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Charge-Transfer in Ion Pairs: Design of Photoreactivity in Solution and Electrical Dark- and Photoconductivity in the Solid.

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Abstract

Weak supramolecular charge-transfer interactions within 1:1 ion pair complexes composed of anionic metal dithiolenes and cationic bipyridinium compounds have astonishing consequences on solution and solid state properties. In solution the relation between thermal and optical electron transfer can be analyzed in terms of the Hush-model. Irradiation of the dissolved complexes induces an electron transfer to molecular oxygen which can be quantitatively controlled by proper selection of the acceptor redox potential. The electrical conductivity of pressed powder pellets is quantitatively predictable within the range of 10^{-11} to 10^{-4} $\Omega^{-1}cm^{-1}$ from the solution redox potentials of the components or from the activation energy of thermal electron transfer calculated from the Hush-model. Finally, the action spectrum of the photoconductivity exhibits a maximum in the range of the optical charge-transfer band.

1. Introduction

Intermolecular charge-transfer interactions, which are a special case of the more general phenomenon of π-π interaction, are of basic importance in many areas of chemistry. For instance they largely determine the tertiary structures of biomolecules [1] and play a dominating role in chemical reactivity [2]. Intermediate CT complexes frequently are involved in thermal [3] and photochemical reactions [4]. The simplest chemical reaction is electron transfer and it was pointed [5] out that kinetic and thermodynamic parameters obtained from an *intramolecular* outer-sphere process are more informative than those from a bimolecular one since they do not contain the contributions for assembling the reactants. The intramolecular nature can be achieved using metal complex ions of opposite charge as the two components . Thermal and photoinduced electron transfer then occurs within a contact ion pair, which can be considered as the simplest case of a "supermolecule". When an ion pair charge-transfer (IPCT) band is observable, application of the Hush-model, originally formulated for intervalence complexes [6], can provide valuable information on the relation between thermal and optical electron

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transfer as reported by Meyer *et al.*[7] for the ion pair $MV^{2+}/[Fe(CN)_6]^{4-}$, MV^{2+} = methyl viologen. Since usually these complexes have not been isolated, basic structural information like relative orientations and short interionic contacts within the ion pair is lacking. Only a few examples of electron transfer within excited metal complex ion pairs are known and in most cases the components had an octahedral geometry [5,8-12]. The latter is not very favorable for π-π interactions which cause the appearance of CT bands [1]. Contrary to that, planar complexes with an extended π-system should be able to facilitate such interactions.

Moreover, physical properties of the solid state like electrical conductivity may depend on CT interaction between the components [13]. An important example are organic CT complexes of the type D-A wherein the acceptor A is a tetracyanoquinodimethane derivative and the donor D can be tetramethoxyselenaanthracene (TMSA) or the better reducing tetrathiafulvalene (TTF) . However, in these complexes there is no obvious relationship between the redox properties and electrical conductivity. In the case of TMSA conductivity increases with increasing oxidizing power of A while it decreases when D is equal to TTF [14]. This may be due to the fact that the structure of these compounds consists of separated -D-D-D- and -A-A-A- columns which enables only weak *intercolumnar* CT interactions while others, *intracolumnar* of non CT-type can be more important. Similar results were obtained for metal dithiolenes in different oxidation states [16, 16d]. Therefore a structure of mixed stacks (-D-A-D-) should be better suited to explore the effect of CT interaction on physical properties.

From this background it seemed worthwhile to synthesize light-sensitive ion pair complexes of CT character with planar components of different redox potentials. A planar geometry is expected to induce an approximately coplanar arrangement of the ions irrespective of the introduction of different substituents in order to vary the electronic part of the interionic interaction. In the following we report on the structure, photoinduced electron transfer in solution and on the electrical dark- and photoconductivity of metal-organic ion pair complexes of the type $\{D^{2-}A^{2+}\}$ and $\{D_2{}^{2-}A^{2+}\}$ wherein both components can undergo reversible electron transfer in the ground state. We address the question whether interionic CT interactions in these composite materials have a significant influence on their chemical and physical properties and how they are influenced by changing the redox potentials of the components. The complexes investigated are summarized in Figure 1. They consist of a planar mono- or dianionic metal dithiolene $[ML_2]^{-/2-}$ and a dicationic 2,2'- or 4,4'-bipyridinium derivative A^{2+} which may have a planar or twisted arrangement of the two pyridinium rings. This combination has the advantage that redox potentials can be easily tuned by changing ligand, metal and substituents in the donor and acceptor, respectively, while keeping the geometry approximately constant. We shall focus on the question whether CT interaction within these composite materials has a significant influence on their chemical and physical properties.

Metal dithiolenes are well known to undergo reversible electron transfer reactions in the ground state and to have electronic absorption spectra which extend down to 2000 nm [16]. Methyl viologen and other bipyridinium derivatives are inhibitors of electron transfer in mitochondria and in chloroplasts [17]. The sensitized photoreduction of bipyridinium derivatives is a key step in the photoproduction of hydrogen from water [18] and therefore a further aspect of this work is the question whether these viologen - metal dithiolene complexes may be used for static electron transfer photosensitization of viologens .

