CHEMISTRY OF VIOLOGENS

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Abstract - Pointing out electron acceptor properties of viologens, the outlines of porphyrin-viologen systems, complexes of viologens with donors and polymeric viologens are described along with biological interest of viologens.

I. INTRODUCTION

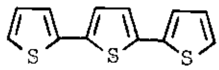
Viologens (methylviologen, MV, 1,1'-dimethyl-4,4'-bipirydinium dibromide, and its analogues) are a special class of N-substituted salts of azaaromatics which are important as synthons in cyclization reactions[1-7] and as species of interesting electrochemical properties;[1,3] they have been used in the synthesis of drugs and as models in the investigation of biochemical processes.[3]

Viologens have drawn considerable attention as redox catalysts and electron relays in photocatalyzed water cleavage for solar energy harvesting;[8-10] they are also used in organic synthesis.[11-14] Polymers incorporating viologen units have special properties,[15-16] while methylviologen (under the name of paraquat) and its analogues are effective herbicides.[17]

The article reviews the chemistry of viologens. The viologens as electron acceptors are described first. Then porphyrin-viologen systems and complexes of viologens are presented, followed by polymeric viologens and biologically interesting ones.

II. VIOLOGENS AS ELECTRON ACCEPTORS

An example of MV^{2+} as an electron acceptor is its reaction with the triplet α-terthienyl (αT^*),



αT

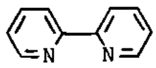
which yields the readily detectable methylviologen radical cation $MV^{\cdot +}$.

$$\alpha T + MV^{2+} \longrightarrow \alpha T^{+} + MV^{\cdot +}$$

This reaction is followed by back electron transfer[18,19].

$$\alpha T^{\cdot +} + MV^{\cdot +} \longrightarrow \alpha T + MV^{2+}$$

It was observed that the photoreduction of tris(acetylacetonato)cobalt(III) ($Co(acac)_3$) with 1-benzyl-1,4-dihydronicotinamide (BNAH) is accelerated in the presence of methylviologen.[20] The hydrophilic MV^{2+} is an electron mediator in the photoreduction of hydrophobic $Co(acac)_3$ by hydrophobic BNAH. It accelerates the reaction through the efficient acceptance of electrons from the photoactivated $BNAH^*$, followed by electron transfer from the electron mediator to $Co(acac)_3$.This process is favored by low polarity of the reaction medium.[21,22]
Photosensitized reduction of MV^{2+} through the triplet-triplet energy transfer from organic dyes to 9-anthracenecarboxylate anion (AC^-) has been investigated. Xanthene and acridine dyes, such as fluorescein, erythrosine, proflavine and acriflavine serve as electron donors. In the dye/AC^-/MV^{2+}/TEOA system the efficiencies of the energy and electron transfer from $^3AC^-$ to MV^{2+} are close to unity (TEOA = triethanoloamine). These investigations are performed in the aspect of application of light energy to optical devices.[23]
In the spectroscopic study of RuL_3^{2+} complexes (L = 1-5), the absorption coefficients of a triplet metal-to-ligand charge transfer (^{3}MLCT) state were determined, and the obtained values were verified by measurement of solvent-cage escape efficiencies for the RuL_3^{2+}/MV^{2+}/EDTA system using pulsed-laser techniques.[24]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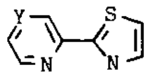
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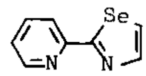
Y
CH
N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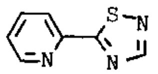
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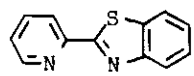
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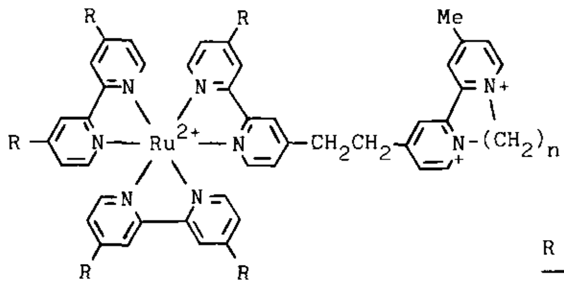
It was also observed that the counterions influence forward and backward electron transfer reactions between $Ru(bpy)_3^{2+}$ and MV^{2+}.[25]

A zeolite-based molecular triad composed of a zeolite L or Y surface-bonded $Ru(bpy)_3^{2+}$ sensitizer is known. It is an electron acceptor which is a diquat (DQ^{2+}) analog oriented into the open anionic structure of zeolite, and a secondary acceptor, benzylviologen BV^{2+}, localized within the zeolite framework.

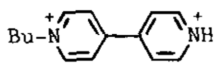

$Ru(bpy)_3^{2+}$ linked with DQ^{2+} analog

R	n
H	3
Me	2
Me	3

In the self-assembling molecular triad a long-lived light-induced charge separation was achieved. These studies may be of use in electron transfer reactions aimed to mimic photosynthetic processes.[26,27]

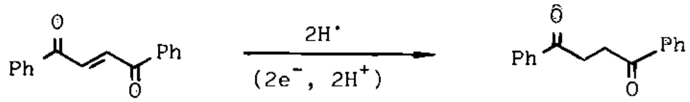
Electron transfer reactions between viologen radical cations $C_nV^{\cdot +}$ (n = 1-18) and quinones have been investigated in aqueous and reverse micellar AOT/isooctane/H_2O solution (AOT = aerosol, OT = bis(2-ethylhexyl)sulfosuccinate sodium salt) using electron pulse radiolysis technique. The viologens showed a distribution equilibrium between water pool and surfactant interface, while quinones were either water- or oil-soluble exclusively. Antraquinone-2-sulfonic acid (AQS^-) sodium salt (water-soluble) as well as dimethylnaphthoquinone and vitamin K (oil--soluble) were used as quinones. The orientation of viologen species in the surfactant interface and the effect of solubilization sites on electron transfer rates were studied. The concentration of water pools was determined using dynamic light scattering techniques. The association of the radical cation with the surfactant AOT tended to increase with the length of the aliphatic chain of viologens. Consequently, the rate constants of the reaction betweeen $C_nV^{\cdot+}$ radical cations and anthraquinonesulfonate ions (AQS^-) are decreased with increase of the aliphatic chain of viologens and in the case of of $n > 12$ no electron transfer to AQS^- ions is observed. It was found that $C_nV^{\cdot+}$ radical cations are more hydrophobic than the oxidized species and that the association of reduced viologens with interfacial region is stronger than that of the oxidized species. The reduced viologens are, therefore, lees accessible for quinones.[28-33] Alkylviologens are usually electron transfer agents, and the reactions are most frequently accomplished by protons providing from a large excess of protic medium.[34,35]

However, a concurrent transfer of electrons and protons may occur. It was observed that 1-butyl-4,4'-bipyridinium radical cation ($BuPPH^{\cdot+}$) acts as hydrogen transfer agent in an aprotic medium.[34,35]

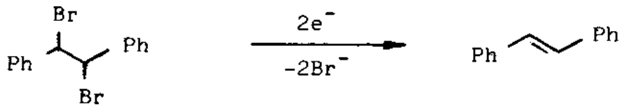


$BuPPH^{2+}$

In order to prove the efficiency of $BuPPH^{\cdot+}$ as hydrogen transfer agent, two substrates, (E)-1,4-diphenyl-2-butene-1,4-dione (6) and meso-1,2-dibromo-1,2-diphenylethane (7) were selected to be reduced. The reduction of 6 to 1,4-diketone (8) requires protons (reaction A), while the reduction of 7 (i.e. its debromination) proceeds by the acceptance of electrons to give the olefin (9)(reaction B).[35]

