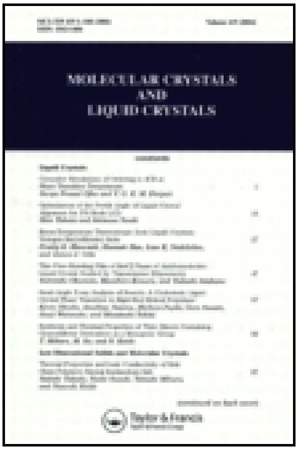

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# Photoconductivity of Ion Pair Charge-Transfer (IPCT)

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# PHOTOCONDUCTIVITY OF ION PAIR CHARGE-TRANSFER (IPCT) COMPLEXES

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Abstract The results of photoelectric measurements in salts of planar complexes of mono- and dianionic metal dithiolenes with a variety of cations, such as 2,2'- and 4,4'-bipyridinium derivatives, are described. It is shown that by specific combinations of ligands, metals, anionic charges and cations photoconductivity gain and spectral response to specific wavelength regions can be tailored. On the basis of ion pair charge-transfer (IPCT) mechanism a model is given according to which photoconductivity of metal dithiolene complexes may be attributed to the photoinduced "reverse" charge-transfer between anionic and cationic sites resulting in conducting anionic stacks of mixed-valence.

## INTRODUCTION

Ion pair charge-transfer (IPCT) complexes consisting of organic and inorganic redox systems are of particular interest. On the one, IPCT salts based on metal dithiolene anions with conductivities up to 1 - 50 $ohm^{-1}cm^{-1}$ may be considered as useful for the synthesis of high conducting organic compounds[1-4]. On the other, photoelectrical properties recently observed in IPCT complexes[5] suggest that for possible technical applications organic photoconductors with relatively low bulk resistivity may become available. However, no experimental results are known to us showing correlations of different combinations of ligands, central metal atoms, anionic charges and cations to the photoelectrical properties of this type of organic charge-transfer compound. Moreover, important data are missing for elaborating mechanism of IPCT photoconductivity.

Therefore, systematic photoelectric studies on IPCT compounds have been started.

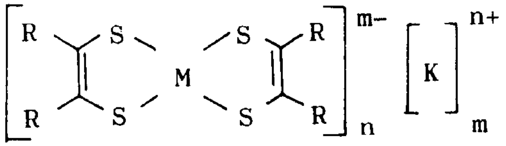
## EXPERIMENTAL

### Methods

The photoelectric properties have been measured without any additive in surface-type cells with electrode distances of 0.2 mm as previously described[6]. Dark- and photocurrents were registered with a Keithley 480 picoammeter in combination with a fast recorder. Monochromatic light in the spectral range 320 - 1900 nm was obtained with bandpass filters with bandwidths of 50 nm.

### Materials

A series of salts of mono- and dianionic bisdithiolene complexes, $[ML2]_n^{m-}[K]_m^{n+}$, (m, n = 1,2; M = Ni, Zn)



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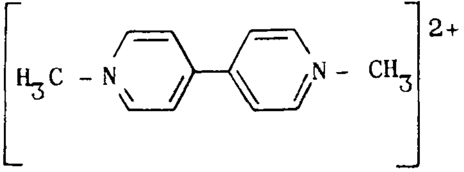
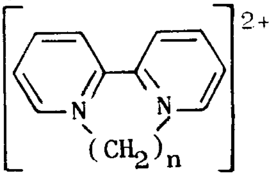
have been examined. The abbreviations are:

(a) Ligands L: mnt (maleonitrilo-1,2-dithiolate) when R = CN; dmit (1,3-dithio-2-thione-4,5-dithiolate) when R-R = $CS_3$; dddt (1,3-dithio-5,6-dihydro-1,4-dithiin-2,3-dithiolate when R-R = $(CH_2)_2S_2$. (b) cations K: $NEt_4^+$ (tetraethylammonium); $NBu_4^+$ (tetrabutylammonium); $MV^{2+}$ (methyl viologene, II); $DQ^{2+}$ (n = 2), $PQ^{2+}$ (n = 3) and $BQ^{2+}$ (n = 4) of the 2,2'-bipyridinium derivatives (III).



(II)



(III)

All the compounds have been prepared as described[7].