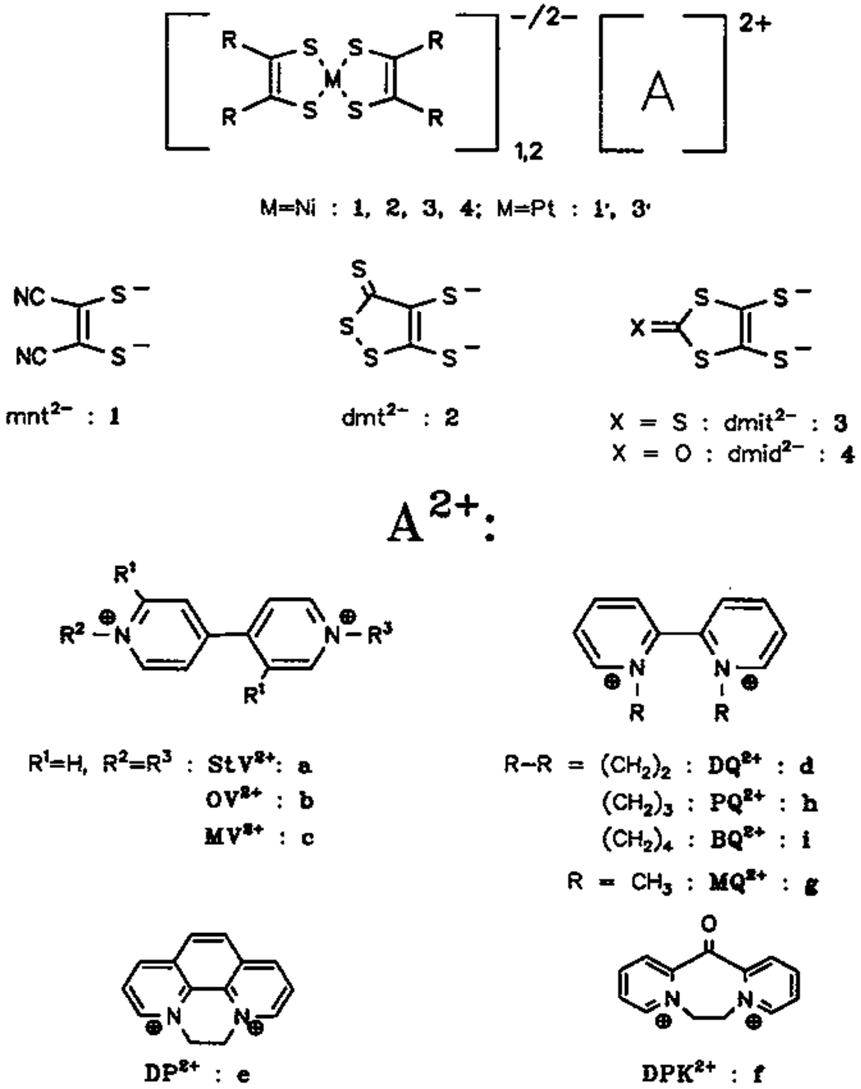


Figure 1

2. Synthesis and Structures

Methyl viologen salts of halogenometallates have been mentioned already more than fifty years ago by Emmert and Lauritzen [19a] and were fully characterized by R.J.P.Williams *et al.*[19b,c]. $\{MV^{2+}[Ir(mnt)(CO)_2]_2{}^{2-}\}$ [20a] and $\{MV(anthracene)\}^{2+}$, were previously synthesized, the latter even in a zeolite cage [20b], and characterized by x-ray analysis. Inclusion complexes with crown ethers are known also [20c]. Very recently the complexes $\{MV^{2+}(eosin)^{2-}\}$ and $\{BV^{2+}[BV^{2+}(eosin)_2{}^{4-}]^{2-}\}$, BV^{2+} = benzyl viologen, and their x-ray structures were reported [21]. The compounds discussed here are conveniently prepared by metathesis which occurs upon combination of acetone solutions of $(NBu_4)_{1,2}[ML_2]$ and $(A)X_2$ ($X= Cl^-, Br^-, [PF_6]^-$) since the products immediately precipitate due to their insolubility in this solvent [22-24].

The structure of the 1:1 ion pair $\{MV^{2+}[Ni(mnt)_2]^{2-}\}$ is shown in Figure 2 [25]. It consists of mixed columns along the a-axis. The planar ions are located face-to-face approximately parallel to each other (the interplanar angle is 5^{o}) with the two planes oriented offset (slipped). Shortest interplanar distances are in the range of 340 pm, a value typical for organic CT complexes [26], and occur between the electron rich sulfur atoms and the electron deficient carbon atoms in ortho-position to the viologen nitrogen [27a]. This orientation therefore maximizes attractive charge-charge interaction and minimizes π-π repulsion [1].

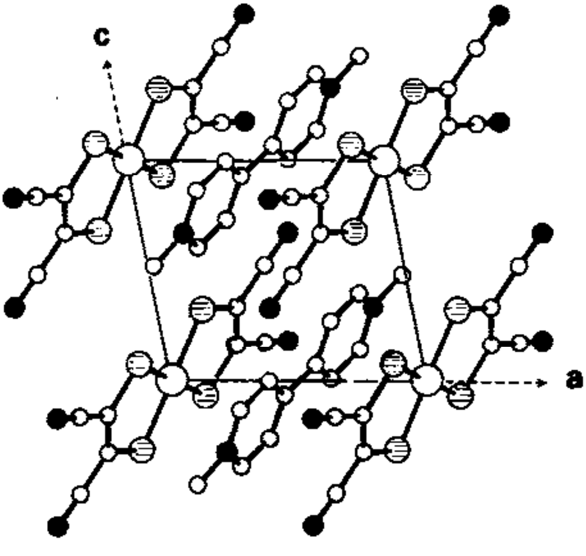


Figure 2: Solid state structure of $\{MV^{2+}[Ni(mnt)_2]^{2-}\}$.