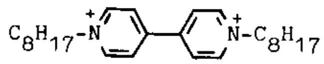


6 8 reaction A



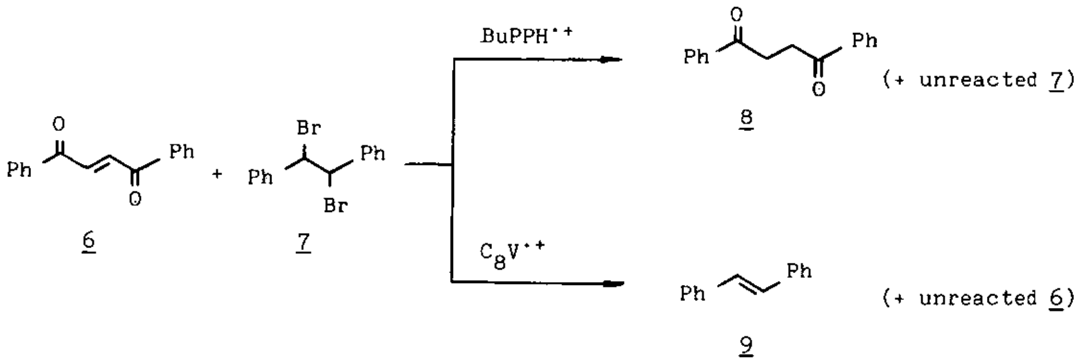
7 9 reaction B

It was shown that $BuPPH^{\cdot +}$ is efficient both as hydrogen reducing agent (reaction A) as well as electron reducing agent (reaction B) in aprotic media (dichloromethane or DMF).[35] On the other hand $C_8V^{\cdot +}$ reacts only as electron reducing agent (reaction B).[35]

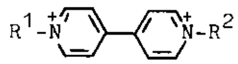


C_8V^{2+}

In the experiments where the equimolecular mixture of 6 and 7 was treated with $BuPPH^{\cdot +}$ or $C_8V^{\cdot +}$ in dichloromethane, hydrogen reduction resulting in 8 took place exclusively in the case of $BuPPH^{\cdot +}$, while $C_8V^{\cdot +}$ was only an electron reducing agent and the reaction led exclusively to 9.[35]



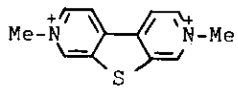
These investigations demonstrated that $BuPPH^{\cdot +}$ can act as hydrogen transporting agent through a hydrophobic liquid membrane.[34,35] Bioelectrocatalytic reduction of NAD^+ to NADH on diaphorase immobilized electrodes was also studied by using viologen derivatives (10), and the effect of viologen structure on this process was examined.[36]



10

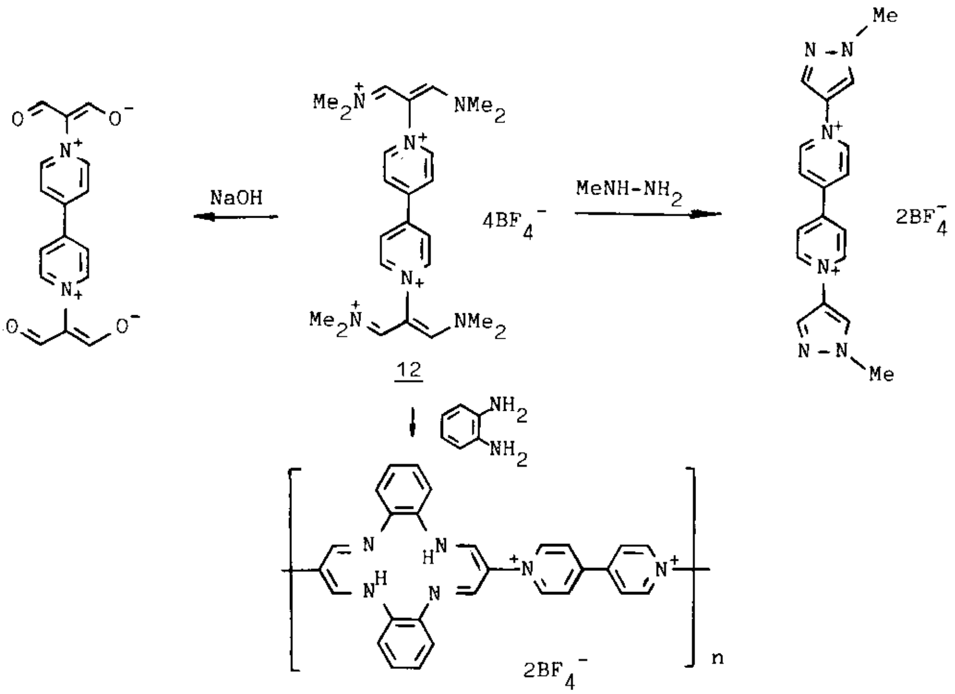
R^1, R^2 = Me, CH_2CONH_2, $(CH_2)_3NH_2$, $(CH_2)_2SO_3H$

It may be noted that the analog of viologen bearing a thiophene moiety (11) is more efficient electron transfer agent in the water cleavage than the parent MV^{2+}.[37,38]



11

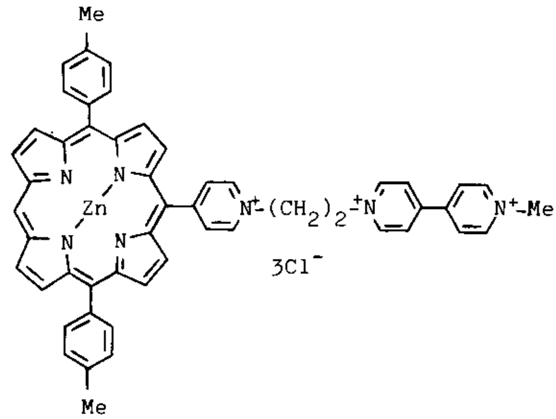
It was found that the reduction of the salt (12) proceeds more easily than that of methylviologen, this fact being rather unexpected. Here the following reactions of 12, carried out from the aspect of synthesis of models for organic superconductors,[39,40] should also be mentioned.



III. PORPHYRIN-VIOLOGEN SYSTEMS

There exist many publications dealing with molecular models capable of mimicing the rapid electron-transfer processes occurring in photosynthesis having views upon the conversion of light to electrical or chemical energy [41–46] Often a porphyrin or a chlorophyll derivative is used as the chromophore, and viologen or quinone linked via a spacer group serves as an electron acceptor. Much works in the area of porphyrin-viologen systems deal with the influence of the mutual orientation, the type of spacer group and the kind of solvent on rates of charge separation and charge recombination.[47–59]

An example is the investigation of photoinduced water cleavage by 13 proceeding in the presence of colloidal platinum and 1,4-dihydronicotinamide, used as an electron donor.[38,54]



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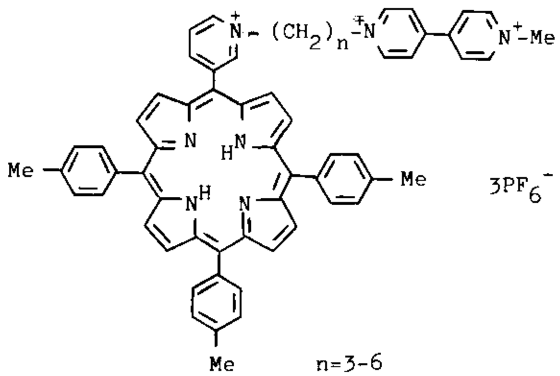
To porphyrin-viologen systems also belongs 14.