## RESULTS AND DISCUSSION

### Correlation between photoconductivity and structure

There are a series of structural factors governing photoconductivity of dithiolate complexes:

The type of the ligand can influence the photoresponse via its size, planarity and mode of stacking in the crystal because of the degree of interaction within the anion system. This is demonstrated by the photoconductive gain

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

which gives, e.g., $G = 1.1\times10^{-3}$ (2500V/cm) in $[Ni(dddt)_2]_2MV$ and $G = 2.8\times10^{-6}$ (500 V/cm) in $[Ni(mnt)_2]_2MV^5$. ($I_{ph}$ = photocurrent, $I_A$ = number of photons per cubic centimeter absorbed per second, and V = volume of the sample).

Photoelectrical sensitivity of dithiolate complexes can be influenced by the size of inert cations and by the redoxproperties of planar cations, respectively; e.g., replacing $MV^{2+}$ by $NBu_4{}^+$ may result in lower photoconductivities in $[Ni(dmit)_2]^-$ complexes as shown in Figure 1.

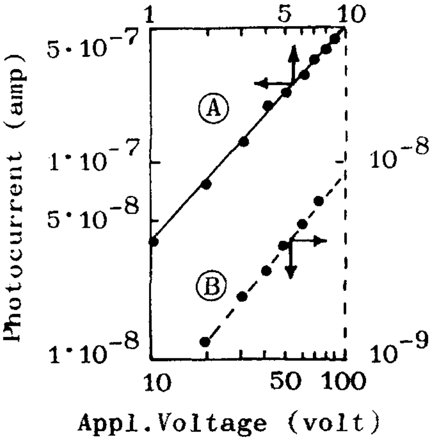


FIGURE 1 $I_{ph} = f$ (voltage): Ⓐ = $[Ni(dmit)_2]_2MV$. Ⓑ = $[Ni(dmit)_2]NBu_4$ ($\lambda = 696$ nm: $I_B = 2.3\times10^{17}$ photons $cm^{-2}$).

As observed for the dark conductivity, monoanionic dithiolate complexes may be more highly photoconducting than dianionic complexes. This is demonstrated by the photoconductive gain, e.g., at 500 V $cm^{-1}$ in monoanionic $[Ni(dmit)_2]_2MV$ ($G = 2\times10^{-4}$) and in dianionic

$[Ni(dmit)_2]MV$ ($G = 2 \times 10^{-6}$) in accordance with the different repulsion energies which are active in mono- and dianionic units.

Photoconductivity may depend on the central metal atom. For instance, photoconductivity of $[Ni(mnt)_2]^{2-}$ complexes decreases by several orders of magnitude when replacing nickel with zinc presumably due to different solid state structures[8] ($G < 10^{-8}$ in $[Zn(mnt)_2]DQ$ at 8000 V $cm^{-1}$).

## Mechanism of IPCT-photoconductivity

In discussing photoconductivity of dithiolene anions ($D^-$) with cations ($A^+$) it must be noted that these compounds exhibit a "reverse" charge-transfer (CT), i.e., an CT from an ionic ground state to a less ionic excited state corresponding to $D^-A^+ \longrightarrow DA$. Photoconductivity spectra are in accordance with this type of CT.

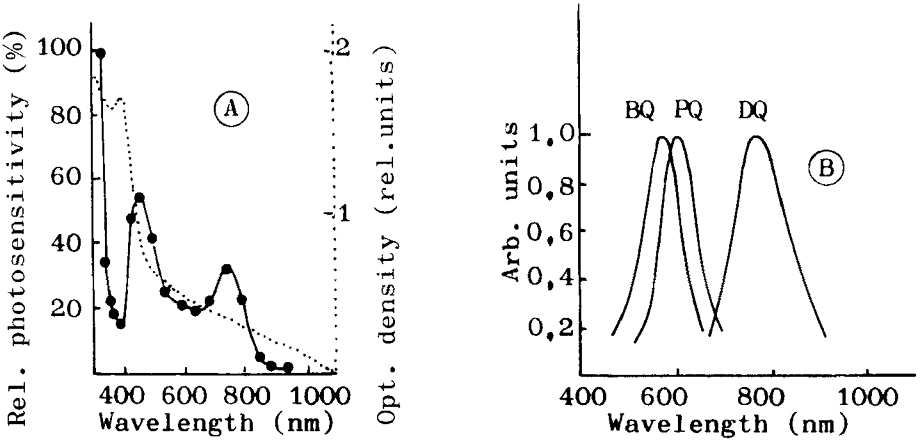


FIGURE 2 Spectral dependence of photoconductivity
Ⓐ $[Zn(mnt)_2]DQ$ (plotted as $I_{ph}^{1/\gamma}/Nq$ vs. $\lambda$)
Ⓑ $[Zn(mnt)_2]^{2-}$ with $K = DQ^{2+}$, $PQ^{2+}$, $BQ^{2+}$ (normalized)