Figure 3 contains the basic features of the structure of the 1:2 pair $\{MV^{2+}[Ni(phdt)_2]_2{}^{2-}\}$ which is analogous to the 1:1 pair along the a-axis but the second monoanion has been placed in between two mixed columns forming an edge-on arrangement with the methyl viologen; the angle between the corresponding planes is 83°. As compared to $\{MV^{2+}[Ni(mnt)_2]^{2-}\}$ the two planes within the mixed stack along the a-axis have a larger interplanar angle (22°) while the shortest intracolumnar distance of 350 pm is similar [25].

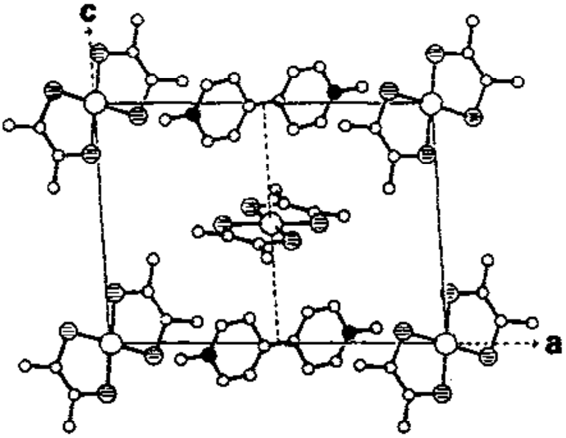


Figure 3: Solid state structure of $\{MV^{2+}[Ni(phdt)_2]_2^{2-}\}$; phenyl groups of the 1,2-diphenylethylenedithiolate ($phdt^{2-}$) are omitted.

When MV^{2+} is replaced by the nonplanar BQ^{2+} (Figure 1), a different structure is obtained. The two pyridinium rings are twisted by 64° and therefore only one of them is oriented face-to-face to one dianion while the second one interacts with another dianion. The angle between the corresponding donor and acceptor planes is 5° [27b].

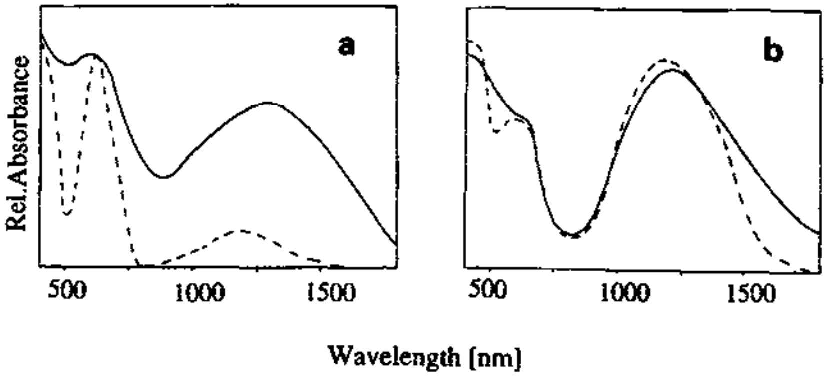


Figure 4: Diffuse Reflectance spectra of $\{DQ^{2+}[Ni(dmit)_2]^{2-}\}$ and $\{DQ^{2+}[Ni(dmit)_2]_2^{2-}\}$, a) and b) respectively, as compared to the tetrabutylammonium complexes (- - -).

Comparison of VIS-NIR spectra of $(NBu_4)_{1,2}[ML_2]$ with those of $\{A^{2+}[ML_2]^{2-}\}$ and $\{A^{2+}[ML_2]_2{}^{2-}\}$ reveals that only for the former a CT band is observable as demonstrated for $DQ^{2+}/[Ni(dmit)_2]^{-/2-}$ pairs in Figure 4. The higher end absorption of $\{DQ^{2+}[Ni(dmit)_2]_2{}^{2-}\}$ as compared to $NBu_4[Ni(dmit)_2]$ does not originate from an IPCT transition since it does not show the expected shift upon changing the redox potentials of donor and acceptor [22].

3. Relation between Optical and Thermal Electron Transfer in Solution.

In DMSO or DMF solutions the compounds are strongly dissociated as indicated by the association constant of $\{PQ^{2+}[Pt(mnt)_2]^{2-}\}$ which is 300 M^{-1} at an ionic strength of 0.016 M [23]. For this complex the maximum of the IPCT band is observed in DMSO solution at 773 ($\varepsilon = 40\ M^{-1}cm^{-1}$), in the solid at 742 nm. In order to gain some information on the relation between optical and thermal electron transfer it was tested whether or not the Hush-model [6] is applicable to these contact ion pairs. According to the model a linear correlation $E_{IPCT} = \chi + \Delta E$, wherein E_{IPCT} and ΔE are the energies of the optical and thermal process, respectively, and χ is the total reorganization energy, should be observed upon variation of ΔE [7]. While E_{IPCT} is directly available from the maximum of the IPCT absorption in DMSO solution, ΔE which is equal to ΔH in condensed phase, is calculated in the following manner [7]. From Scheme 1 it follows that the free energy change for electron transfer between the solvent separated ion pairs, as calculated from the redox potentials, is given by $\Delta G_{12} = \Delta G_{IP} + \Delta G_1 - \Delta G_2$. The two latter values are obtained from calculated association constants and therefore the free energy change for the reaction in the contact ion pair, ΔG_{IP}, becomes accessible. The values of ΔG_{12}, ΔG_{IP}, $\Delta G_1{}^A$, and $\Delta G_2{}^A$ applying for Scheme 1 are 84, 100, -18, and -2 as compared to 80, 87, -12, and -5 $kJmol^{-1}$, respectively, reported for $MV^{2+}/[Fe(CN)_6]^{4-}$ [7]. To obtain ΔE the term $T\Delta S_{IP}$ has to be added to ΔG_{IP}. Since the reaction entropy for the pair $MV^{2+}/[Fe(CN)_6]^{4-}$ is rather small (80 ± 21 $JK^{-1}mol^{-1}$) [7] one expects that in the present case it should be even smaller due to the highly π-delocalized nature of the dithiolene donor which should lead to a decreased interaction with the solvent dipoles.

