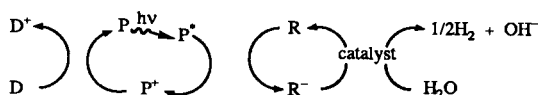


Lindsay A. Summers

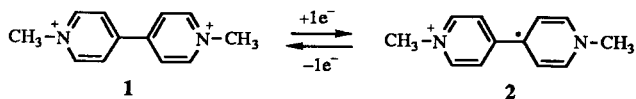
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I. Introduction.

For the past twelve years or so there has been considerable interest in model systems for the production of hydrogen by the photoreduction of water. One of the systems most actively studied is an electron transfer sequence containing four components: a sacrificial electron donor D, a photosensitizer P, an electron relay R and a catalyst [1-4]. Typically in this system a photosensitizer P is illuminated



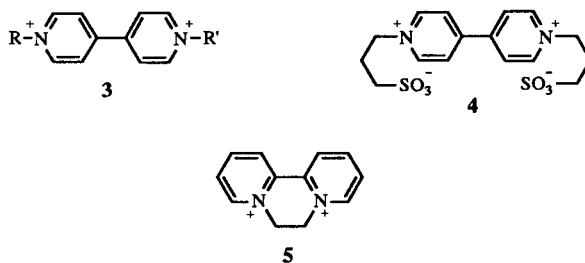
with light and converted to its excited state P*. An electron is passed from the excited state of the photosensitizer by quenching to a suitable electron relay R converting the electron relay to its one electron reduced form R-. In the process the photosensitizer is oxidized to P+. The oxidized photosensitizer P+ is reduced back to its original state P by a sacrificial electron donor D. In the presence of a suitable catalyst the reduced form of the electron relay R- is able to reduce water to hydrogen ($\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^-$) and is itself in the process oxidized back to R. The overall process thus involves reduction of water to hydrogen at the expense of a sacrificial electron donor. The electron donor is frequently ethylenediaminetetraacetic acid (EDTA) or 2-mercaptoethanol, the photosensitizers are often ruthenium complexes such as $\text{Ru}(\text{bpy})_3^{2+}$, where bpy stands for 2,2'-bipyridine, or zinc porphyrins while the catalyst is usually a form of platinum or a hydrogenase. The electron relay is usually methyl viologen (MV^{2+}) (**1**) or one of its



derivatives. Methyl viologen is named as 1,1'-dimethyl-4,4'-bipyridinium dichloride and is the widely used herbicide paraquat. Methyl viologen has long been known to be reversibly reduced in aqueous solution by a one electron transfer at a potential (E_o) of -0.45 V to the violet stable radical cation (MV^+) (**2**). While methyl viologen was the electron relay used in many of the early experiments on the photoreduction of water in the past decade several relatives of it have been studied as electron relays or mediators.

Continuing our longstanding interest in the chemistry and uses of bipyridinium salts [5,6] the purpose of this article is to review diquaternary salts of 4,4'-bipyridine (*i.e.* analogues of methyl viologen) which have been investigated as potential electron relays for the photolysis of water. The review provides coverage of work reported to mid-1990. Because of the diversity of journals in which work on this topic is published comprehensiveness is not claimed.

The review is divided into the following sections: diquaternary salts of 4,4'-bipyridine (**3**, $\text{R} = \text{R}'$) and (**3**; $\text{R} \neq \text{R}'$), diquaternary salts of 4,4'-bipyridine containing ring substituents, zwitterion diquaternary salts of 4,4'-bipyridine (*e.g.* **4**), diquaternary salts of 2,2'-bipyridine (*i.e.* the herbicide diquat **5** and its derivatives), viologens linked to porphyrins, viologen polymers and pendant viologens on polymers, and miscellaneous viologens.

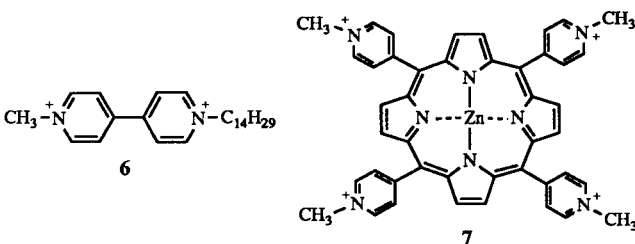
II. Diquaternary Salts of 4,4'-Bipyridine (**3**, $\text{R} = \text{R}'$) and (**3**, $\text{R} \neq \text{R}'$).

Several papers have reported results which confirm that simple higher alkyl analogues of methyl viologen (*e.g.* **3**, $\text{R} = \text{R}' = \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{CH}(\text{CH}_3)_2, \text{C}_4\text{H}_9, \text{C}_7\text{C}_{15}, (\text{CH}_2)_2\text{OH}$, benzyl) also quench the excited state of $\text{Ru}(\text{bpy})_3^{2+}$ [7,8] and metal porphyrin sensitizers [9,10] in homogeneous aqueous systems and if a catalyst is present hydrogen is produced although there is no evidence to suggest that these higher homologues are more effective than methyl viologen itself in producing hydrogen [1, 10-13]. Sometimes unwanted complex formation between viologen and sensitizer has been observed when the sensitizer is an anionic one such as a metal *meso*-tetraphenylporphyrintrisulfonate [10,14]. Hydrogen production rates are best when the viologen has a reduction potential (E_o) of about -0.45 V which is close to the value for methyl viologen [1,15] and when experiments are conducted near pH 5.0 [15]. Other photosensitizers have also been investigated

[8,16-19]. Two reports claim no ruthenium or porphyrin photosensitizer is required [11,20].