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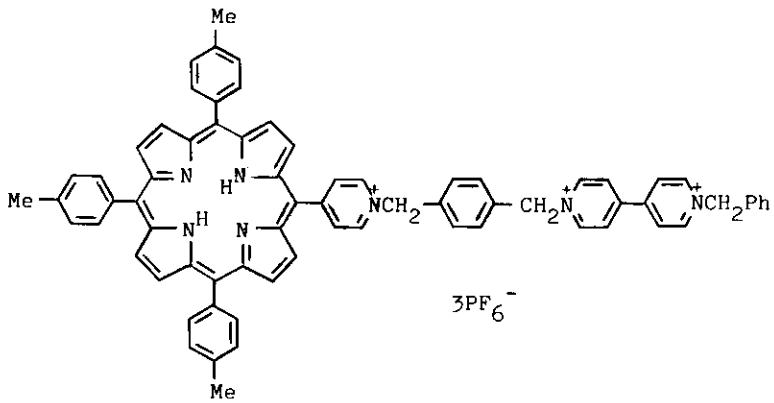
The ^1H nmr results showed that the viologen unit does not fold back above the porphyrin plane in spite of the fact that linking chain is flexible.[60]

In the study of excited state properties in porphyrin-viologen systems, the pulsed laser excitation of pyridyltritolylporphyrin chromophore covalently linked to benzylviologen (15) was performed.[61]



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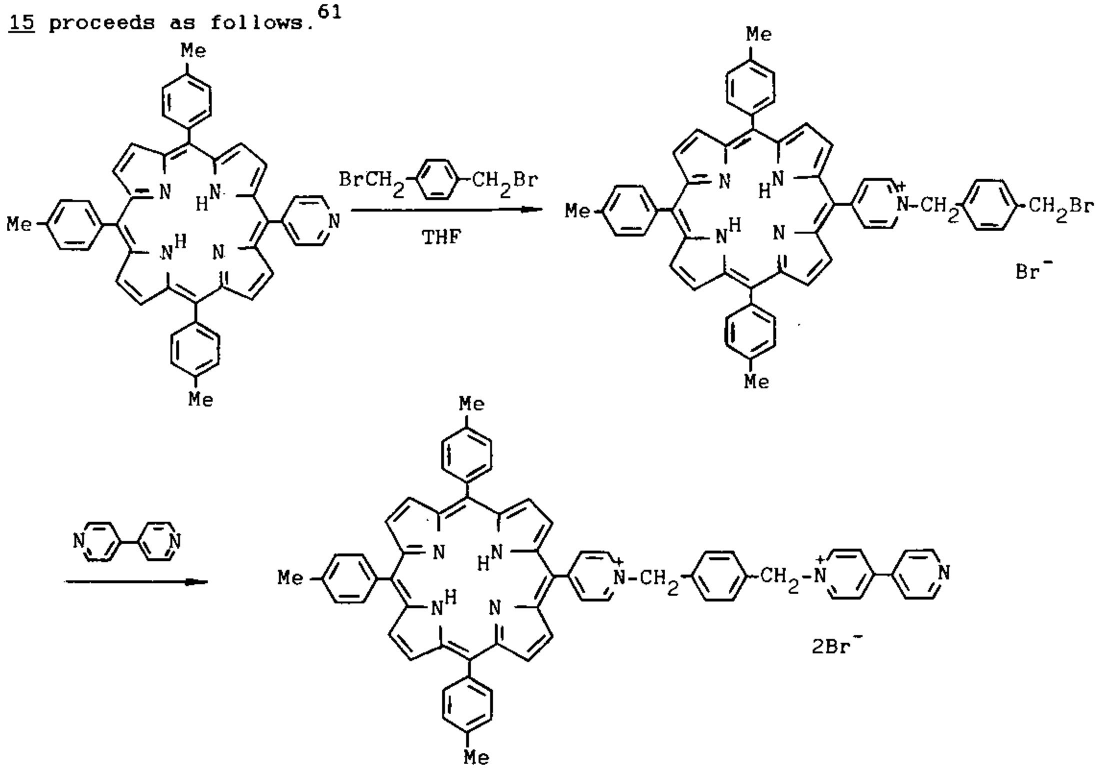
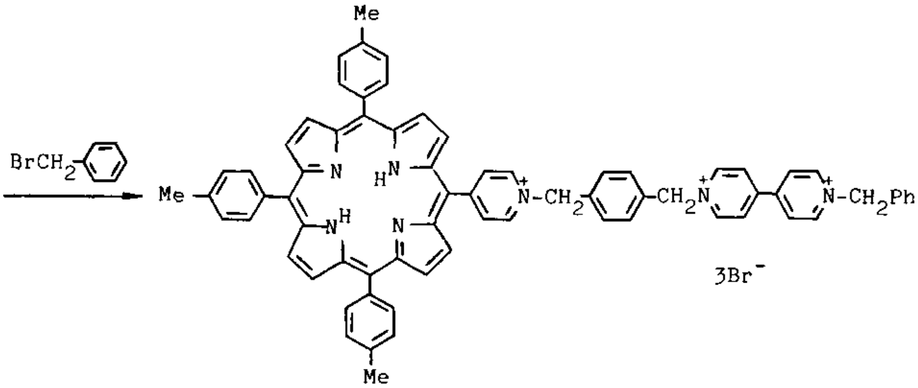
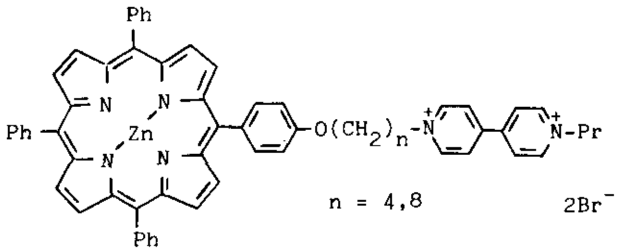
Benzylviologen was chosen as an electron acceptor due to the easy detection of its one electron reduction product by resonance Raman spectroscopy. The synthesis of 15 proceeds as follows.[61]





It was observed that photoexcitation leads to an intramolecular electron transfer, reducing the viologen moiety to radical cation. The results were confirmed by pulsed resonance Raman spectroscopy as well as by fluorescence quenching and direct fluorescence lifetime measurements.[61]

In donor-acceptor linked compounds, the electron transfer rates decrease with the donor-acceptor distance in the singlet state.[59,62] In porphyrin-viologen systems electron transfer processes are affected by counterions of viologen units. In 16 the influence of counterions on the electron transfer processes was investigated in aqueous acetonitrile, in micelles, and in molecular bilayers of cationic surfactants in water .[49,63,64]



16

The photoinduced electron transfer rates decrease considerably when the counterion of viologen moiety is changed from chloride to bromide ion. This fact is presumably associated with the CT interaction between viologen and bromide ions. It was also established that halide ions accelerate the decay of radicals more efficiently than sulfate or perchlorate ions.[64]

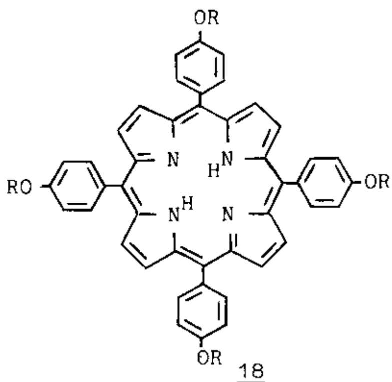
For investigation of the heavy atom effects, 16 was incorporated into comicelles of cetyltrimethylammonium chloride (17a) and bromide (17b) at various 17a : 17b molar ratios. It was found that the decay rate increases with an increase in bromide ions i.e. with the amount of 17b.[64]