$$\begin{tikzcd}
PQ^{2+} + [Pt(mnt)_2]^{2-} \arrow[r, shift left, "\Delta G_1{}^A"] \arrow[d, "\Delta G_{12}"] & \{PQ^{2+}[Pt(mnt)_2]^{2-}\} \arrow[l, shift left] \arrow[d, "\Delta G_{IP}"] \\
PQ^{+} + [Pt(mnt)_2]^{-} \arrow[r, shift left, "\Delta G_2{}^A"] & \{PQ^{+}[Pt(mnt)_2]^{-}\} \arrow[l, shift left]
\end{tikzcd}$$

Scheme 1

As a rough approximation this term was therefore neglected and ΔE becomes equal to ΔG_{IP}. One can estimate that the true values of ΔE may be 20-30 % higher [27c].

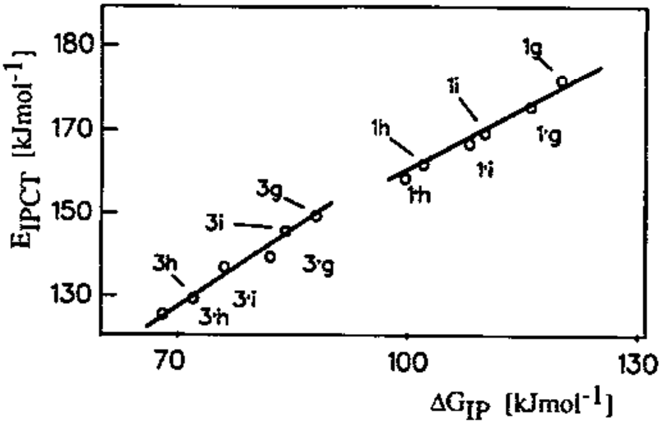


Figure 5: Dependence of the energy of the IPCT band on the driving force of electron transfer within the contact ion pairs of $\{A^{2+}[ML_2]^{2-}\}$; $L=dmit^{2-}$: M=Ni (3), Pt (3') and $L=mnt^{2-}$: M=Ni(1),Pt(1'); $A^{2+}=PQ^{2+}$ (h), BQ^{2+}(i), MQ^{2+} (g).

Remarkably, the linear dependence of E_{IPCT} on ΔG_{IP} also holds for these ion pairs as shown in Figure 5. As expected from the better reducing properties of $[Pt(mnt)_2]^{2-}$ and $[Pt(dmit)_2]^{2-}$ as compared to the corresponding nickel complexes, 0.23 and -0.14 as compared to 0.25 and -0.11 V (MeCN, vs.SCE), respectively, E_{IPCT} for a given acceptor is always smaller for the platinum complex. From the intercepts one calculates 64 ± 5 and 47 ± 9 kJmol^{-1} for $\{A^{2+}[M(mnt)_2]^{2-}\}$ and $\{A^{2+}[M(dmit)_2]^{2-}\}$, respectively. These values largely reflect the solvent contribution χ_o since the inner part χ_i should be negligibly small due to the presence of delocalized electronic systems in both ions before and after electron transfer. A value of 8 kJmol^{-1} was reported for χ_i for the octahedral pair $\{[Fe(CN)_6]^{4-}/[Ru(NH_3)_5(pyridine)]^{3+}\}^-$ [28]. The smaller reorganization energy of the dmit-complexes as compared to the mnt-compounds is in agreement with the weaker solvent effect on the redox potentials [23]. Note however that according to the neglection of ΔS_{IP} the absolute values of χ may be 20-30 % higher. Values of χ_o, calculated according to a dielectric continuum model [6,7], are 113 and 90 kJmol^{-1} for $\{PQ^{2+}[Ni(mnt)_2]^{2-}\}$ or $\{PQ^{2+}[Ni(dmit)_2]^{2-}\}$, respectively, and therefore reproduce the ligand influence although they are much higher than the experimental ones [23]. The fact that higher values were also calculated for the above mentioned iron - ruthenium pair [28], suggests that specific solvent effects, which are not included in the model, may cause this difference. Contrary to the case of these ion pairs, the model affords good results for large mixed-valence complexes [29-33]. Total reorganization energies of 111 and 234 $kJmol^{-1}$ were reported for $MV^{2+}/[Fe(CN)_6]^{4-}$ and $\{MV^{2+}[Ir(mnt)(CO)_2]_2^{2-}\}$, respectively [7,20a].

The activation energy for the thermal electron transfer within the twelve complexes mentioned in Figure 4 is in the range of 130 -170 $kJmol^{-1}$ as calculated from E_{IPCT} and ΔG_{IP} according to $E_a = E^2_{IPCT}/4(E_{IPCT} - \Delta G_{IP})$ [6]. From these values approximate potential energy curves can be constructed as shown in Figure 6 for the thermal electron transfer according to Equation 1. Since the minima of the curves which represent the system after reaction are located within the curve for the system before reaction, the back-reaction is in the range of the Marcus "inverted region". For $\{PQ^{2+}[Pt(mnt)_2]^{2-}\}$ the values of E_{IPCT}, ΔG_{IP}, and E_a are 160, 100, and 106 $kJmol^{-1}$, respectively. Substitution of PQ^{2+} by the poorer acceptors BQ^{2+} and MQ^{2+} each time increases E_a by 12 kJ/mol in good agreement with the change of the reduction potentials from -0.56 to -0.67 and -0.76 V (MeCN, vs. SCE), respectively [23]. From Figure 6 can be seen that $E_a - \Delta E(\Delta G_{IP})$, the distance between crossing point and minimum of the upper curve, corresponds to the activation energy for the back-reaction. In the same acceptor sequence as above it increases from 7 to 10 and 17 $kJmol^{-1}$.