On the one, spectra of $[Ni(mnt)_2]^{m-}$, $[Ni(dddt)_2]^-$ and $[Ni(dmit)_2]^{m-}$ complexes with photoconductive peaks at about 320, 370, 440 - 460, 500, 900 and 1200 nm can be identified with intense intraanion and IPCT transitions resulting in less ionic excited states, e.g., $[ML_2]^0$ species in $[ML_2]^-$ stacks[9]. On the other, in $[Zn(mnt)_2]^{2-}$ complexes with clearly resolved IPCT bands (see Figure 2 A) the photoconductive peaks at lower energies shift from 760 to 600 and 570 nm when $DQ^{2+}$ is replaced by $PQ^{2+}$ and $BQ^{2+}$ (see Figure 2 B). The acceptor strength decreases in the same sequence as indicated by the reduction potentials of $E(A^{2+}/A^{+})$ = -0.12, -0.56 and -0.67 V (vs SCE in $CH_3CN$) so that photoconductivity maxima can be described by a linear relationship between $\tilde{\nu}_{ph}^{max}$ and $E(A^{2+}/A^{+})$ which may be used as evidence for IPCT excitation in photoconductivity of dithiolate complexes[9].

The electric field dependence of the photoconductive efficiency, $\bar{\eta}$, can be fitted to a Poole-Frenkel-type formula

$$\ln\bar{\eta} = \ln\bar{\eta}_o + \beta E^{1/2} \qquad (2)$$

From least-square analysis of these plots (see Figure 3), Poole-Frenkel coefficients $\beta$ of 6.6 x $10^{-23}$ $(Vcm)^{1/2}$As for $[Ni(dmit)_2]MV$ at T = 263 K and 3.4 x $10^{-23}$ $(Vcm)^{1/2}$As for $[Zn(mnt)_2]DQ$ at T = 313 K are obtained which are in the order given by theory[5]. Consequently, the relationship

$$\bar{\eta} = \bar{\eta}_o \exp\left[-(E_o - \beta E^{1/2})\right]/kT \qquad (3)$$

can be approximately taken for a description of field dependence and temperature dependence of photoconductivity in dithiolate complexes ($E_o$ = Coulombic barrier, $\bar{\eta}_o$ = const[9]).

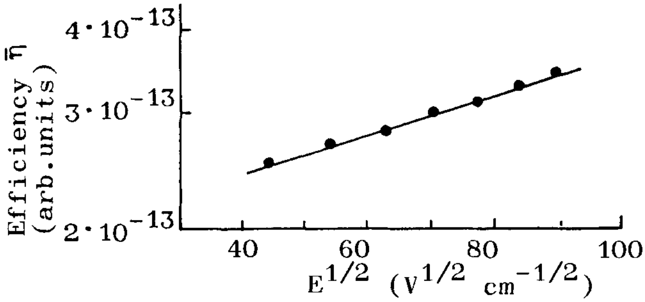


FIGURE 3 Field dependence of photocurrent plotted on log $\bar{\eta}$ vs $E^{1/2}$ scale: $[Zn(mnt)_2]DQ$ at 453 nm, T = 313 K.

According to the given results photoconductivity seems to be attributed to photo-switching of conducting anionic stacks of mixed-valence[10,11] containing, on a short time scale, in monoanionic salts both neutral $[ML_2]^0$ and ionic $[ML_2]^-$ molecules, and in dianionic salts both $[ML_2]^-$ and $[ML_2]^{2-}$ molecules. I.e., the situation of excited dithiolate complexes composed of chains of planar anions and cationic counterions may be analogous to quasi-one-dimensional CT-salts, e.g., TCNQ-salts, with incomplete transfer of charge between donor and acceptor stacks.

## CONCLUSION

In conclusion it can be stated that photoconductive properties of metal dithiolate complexes can be tuned by specific combinations of ligands, anionic charges, metals and cations. On the basis of ion pair charge-transfer (IPCT) mechanism photoconductivity of IPCT complexes may be attributed to photo-switching of mixed-valence anionic stacks with delocalized electrons.

## Acknowledgement

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