$Me_3N^+(CH_3)_{15}Me \quad X^-$

17	X
a	Cl
b	Br

The counterion influences the electron transfer processes via two types of perturbation - reduction of the electron accepting properties of viologen units through charge-transfer interaction, and enhancement of intersystem crossing of the photogenerated radical pair via spin-orbit interaction.[49,63,64]

For a porphyrin linked with four viologen molecules via 1,3-propoxy-4-phenyl chains (18), the rate constants of the photoinduced charge separation and charge recombination have been determined by using time-resolved fluorescence spectroscopy and ultrafast flash photolysis.[65,66]



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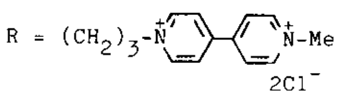


One covalently-bonded viologen molecule quenches the excited singlet and triplet states of a porphyrin in polar solvents only moderately, but when two viologen units are appended to the porphyrin molecule this process is more effective. In the case of four viologen units, as in 18, a very efficient fluorescence quenching takes place.[47,48]

In DMSO solution of 18 a rapid charge separation from the first excited singlet state of the porphyrin affords long-lived redox products.

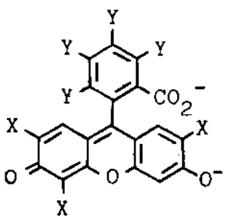
These products recombine to restore the ground-state reactants. Similar, but slower, charge transfer occurs from the porphyrin triplet excited state, which is formed in competition to charge transfer from the singlet state. It was established that the rates of both the charge transfer and charge recombination processes are solvent dependent, protic solvents favoring a fast charge recombination.[65,66]

IV. COMPLEXES OF VIOLOGENS

Various types of viologen complexes are known.[67-76] Most research works deal with CT complexes of xanthene dyes and viologens.[67] Determination of the formation constants of complexes of eosin with viologens reveals that they consist of two additive components, one reflecting the electrostatic potential energy between charged moieties and the other showing the substituent donor-acceptor interactions.[67]

The formation of ground-state complexes of xanthene dyes and viologens has been investigated and the effect of SiO_2 colloids on the separation of these complexes has been examined. Back electron-transfer reactions and electron transfer quenching were followed by laser flash photolysis methods. When an aqueous solution of Rose Bengal (RB^{2-}) is treated with MV^{2+}, the 1 : 1 ground-state complex is formed.[68,69]

$$RB^{2-} + MV^{2+} \longrightarrow [RB^{2-}...MV^{2+}]$$



		X	Y
Rose Bengal	RB^{2-}	I	Cl
Eosin	EO^{2-}	Br	H

Static electron-transfer quenching of excited RB^{2-} takes place in the complex structure, but charge separation is impossible due to a rapid back electron transfer. Addition of a SiO_2 colloid to an aqueous solution (pH = 9.3) of the complex $[RB^{2-}...MV^{2+}]$ results in its dissociation. This process occurs by electrostatic interactions between the complex components and the SiO_2 colloid particles. The positively charged MV^{2+} is attracted by the negatively charged colloid interface, while RB^{2-} is repelled. It was observed that illumination of a system containing RB^{2-} as photosensitizer, MV^{2+} as an electron acceptor and TEOA as sacrificial electron donor, carried out in the presence of SiO_2 colloid results in the effective photoreduction of MV^{2+} to $MV^{\cdot +}$.[69]

TEOA reduces excited RB^{2-} in the primary electron transfer process.[69]

$$^3RB^{2-} + TEOA \longrightarrow RB^{\cdot 3-} + TEOA^{\cdot +}$$

The intermediate photoproducts $RB^{\cdot 3-}$ and $TEOA^{\cdot +}$ are stabilized against back electron-transfer reaction by electrostatic interactions with SiO_2 particles, resulting in the repulsion of $RB^{\cdot 3-}$ from the colloid interface.

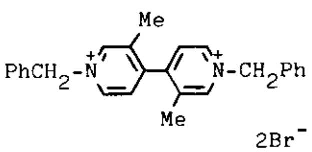
$$RB^{\cdot 3-} + TEOA^{\cdot +} \longrightarrow RB^{2-} + TEOA$$

In the presence of MV^{2+} a rapid decay of the reduced dye, $RB^{\cdot 3-}$ takes place. This process occurs due to the reduction of MV^{2+} to $MV^{\cdot +}$.[69]

$$RB^{\cdot 3-} + MV^{2+} \longrightarrow RB^{2-} + MV^{\cdot +}$$

The photosensitized reduction of bipyridinium compounds by xanthene dyes in the presence of SiO_2 colloid was also carried out in basic aqueous media (pH > 9).

For the hydrogen evolution at this pH, the radical cation $MV^{\cdot +}$ cannot be used because it does not have a suitable reduction potential. For this purpose, benzylviologen (1,1'-dibenzyl-3,3'-dimethyl-4,4'-bipyridinium dibromide, BMV^{2+}) was applied. Bulky substituents at 3,3' positions are a steric hindrance for the planar conformation, therefore, the reduction of BMV^{2+} is more difficult than that of MV^{2+}.[69]



BMV^{2+}

Since Rose Bengal in its reduced form is not able to reduce BMV^{2+}, RB^{2-} was replaced by eosin, EO^{2-}. EO^{2-} forms a ground-state complex with BMV^{2+}.

$$EO^{2-} + BMV^{2+} \rightleftharpoons [EO^{2-} \ldots BMV^{2+}]$$

The complex is separated by the SiO_2 particles through electrostatic association of BMV^{2+} to the colloid interface and repulsion of EO^{2-}. When the $EO^{2-}/BMV^{2+}/TEOA$ system is illuminated, the radical cation $BMV^{\cdot +}$ is formed in the following way.

$$EO^{2-} + TEOA \longrightarrow EO^{\cdot 3-} + TEOA^{\cdot +}$$

$$EO^{\cdot 3-} + BMV^{2+} \longrightarrow EO^{2-} + BMV^{\cdot +}$$

Illumination of an aqueous SiO_2 colloid containing EO^{2-}, BMV^{2+} and TEOA in the presence of Pd^{2+} ions results in hydrogen evolution. This observation is explained by the fact that $BMV^{\cdot +}$, formed upon the photosensitized electron-transfer process, reduces Pd^{2+} to Pd^{o}.[69]

$$2BMV^{\cdot +} + Pd^{2+} \longrightarrow 2BMV^{2+} + Pd^{o}$$

The SiO_2 colloid affects the separation of the ground-state eosin-viologen complex and therefore the recombination of the photogenerated products is retarded. Due to the stabilization of the photoproducts against back electron transfer, $BMV^{\cdot +}$ is formed which mediates hydrogen evolution in the presence of the Pd catalyst.[68]

$$2BMV^{\cdot +} + 2H^{+} \xrightarrow{Pd^{o}} 2BMV^{2+} + H_2$$

It was established that the SiO_2-Pd system including EO^{2-}, BMV^{2+} and TEOA can also be used in the hydrogenation of ethylene.[69]

It may be concluded that xanthene dyes form the ground-state dye-bipyridinium complexes. Therefore, they cannot be used for the photoreduction of bipyridinium electron acceptors. However, in the presence of SiO_2 colloid particles, the resulting microheterogeneous system is able to separate the ground-state dye-bipyridinium complex by means of the electrostatic interactions. In this process, the positively charged component of the complex is attracted to the colloid interface. Due to the stabilization of photoproducts against back-electron transfer, the effective reduction of the bipyridinium acceptor is possible.[69,70]