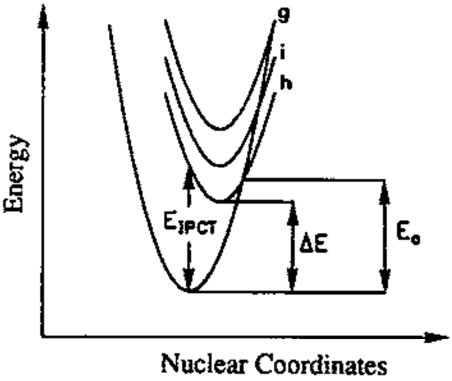


Figure 6: Potential energy diagram for electron transfer within $\{A^{2+}[Pt(mnt)_2]^{2-}\}$. Energetic separations within upper curves are not in scale to lower curve (see text); A^{2+}=**h**, **i**, **g**.

$$\{A^{2+}[ML_2]^{2-}\} \quad \rightleftarrows \quad \{A^{+}[ML_2]^{-}\} \qquad (1)$$

The extent of charge delocalization between $[ML_2]^{2-}$ and A^{2+} within the contact ion pair is described by the parameter α^2 which is directly proportional to the integrated intensity of the IPCT band and indirectly proportional to E_{IPCT} and the square of the interreactant distance between the two ions [7]. Taking the latter as 560 pm one arrives at a value of 2.2×10^{-4} for $\{PQ^{2+}[Pt(mnt)_2]^{2-}\}$ [21]. This is almost identical with the value reported for $MV^{2+}/[Fe(CN)_6]^{4-}$ [7] and indicates a very small extent of delocalization which is typical for outer-sphere complexes [31,34]. Correspondingly, the electronic coupling between the two redox states is rather weak as indicated by the values of 220 and 200 cm^{-1} (2.7 and 2.4 kJ/mol), obtained for the electron exchange matrix element V_{ab} from the relation $V_{ab}= \alpha \cdot E_{IPCT}$ [6] for the platinum [23] and iron [7] complex, respectively.

4. Photoinduced Electron Transfer in Solution

As mentioned in the introduction, one aim of this work was to sensitize the photoreduction of viologens by irradiation into the IPCT band of a ground state CT complex. As a first example $\{MV^{2+}[Zn(mnt)_2]^{2-}\}$ was selected since in this tetrahedral d^{10} complex the IPCT band does not interfere with MC bands as often observed for the transition metal complexes. In DMSO this compound has a broad IPCT absorption at 450-550 nm while the two intense maxima at 380 and 269 nm originate from IL transitions of the mnt^{2-} ligand [35,36]. Laser flash excitation at 530 nm affords a transient spectrum with major maxima at 470 and 610 nm which correspond to $[Zn(mnt)_2]^-$ and MV^+, respectively, (Figure 7). The transient has a half-life of 11 microseconds and decays by a second order rate law from which the rate constant k_{-2} of 3×10^9 $M^{-1}s^{-1}$ has been calculated [35]. These observations indicate that photoinduced electron transfer according to Equation 2 has occurred after excitation and therefore CT sensitization of the viologen was achieved. Upon repeated flashing partial decomposition oc-

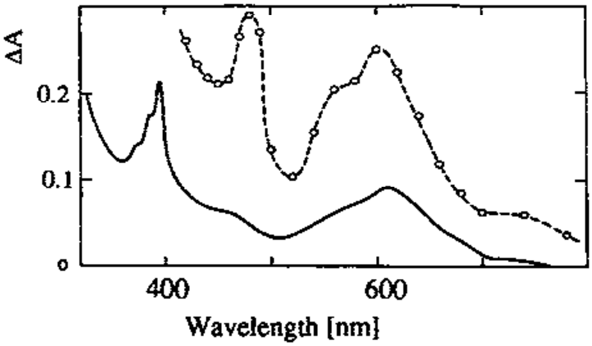
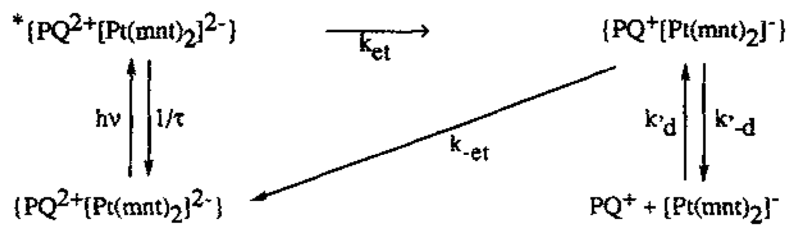


Figure 7: Transient absorption spectrum (- - -) obtained upon laser flash photolysis (λ=530 nm) of $\{MV^{2+}[Zn(mnt)_2]^{2-}\}$ in DMSO; ——— : spectrum of the MV^+ radical.