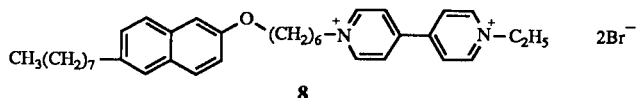
One of the most important problems in the four component system for the photoreduction of water is the rate of the back electron transfer from the reduced relay R^- to the oxidized photosensitizer P^+ resulting in regeneration of the original compounds R and P . Unfortunately this back reaction is fast when, for example, the reduced relay is the methyl viologen radical cation (**2**) and the oxidized photosensitizer is $Ru(bpy)_3^{3+}$. This problem curtails considerably the efficiency of the overall electron transfer process for the photoreduction of water. Much effort has gone in to trying to overcome this difficulty.

One approach to retarding the rate of the back electron transfer has been to use surfactant diquaternary salts of 4,4'-bipyridine containing a long alkyl quaternizing group such as the 1-methyl-1'-tetradecyl-4,4'-bipyridinium cation ($C_{14}MV^{2+}$) (**6**) as electron relay in the presence of cationic micelles such as cetyltrimethylammonium chloride (CTAC). The forward electron transfer from the sensitizer



$Ru(bpy)_3^{2+}$ to relay occurs in the aqueous phase. The back electron transfer, however, is considerably retarded. This is attributed to rapid solubilization of the reduced form of $C_{14}MV^{2+}$, that is the radical cation $C_{14}MV^+$, into the micelles due to its increased hydrophobicity and subsequent electrostatic repulsion between the cationic assemblies and the oxidized form of the photosensitizer $Ru(bpy)_3^{2+}$, namely $Ru(bpy)_3^{3+}$ [21]. Similar results were achieved with a number of other surfactant diquaternary salts of 4,4'-bipyridine (**3**, $R = CH_3$, $R' = C_{12}H_{25}$, $C_{16}H_{33}$ or $C_{18}H_{37}$) using the cationic zinc porphyrin photosensitizer **7** ($ZnTMPyP^{4+}$) as well as $Ru(bpy)_3^{2+}$. Cationic micelles such as octadecyltrimethylammonium chloride and dodecyltrimethylammonium chloride can replace CTAC [22]. The back electron transfer rate constant can in favorable cases be decreased 500-1000 fold. The stabilization and yield of redox products are optimal in a system containing $ZnTMPyP^{4+}$ as sensitizer, $C_{14}MV^{2+}$ as relay and CTAC micelles [22]. In the presence of platinum catalyst and a sacrificial electron donor, EDTA or nicotinamides, hydrogen is produced on illumination of the system [23]. These aspects have been reviewed [24-27] and extended to include the use of the hydrophobic sensitizer zinc tetraphenylporphyrin ($ZnTPP$) solubilized in the redox surfac-

tant [28,29] and an amphipathic sensitizer $Ru[N,N'$ -di(dodecyl)-2,2'-bipyridine-4,4'-dicarboxamide-bis(2,2'-bipyridine)] $^{2+}$ [30,31]. The surfactant and micellar properties of long-chain viologens have been the subject of further study [32-38] and improved platinum catalysts for use in these systems have been developed [39]. Of interest is a study of amphipathic viologens with long alkyl chains with a naphthyloxy group such as **8**. Viologens of this type form micelles and show charge transfer absorptions between the naphthyloxy group as donor and the viologen group as acceptor. In this case the charge transfer complexes were shown to be of value in assisting electron transfer between the viologen and amphipathic metal complex sensitizers in molecular assemblies [40].

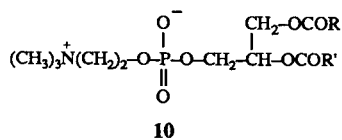
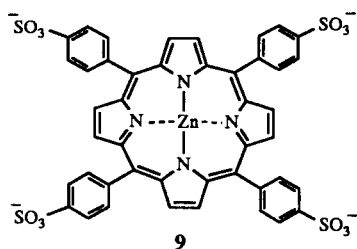