Study of the influence of pH and oxalate anion as counterion on photoreduction of MV^{2+} revealed an increased formation of radical cation $MV^{\cdot +}$ at higher pH. It was found that the pH dependence of the formation of $MV^{\cdot +}$ results from the influence of pH on the concentration of the $MV^{2+} - C_2O_4^{\ 2-}$ complex.[71-75]

In the investigations of zeolite supercages, the shape-selective formation of CT complexes of various arenes with MV^{2+} and diquat (DQ^{2+}), used as electron acceptors directly in zeolite, was examined.[76] The MV^{2+} and DQ^{2+} cations are readily incorporated into zeolite Y by ion exchange of Na^{+}. When these acceptor-doped colorless powders are exposed to dichloromethane solution of aromatic hydrocarbons serving as electron donors, intensive coloration occurs immediately. In these processes the steric reasons, i.e. the shape of electron donors and electron acceptors play an important role. For example, xylenes as well as mesitylene, durene and pentamethylbenzene give colored CT complexes with MV^{2+} and DQ^{2+} doped zeolite Y, while hexamethylbenzene does not despite its high electron donor strength. Similarly 1-methyl- and 1,4-dimethylnaphthalenes as well as 9-methylanthracene form CT complexes, but 1,4-dimethoxynaphthacene and 9-phenylanthracene do not.

The size of electron acceptors is also important. For example, tetracene gives complexes with DQ^{2+} doped zeolite Y, while no complex formation takes place in the case of MV^{2+}.[76] Similar shape selectivity occurs with zeolite X of the dimensions related to zeolite Y, but not with zeolite A.[76]

Here the photoeffects in thin films in the presence of MV^{2+} as an oxidative quencher and TEOA as a reductive scavenger should also be mentioned. Thin polymeric films of chlorosulfonated polystyrene bearing light absorbers were prepared. The used light absorbers contained a primary amino group and were chemically bonded in precast chlorosulfonated polystyrene films by sulfonamide bond.

Examples of light absorbers are the following : $[Ru(bpy)(5\text{-}NH_2phen)_2]^{2+}$, $[(5\text{-}NH_2phen)Re(CO)_3(py)]^{+}$, 9-aminoacridine, acridine yellow G, azure A, o-aminotetraphenylporphine and Zn(o-aminotetraphenyl)porphine.[77] (bpy is 2,2'-bipyridine; phen is 1,10-phenanthroline).

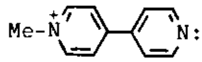
It was observed that visible photolysis of films in the presence of MV^{2+} and TEOA results in a photocurrent response. For a series of light absorbers, photolysis in the presence of MV^{2+} and TEOA gives rise to oxidative photocurrents which may be sustained without degradation for several minutes to hours. The highest photocurrents (several amperes) are obtained in the case of films containing porphines.

In these processes, especially at high concentrations of TEOA, direct excitation of the donor-acceptor complex of MV^{2+} and TEOA occurs.[77]

$$MV^{2+}.TEOA \xrightarrow{h\nu} MV^{+}.TEOA^{+}$$

The photocurrents result by irreversible decomposition of $TEOA^{+}$ and the subsequent oxidative capture of MV^{+} at the electrode.[77-81]

Electronic spectra of methylviologen radical cation $MV^{\cdot +}$,[82-83] the resonance Raman spectra of $MV^{\cdot +}$ and fully-reduced methylviologen MV^{0},[84-87] as well as the Raman and SERS spectra of 1-methyl-4,4'-bipyridinium (monoquat)[88] have been investigated.

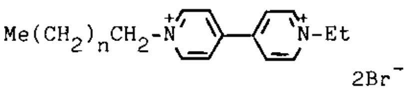


monoquat (MQ^{+})

Enhancement of Raman and resonance Raman (RR) scattering from MV^{2+} and its reduction products at polished and roughened silver electrodes was also examined. The spectrum of $MV^{\cdot +}$ on polished silver electrode (spectrum A) is similar to that of $MV^{\cdot +}$ in solution, while the spectrum observed on roughened silver electrode (spectrum B) is different.[82]

The results show the existence of two different absorption interactions between the reduction products of MV^{2+} and the silver surface, leading to the different enhancement mechanisms in the SERS effect.[89,90] The difference between spectra A and B may be explained by the formation of a complex involving methylviologen, the counterion, and a silver ion or a silver atom cluster on the silver electrode during the roughening process.[91] There was found that the SERS/SERRS spectra of type A appear when viologen is added after the anodization procedure, while those of the type B appear when viologen is present during the anodization and that spectra A and B result from the electromagnetic and chemical enhancement, respectively.[82,84,92]

While describing inclusion complexes of viologens with cyclodextrins serving as hosts,[93] it should be noted that salts (19) may be used as electroactive probes to assess interactions between surfactants and α- and β-cyclodextrins.

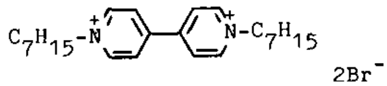


19

n = 14,16

Using cyclic voltammetry, formation of inclusion complexes in which hydrophobic tails of surfactant viologens penetrate the cyclodextrin cavity was demonstrated. In the presence of α-cyclodextrin dimerization of viologen radical cations is considerably suppressed, while in the case of β-cyclodextrin no effect is observed.[94] A stable inclusion complex of methylviologen radical cation $MV^{\cdot+}$ with β-cyclodextrin was prepared and its electronic absorption spectra, esr and induced circular dichroism spectra were discussed.[95]

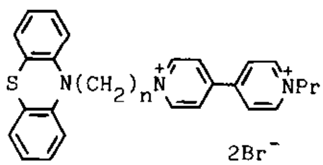
From induced circular dichroism spectrum of the complex of heptylviologen (20) with α-cyclodextrin, its rotational strength was calculated by using Kirkwood-Tinoco expression.[96]



20

Comparison of the calculated and experimental values of the rotational strength indicates that the alkyl chain of heptylviologen is situated within the cavity of cyclodextrin, while the bipyridinium moiety is localized out of the cavity.[96-98]

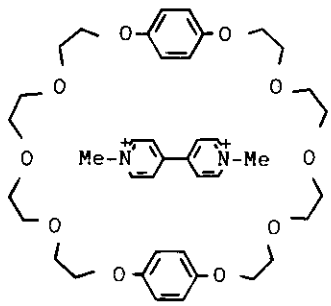
For the complexes of phenothiazine-linked viologens 21 with α- and β-cyclodextrins, the external magnetic-field effects on the photoinduced electron-transfer reactions were examined.[62]



21

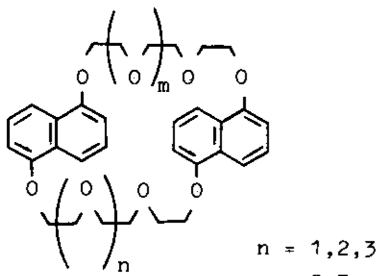
n = 4,12

There exist inclusion complexes where viologen is a guest and a macrocycle serves as a host, an example is a 1 : 1 inclusion complex (22), existing in solution and in the solid state.[99-102]

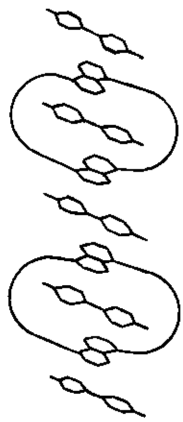


22

Solution studies indicate that MV^{2+} forms a 1 : 1 inclusion complex with macrocycle (23), but a single-crystal X-ray examination has shown a continuously stacked Π-donor / Π-acceptor structure (24) with viologen : 23 stoichiometry 2 : 1 Here two viologen dications are alternately included inside (23) and sandwiched between adjacent molecules of 23.[103-105]