$$\{A^{2+}[M(mnt)_2]^{2-}\} \quad \underset{k_{-2}}{\overset{h\nu}{\rightleftarrows}} \quad A^+ + [M(mnt)_2]^- \qquad (2)$$

curs in agreement with the opening of the Zn-S bond and cis-trans isomerization of the ligand as reported for $(NBu_4)_2[Zn(mnt)_2]$ [37]. When zinc is replaced by platinum and MV^{2+} by PQ^{2+} and the complex is excited at 347 nm under otherwise identical experimental conditions, analogous results are obtained but the system behaves completely reversible now, $k_{-2} = 10x10^9\ M^{-1}s^{-1}$ [38]. The intensity of the transient decreases when the ionic strength is increased. The fact that the transient's disappearance obeys a second order rate law, indicates that the back-reaction occurs from solvent separated ions. This requires diffusion followed by electron transfer (Scheme 2). Therefore k_{-2} can be formulated as $k'_d k_{-et} / (k_{-et}+k'_{-d})$. The measured value of k_{-2} is about two times larger than the calculated diffusion constant k'_d (vide infra). This implies that the back-reaction is diffusion controlled and $k_{-et} \geq k'_{-d}$.



Scheme 2

Under the experimental conditions given, about 60 % of the complex exist as contact ion pair. Since this percentage should decrease upon increasing the ionic strength, it is most likely that only light absorbed by the contact ion pair promotes electron transfer (Scheme 2), i.e. static quenching occurs. This is corroborated by the short life-time of $\tau \leq 1x10^{-8}$ s measured for $(NBu_4)_2[Pt(mnt)_2]$ [39]. From the calculated diffusion rate constant in the order of $1x10^{10}\ M^{-1}s^{-1}$ and the concentration of $[PQ^{2+}] = 3.33x10^{-3}$ M the pseudo-first order rate constant for dynamic quenching is obtained as $\leq 3.33x10^7\ s^{-1}$. This process therefore seems to be too slow to compete with excited state deactivation of the platinum dithiolene [38]. Assuming that diffusional electron transfer is absent, the quantum yield of product formation is given by $\Phi = \Phi_{IP}\eta_{et}\eta_{ce}$ wherein Φ_{IP} is the fraction of contact ion pairs, η_{et} and η_{ce} are the efficiencies of electron transfer and cage escape, respectively. From the measured quantum yield of 0.07 the product $\eta_{et}\eta_{ce}$ is calculated as 0.11. When PQ^{2+} is replaced by the monocationic $EPSP^+$ (R^2 = Et, $R^3 = (CH_2)_3SO_3^-$, Figure 1) this product is ten times larger while the quantum yield changes almost negligibly. This is most likely a charge effect on η_{ce} since the rate constant of cage escape, k'_{-d}, should be larger in the case of a monopositive acceptor. Calculated constants of k'_d ($M^{-1}s^{-1}$) and k'_{-d} (s^{-1}) for the pairs $PQ^+/[Pt(mnt)_2]^-$ and $EPSP^0/[Pt(mnt)_2]^-$ are $5.6x10^9$, $2.2x10^9$ and $2.8x10^9$, $5.9x10^9$, respectively [38,40].

Since the flash photolyses indicated that photoinduced electron transfer affords the expected primary redox products, we tested whether these could be intercepted by appropriate scavengers in order to introduce chemical reactions [41]. While no spectral changes are observed upon continuous irradiation ($\lambda \geq 360$ nm) of $\{A^{2+}[Pt(mnt)_2]^{2-}\}$ in dinitrogen saturated DMSO solution, a clean oxidation to $[Pt(mnt)_2]^-$ occurs in the presence of air when A^{2+} is BQ^{2+} and MQ^{2+} (Figure 8). At an irradiation wavelength of 334 nm the quantum yields of monoanion formation are 0.06 and 0.03 for the two cases, respectively. This reaction differs from the photooxidation of dianionic metal dithiolenes by chloroform [42] and from the photoinduced electron transfer to the solvent which occurs only at wavelengths shorter than 353 nm [35]. No reaction takes place when the acceptor is MV^{2+}, PQ^{2+} or tetrabutylammonium. This suggests that the reduced acceptor A^+ formed according to Equation 2, transfers an electron to oxygen (Equation 3), thus intercepting the back-reaction. In fact, the superoxide anion radical can be scavenged with a spin-trap only in the case of $A^{2+} = BQ^{2+}$ and MQ^{2+}.

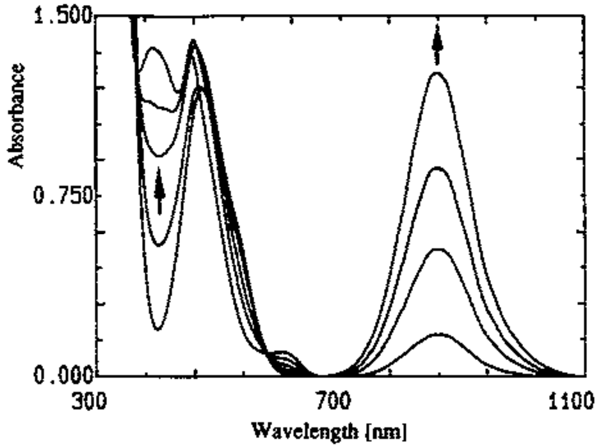


Figure 8: Spectral changes observed upon irradiating ($\lambda \geq 570$ nm) an aerated solution of $\{MQ^{2+}[Pt(mnt)_2]^{2-}\}$ in DMSO.

$$A^+ + O_2 \longrightarrow A^{2+} + O_2^- \tag{3}$$

These two acceptors in DMSO solution have reduction potentials of -0.67 and -0.73 V which compare well with the value of -0.78 V for $E^o(O_2^{o/-})$ in the same solvent [41,43]. Thus, the failure of MV^{2+} and PQ^{2+} to induce the reaction, originates in their potentials of -0.47 and -0.57 V, respectively, which are too positive. In summary, photoinduced electron transfer to molecular oxygen, which is the basic step of oxygen activation in artificial [44] and biological [45] systems, can be controlled by proper selection of the acceptor component.

