(Cl_4dib)]_n$.

Photoconductivity may depend on the central metal atom. For instance, the photoelectrical sensitivity of cyano-bridged complexes decreases when replacing cobalt with chromium and manganese: $G = 0.07$ at 2000 V/cm in $[PcCoCN]_n$, $G = 5.6 \times 10^{-6}$ in $[PcCrCN]_n$, and $G = 1.3 \times 10^{-6}$ in $[PcMnCN]_n$.

It is remarkable 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, σ_D, were higher in $[PcM(dib)]_n$ than in $[PcM(pyz)]_n$ as shown in Table II.

TABLE II Influence of the size of bridging ligands.

Complex	G (2000 V/cm)	d (pm)	σ_D (S/cm)
$[Me_8PcFe(dib)]_n$	1.6×10^{-3}	~ 1190	2×10^{-6}
$[PcFe(pyz)]_n$	4.2×10^{-6}	~ 700	2×10^{-9}
$[PcRu(dib)]_n$	2.3×10^{-5}	~ 1190	6×10^{-9}
$[PcRu(pyz)]_n$	4.7×10^{-8}	~ 700	3×10^{-11}

This effect may be explainable by discussing

(a) the formation of an energy band along the central chain and

(b) a direct photogeneration of charge carriers because measurements for testing the Onsager and Poole-Frenkel theories[14-15,17] failed.

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 from the HOMO of the transition metal d-orbital to the LUMO of the bridging ligand[18-19].

CONCLUSION

In conclusion it can be stated that bridged macrocyclic metal complexes can be synthesized which show, on suitable choice of central metal atom and bridging ligand, good to very good photoconducting properties. Moreover, by specific combinations of macrocycles, bridging ligands and central metal atoms photoelectric properties can be tailored to specific wavelength regions.

Acknowledgement

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