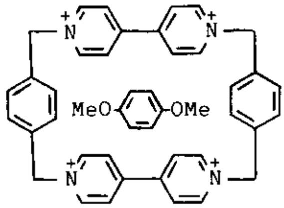
23



24

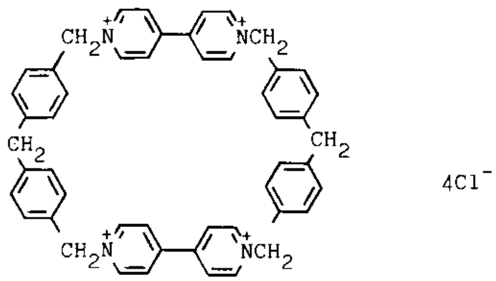
(schematic representation)

The complexes where the roles are reversed, i.e. cyclic systems incorporating viologen units serve as cationic host molecules [101] are also known. An example 25 of the inclusion complexes is demonstrated here.[102]



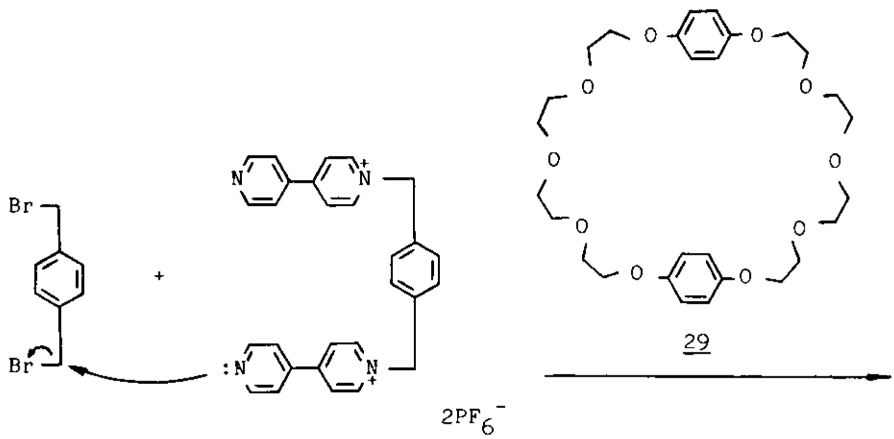
25

Another example of macrocyclic compound (26) containing viologen units which serves as a cationic host is able to form inclusion complexes with some arenes.[106]

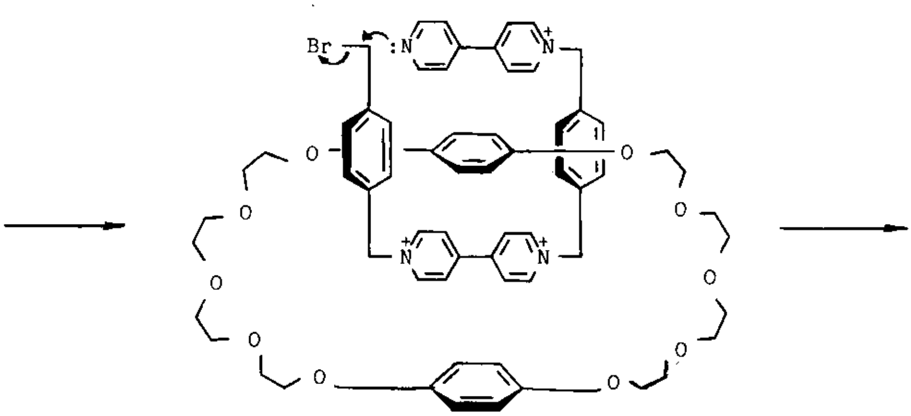


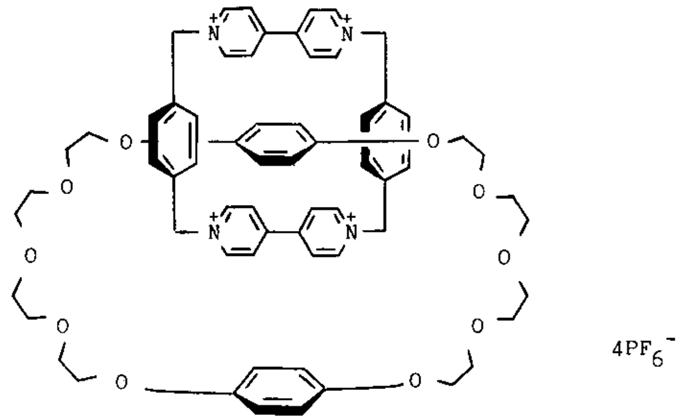
26

There was obtained an interesting catenane (27); its synthesis involved the reaction of the salt (28) with p-bis(bromomethyl)benzene and bisparaphenylene-34-crown-10 (29).



28





27

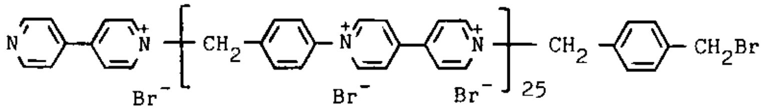
The result was confirmed by positive ion FAB-MS and by X-ray crystallographic analysis.[102]

Examination of the packing of the anions, tetracations and MeCN used as solvent has shown the existence of continuously-stacked catenane units, similar to that of 24. This result may be of use in the design of highly-ordered electron donor-acceptor polymer chains. In should be pointed out that the ordered arrangement of the catenane (27) is retained also in solution.[102]

V. POLYMERIC VIOLOGENS

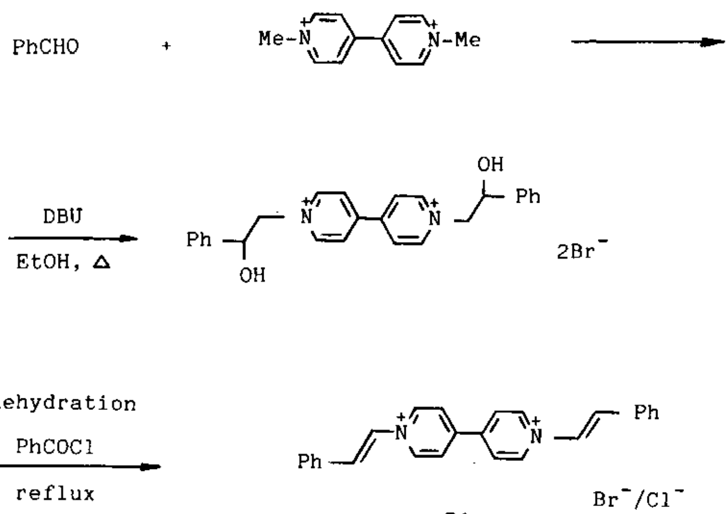
Polymeric viologens can be divided into two groups : (1) polymers where the viologen is incorporated into the chain as an interconnecting member, and (2) polymers bearing pendant viologen moieties.