5. Electrical Dark- and Photoconductivity

As mentioned in the introduction, the specific electrical conductivity (σ) of organic CT complexes is known to depend in an irregular fashion [13,14,46,47] on the difference of the components redox potentials. The same is observed [22,48] for the 1:2 complexes of type $\{A^{2+}[ML_2]_2{}^{2-}\}$ which do not posses an IPCT band. Contrary to that, a regular dependence is found for the 1:1 pairs $\{A^{2+}[ML_2]^{2-}\}$ as long as the acceptor can adopt a planar geometry [24]. The surprising linear correlation between log σ and the redox potential difference, expressed as ΔG_{12}, the driving force of the thermal electron transfer between the solvent-separated ions according to Equation 4, is followed by fifteen complexes (Figure 9). In all of these complexes the lowest absorption band has IPCT character.

$$A^{2+} + [ML_2]^{2-} \longrightarrow A^{+} + [ML_2]^{-} \qquad (4)$$

In the case of the six considerably deviating complexes the acceptors are the non-planar 2,2'-bipyridinium derivatives PQ^{2+} (**h**), BQ^{2+} (**i**), and MQ^{2+} (**g**) (Figure 1) and the absorption lowest in energy is of MC character.

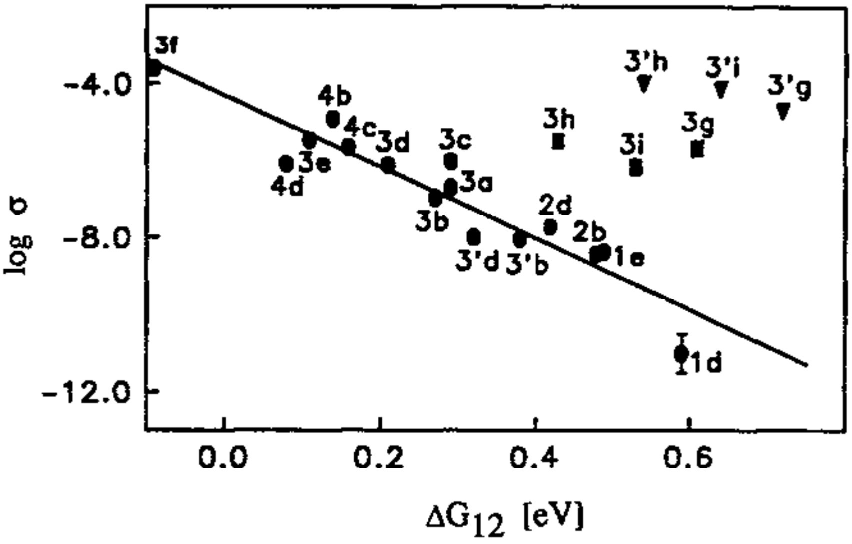


Figure 9: The dependence of log σ ($\Omega^{-1}cm^{-1}$) of pressed powder pellets on the driving force of electron transfer in solution.

It was shown above that in solution for a number of mnt- and dmit-complexes E_{IPCT} increases linearly with ΔG_{IP} (Figure 4) since the reorganization energy stays constant. As a reliable approximation ΔG_{IP} is taken as equal to ΔG_{12} [49] which means that E_{IPCT} depends linearly on ΔG_{12}. The equation for α^2 [7] can then be written as

$$\alpha^2 = \mathrm{const.}\varepsilon_{max}\Delta\bar{\nu}_{1/2}/\Delta G_{12}d^2 \tag{5}$$

wherein the constant contains the reorganization energy χ. Equation 5 means that for a group of ion pairs with IPCT bands of similar oscillator strength and with approximately the same interionic distances d [50], the CT interaction increases linearly with more negative values of the driving force. This explains the observation that only the complexes with planar acceptors do follow the linear correlation while those having different amounts of twisting around the central C-C bond, due to the presence of a bridging propylene or butylene group (h,i) or two methyl groups (g), do not (Figure 9).

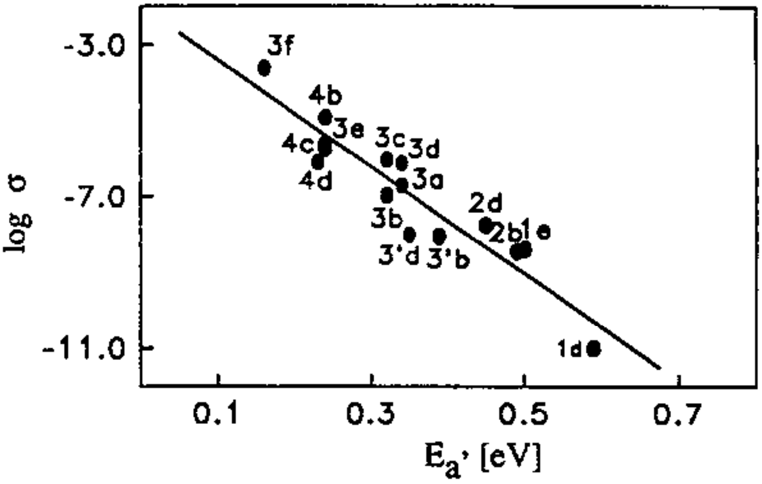


Figure 10: The dependence of log σ ($\Omega^{-1}cm^{-1}$) of pressed powder pellets on the E_a, the activation energy of thermal electron transfer as calculated, from ΔG_{12} and E^{on}_{IPCT}

These results suggest that the mechanism of conductivity basically consists of a solid state electron transfer. If that is the case, the conductivity should depend on the activation energy E_a, obtainable within the Hush-model from the E_{IPCT} and ΔG_{12} values as discussed in Chapter 3. As the energy of the optical electron transfer E^{on}_{IPCT}, the onset of IPCT band in the Diffuse Reflectance spectrum was taken since the determination of the maximum of these very broad bands is too erratic. In fact a plot of log σ as function of E_a, affords a straight line as shown in Figure 10. This clearly demonstrates that the electrical conductivity of these composite solids can be quantitatively predicted from the activation energy of electron transfer obtained *via* the Hush-model [48].