To the first group belongs 30, a redox polyelectrolyte. Polarographic reduction of 30 in the presence of $CdSO_4$ showed that reduction of the protonated from is accompanied by complexation with Cd^{2+}.[107]



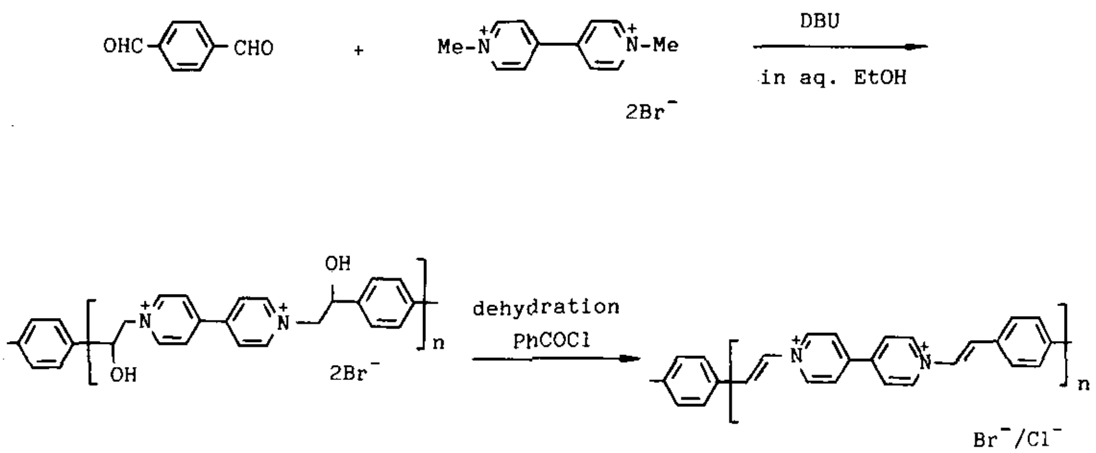
30

The following reaction leading to styryl viologen (31), possesing an extended Π-system was performed as a model process for the synthesis of 32 which is a conductive Π-conjugated polymeric viologen.[108,109]



31

Polymer (32) was obtained in an analogous way.[108]

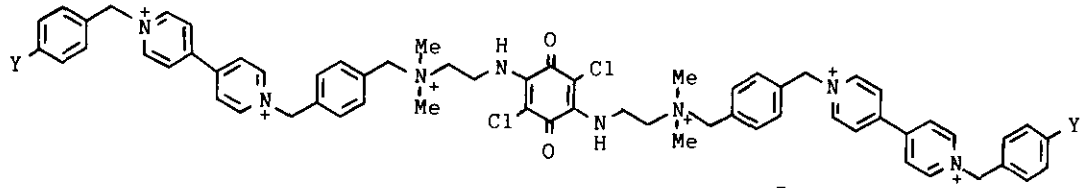


32

It was observed that the charge associated with the reduction of quinone

$$Q + 2e^- + 2H^+ \longrightarrow QH_2$$

can be trapped at low pH in the electrode-confined siloxane polymer, containing benzoquinone unit flanked by two benzylviologen moieties, derived from base hydrolysis of the pendant trimethoxysilyl units on 33.[110,111]

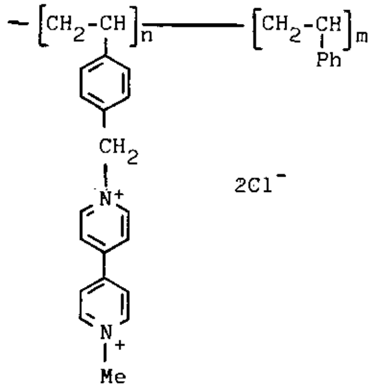


Y = $Si(OMe)_3$ $4Cl^-$

33

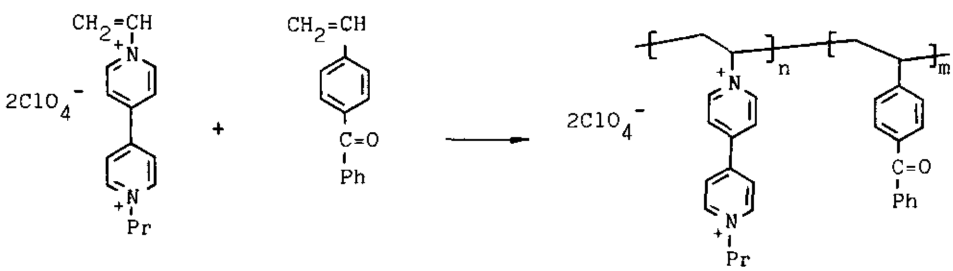
Electrons can be released from the polymer by raising the solution pH to neutral or basic, where the viologen can reoxidize the QH_2 to Q, delivering the charge to the electrode.[112] It was observed that redox reagents, such as I_3^-/I^- and $Fe(CN)_6^{3-/4-}$, are charge-release mediators capable of releasing the charge and delivering it to the electrode at acidic pH. In order to achieve the charge release, i.e. to oxidize QH_2 which will return charge to the electrode, the reduced form of a reversible redox couple, for instance I^-, is added.[113,114]

The $Fe(CN)_6^{3-/4-}$ redox couple can also catalyze the oxidation of QH_2. In this case, $Fe(CN)_6^{3-/4-}$, like other large multicharged inorganic anions, is concentrated by the polycationic $(BV\text{-}Q\text{-}BV^{6+})_n$ polymer. It should to be noted that only very low solution concentrations (ca 1 μM) are necessary to mediate the oxidation of QH_2.[113,114] The system (34) belongs to polymers with pendant viologen units.[115]



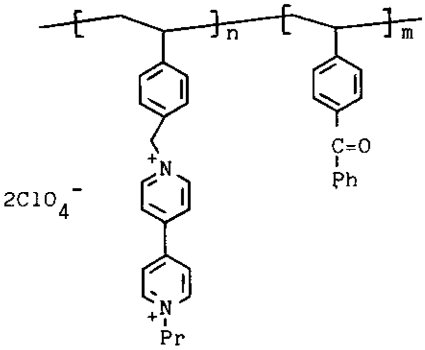
34

Another example is the polymer (35) obtained by the radical copolymerization of 1-propyl-1'-vinyl-4,4'-bipyridinium diperchlorate (36) and vinylbenzophenone (37).[116]

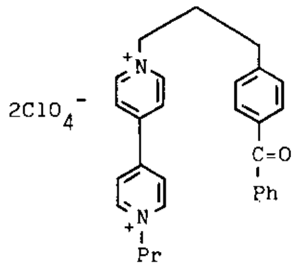


36 37 35

Copolymer (38), bearing a benzyl group as a spacer between a polymer main chain and viologen moiety was prepared by copolymerization of 1-propyl-1-vinylbenzyl-4,4'-bipyridinium diperchlorate and 37. Also, 39 was synthesized as a model compound.[116]