Thus, the linear relationship between log σ and ΔG_{12} or E_a, most likely originates from two basic properties of these ion pairs. One is the fact that their structure consists of mixed donor/acceptor columns (-D-A-D-) which allows more favorable *intracolumnar* π-π interactions than in the case of separated donor (-D-D-D-) and acceptor (-A-A-A-) stacks observed for the most organic CT complexes [14]. The other one is the planar geometry of both components which maximizes the electronic interaction and preserves the key structure. Therefore the reorganization energy of electron transfer stays approximately constant when substituents and ligands are varied. One should note that although the electronic perturbation caused by the CT interaction is very small as indicated by the value of $\alpha^2 \cong 10^{-4}$, it causes a change in conductivity over seven orders of magnitude. An excellent summary of solid state properties of metal dithiolenes has appeared recently [16d].

When the above conclusion, that the electrical conductivity strongly depends on the amount of electron delocalization from the donor to the acceptor, is valid, one expects that irradiation should have a pronounced effect in the case of the ion pairs having CT character since the solution experiments have demonstrated that photoinduced electron transfer takes place. In fact, when in $(NBu_4)_2[Pt(mnt)_2]$ the cation is replaced by the redoxactive MV^{2+}, the photoconductivity (λ= 696 nm) increases from $\leq 10^{-12}$ to 4×10^{-9} $\Omega^{-1}cm^{-1}$ while it changes only from 1×10^{-9} to 2×10^{-9} $\Omega^{-1}cm^{-1}$ when $NBu_4[Ni(mnt)_2]$ is compared with

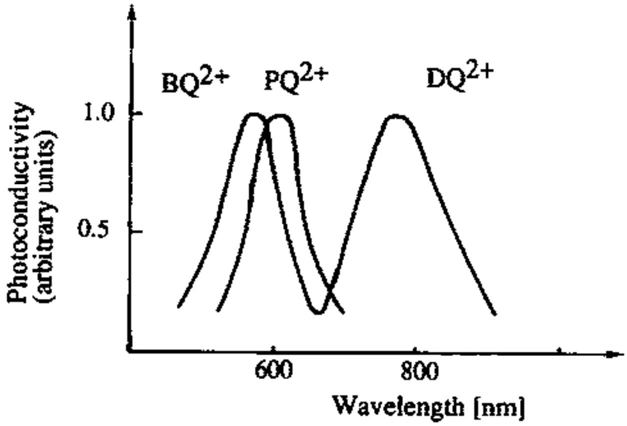


Figure 11: Changes in the action spectra of the photoconductivity upon varying the acceptor in $\{A^{2+}[Zn(mnt)_2]^{2-}\}$.

$\{MV^{2+}[Ni(mnt)_2]_2^{2-}\}$ [51,52]. This parallels the results obtained for the electrical dark conductivity which exhibits a clear dependence on the redox properties only in the case of 1:1 ion pairs but not for the 1:2 pairs which do not have CT character.

Further evidence for the promoting effect of charge-transfer states stems from the wavelength dependence of the photoconductivity. In order to prevent interference by MC states, the zinc complexes $\{A^{2+}[Zn(mnt)_2]^{2-}\}$ were examined. Surprisingly, a maximum is obtained in the region of the IPCT band (Figure 11). Such a behavior has been predicted for intervalence complexes [6] and again supports the validity of the Hush-model for these redoxactive ion pairs. In the sequence $A^{2+} = DQ^{2+}, PQ^{2+}, BQ^{2+}$ the photoconductivity maxima are located at 760, 600 and 570 nm and their wavenumbers increase even linearly with the redox potential of the acceptors [51,52].

6. Summary

The results summarized above demonstrate that light-sensitive redox ion pairs consisting of both planar inorganic complex anions and organic cations are excellent candidates to study the effect of weak CT interactions on photochemical reactivity in solution and electrical dark and photoconductivity in the solid state. The relations between thermal and optical electron transfer can be analyzed in terms of the Hush-model and have surprising *quantitative* consequences on chemical solution and solid state properties. In solution photoinduced electron transfer to molecular oxygen proceeds via initial reduction of the acceptor component and can be therefore controlled by proper adjustment of its reduction potential. The reorganization energy of thermal electron transfer in solution stays fairly constant when only the acceptor part is varied while the donor complex is kept constant. This seems to be the prerequisite for the linear dependence of the logarithm of the specific electrical conductivitiy on both the driving force of thermal electron transfer and the activation energy of this process as calculated from the spectral properties of the IPCT band and the solution redox potentials. Thus, it is possible to quantitatively predict this important solid state property from easily obtainable molecular parameters, a central topic of materials research. In accord with an CT mechanism of the electrical conduction the action spcetrum of the photoconductivity exhibits a maximum in the region of the optical IPCT band. - These results clearly reveal that small changes in the electronic interaction within ion pairs can be used to quantitatively design solution and solid state photosensitivity of these composite materials.

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