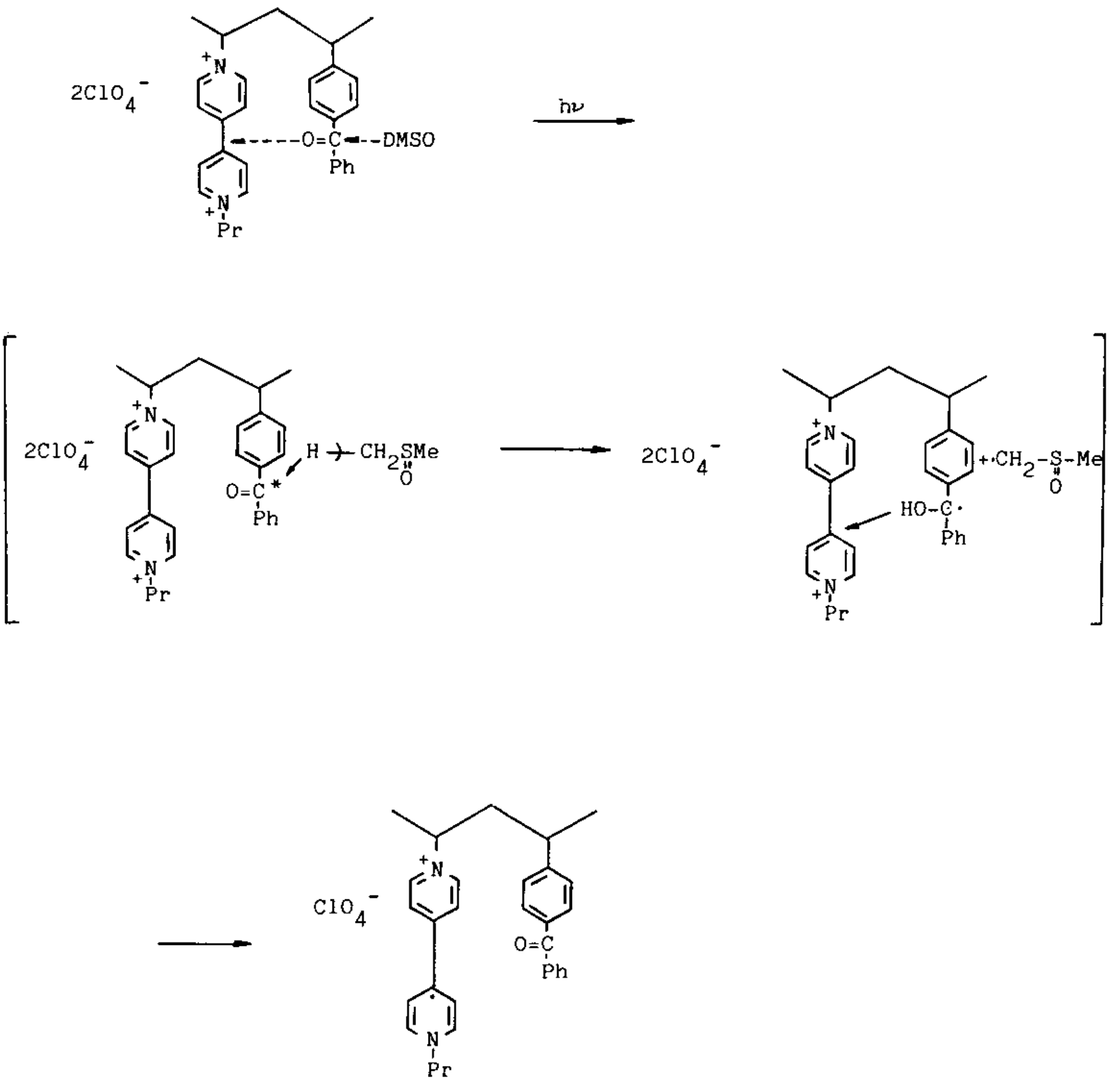
38



39

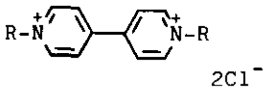
A rather unusual photoreduction of viologen by DMSO proceeds on copolymer (35) in an aprotic medium. The electronic spectra show that, in 35, the CT complexation assisted by the solvent occurs between the viologen and benzophenone structures. Similar behaviour was observed in the copolymer of 36 and methyl methacrylate.[117] It was found that the conversion of V^{2+} to $V^{\cdot +}$ by photoirradiation decreases in the order : 35 > 39 > 38. This observation is associated with the fact that in 35 and 39 the viologen and benzophenone moieties are bonded by C_3 linkage, therefore they can stack each other (more efficiently in the case of 35) and show the solvent-assisted CT interaction. Benzophenone activated by this interaction abstracts hydrogen from DMSO to form ketyl radical, which subsequently reduces the viologen to give radical cation.[118]

The investigated photoreduction of 35 is of interest in photochromic materials designing.[118]



VI. VIOLOGENS OF BIOLOGICAL INTEREST

Methylviologen, (paraquat, PQ), which is an effective herbicide and pesticide is the topic of a number of publications.[119-122] The homologues of PQ, e.g. 40 as well as diquat (DQ) also possess herbicidal activity.[123]



40 $R = C_{1-5}$

Much research deals with the poisonous properties of PQ. The absorption of PQ through the intact human skin is rather low but it is considerably enhanced in the case of the damaged skin.[124]

Study of acute PQ poisoning has shown that the induced circulatory failure is due to the irreversible decrease of systemic vascular resistance.[125]

Investigations of behavioral and electrocortical changes induced by PQ after injection in specific areas of the rat brain showed that paraquat produces central neurotoxicological effects which presumably are not specific for the dopamine nigrostriatal system.[126] From studies of canine lungs exposed on the PQ (i.v. administration during the proliferative phase of PQ toxicity) it was established that the detachment of alveolar epithelial cells and alveolar macrophage play an important role in PQ-induced pulmonary fibrosis. [127] Examination of the damage of lungs by PQ indicated that pretreatment with vitamin E has no protective influence on lung function.[128]

For the investigation of PQ-induced pulmonary fibrosis, a model in which doses of PQ are instilled into the right lung of rats was shown to be useful. In this model, graded degrees of lung injury and fibrosis may be produced by varying the PQ dose.[129]

The diquat toxicity to lungs was also examined.[130,131] The degeneration changes in rat lungs resulting from intratracheal administration are similar to those caused by paraquat. However, a much larger dose of DQ is needed as compared to PQ. It was observed that the initial alveolar damage induced by DQ is followed by lung fibrosis, as in the case of paraquat.[130]

A microcomputer-interfaced monitoring system which can be installed on a Benoit-type serial diluter should be mentioned here. The system is useful for monitoring flow rates of test solutions and for measurements of a number of water quality parameters. It provides an information on the progress of the test.[132]

In the study of the clastogenicity of paraquat in cultured Chinese hamster cells, it was found that the induction of chromosomal aberrations by PQ is enhanced by diethyl maleate (a glutathione scavenger) and by diethyl dithiocarbonate (an inhibitor of superoxide dismutase). However, no such effect was observed in the case of 3-aminotriazole, an inhibitor of catalase. It was shown that the induction of chromosomal aberrations by PQ may be related to the generation of O_2^-,rather than to the formation of H_2O_2 by the dismutation reaction of O_2^- or of hydroxyl radical and singlet oxygen.[133]

With the use of paraquat, the ability of radical-driven Fenton reactions to oxidize formate or deoxyribose was investigated. The process was catalyzed by citrate, ATP and ADP iron chelates. It was shown that Fe^{2+} ions available physiologically may take part in the Fenton reaction in a nonchelated form and produce a ferryl species rather than hydroxyl radical. It should be pointed out that equivalent reactions of superoxide are catalyzed by the same iron chelates only to a very small extent. Thus it may be suggested that Fenton reactions driven by organic reducing radicals contribute more to the toxicity of redox cycling compounds than reactions of superoxide.[134]

Examination of effects of PQ in Escherichia coli revealed a complete correlation of the damage of the cytoplasmic membrane with the levels of adventitious Cu or Fe. Exposure of bacterial cells to a combination of PQ and Cu causes a considerable decrease of levels of cellular ATP and K, and of the cellular capacity to accumulate radiolabeled leucine. However, no such effects in the cellular structure are found in the case of PQ alone or Cu alone. These observations are consistent with the metal-mediated Haber-Weiss mechanism of the PQ toxicity.[135]

A new simple method of the direct extraction of PQ from plasma or serum without deproteinization utilizes Sep Pak C_{18} cartridges. Its simplicity is associated with the fact that the extraction does not require a saturated curve and gives a complete recovery.[136]

For the analysis of PQ and DQ, a useful method appears to be the FAB/MS combined with tandem MS/MS.[137]

It was observed that the adsorption rate of PQ in vitro by cation exchange resins is influenced mainly by the degree of their crosslinkage.[138]

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