As well as cationic micelles, cationic vesicles have been used to induce charge separation and electron storage effects. Vesicles have the advantage over conventional micelles in that they are formed at much lower surfactant concentrations. Moreover, they provide compartmented systems of inner and outer phases allowing for the local separation of processes involved in the photoreduction of water. Typical cationic vesicles or bilayer membranes can be formed from dioctadecyldimethylammonium chloride (DODAC) which forms spherical aggregates. Using $C_{14}MV^{2+}$ as relay and $Ru(bpy)_3^{2+}$ or $ZnTMPyP^{4+}$ as sensitizer, the reduced form of $C_{14}MV^{2+}$, that is $C_{14}MV^+$, is readily entrapped in the DODAC aggregates. Retardation of the back reaction is achieved being at least fifty times slower than in the vesicle free solution. When EDTA and a platinum catalyst were added and the heterogeneous mixture illuminated hydrogen was generated although at a slower rate than for the homogeneous system using methyl viologen [41]. Further study of alkylmethyl viologens in DODAC aggregates has been reported [42]. In earlier reports the viologen (**3**; $R = C_2H_5$, $R' = C_{16}H_{33}$) was incorporated into the bilayer membrane of didodecyldimethylammonium bromide along with the amphipathic ruthenium sensitizer $Ru[N,N'$ -di-(dodecyl)-2,2'-bipyridine-4,4'-dicarboxamide-bis-(2,2'-bipyridine)] $^{2+}$. It was shown that in some circumstances the photochemical behaviour of the system would allow the electron to migrate sufficiently from the sensitizer so that the reverse electron transfer could not easily take place [43,44].

Anionic micelles and vesicles have also been investigated. In the presence of sodium dodecylsulfate (SDS) micelles, the rate of quenching of excited $Ru(phen)_3^{2+}$ sensitizers, where phen stands for 1,10-phenanthroline, decreased as the alkyl chain length increased with the viologens (**3**, $R = R' = C_2H_5$, C_3H_7 , C_4H_9 , iso- C_4H_9 ,

C_6H_{13}) and (**3**, $R = CH_3$, $R' = C_6H_{13}$) due to the alkyl chain being buried in the interior of the micelle [41,45]. Further studies with ruthenium [46] and anionic palladium porphyrin [27] sensitizers and viologens in SDS micelles have been reported. Quenching of excited $Ru(bpy)_3^{2+}$ by the viologen (**3**, $R = C_2H_5$, $R' = C_{16}H_{33}$) in ethylene glycol-water mixtures in the presence of SDS micelles has also been reported [47] at room and low temperatures and an electron spin resonance study of charge separation in frozen SDS micellar solutions containing $Ru(bpy)_3^{2+}$ and various alkyl methyl viologens has been described [48].

Some interest has also been shown in anionic vesicles from dihexadecyl phosphate (DHP). Photoexcited $ZnTMPyP^{4+}$ adsorbed onto DHP vesicles is quenched by alkylmethyl viologens (**3**, $R = CH_3$, $R' = C_{14}H_{29}$ or $C_{16}H_{33}$) which were also DHP bound. When amine donors are present in the solution cyclic photosensitized redox transfer occurs with the net formation of viologen radical cations. When an oxidant, such as $Fe(CN)_6^{3-}$ is incorporated within the vesicle inner aqueous phase accumulation of reduced viologen is retarded suggesting that the viologens are capable of acting as transmembrane charge relays [49]. If an anionic sensitizer is used such as $ZnTPPS^{4-}$ (**9**), negligible photoredox chemistry occurs with alkylmethyl viologens C_nMV^{2+} because the sensitizer and viologen are nearly completely ion-paired. However, in the presence of DHP vesicles the alkylmethyl viologens bind preferentially to DHP vesicles whose negative charge provides electrostatic repulsive forces sufficient to prevent $ZnTPPS^{4-}$ association. Consequently formation of discrete photoproducts, $ZnTPPS^{3-}$ and C_nMV^+ becomes possible. Because C_nMV^+ remains bound to DHP, from which $ZnTPPS^{3-}$ is also repelled the back reaction is effectively retarded [50]. The binding environment of long chain viologens in DHP vesicles has been the subject of chemical studies [51,52] and related electron spin resonance investigations have been reported [42].



There has been considerable interest in the use of zwitterionic phospholipid vesicles such as phosphatidylcholine derivatives **10** which afford bilayer membranes. In a basic study with this type of system an amphiphilic ruthenium complex, $Ru[N,N'$ -di-(dodecyl)-2,2'-bipyridine-4,4'-dicarboxamide-bis(2,2'-bipyridine)] $^{2+}$ as sensitizer was incorporated in the membrane wall. An electron donor EDTA was entrapped in the inner aqueous compartment of the vesicle and heptyl viologen (**3**, $R = R' = C_7H_{15}$) (HV^{2+}) as electron acceptor was introduced into the outer aqueous phase. On illumination an electron transfer process across the vesicle wall was initiated and reduced HV^+ was produced. The excited sensitizer transfers an electron to HV^{2+} in the primary event. The oxidized sensitizer Ru^{3+} thus produced oxidizes a Ru^{2+} species to Ru^{3+} located at the inner surface of the vesicle and thereby separation of the intermediate photoproducts is assisted. The further oxidation of EDTA regenerates the sensitizer and consequently the separation of the reduced species HV^+ from the oxidized product is achieved. However the quantum yield for the reaction is very low. The transmembrane electron transfer was found to be the rate limiting factor for the overall reaction and the origin of the low efficiency. Incorporation of cation carriers into the vesicle system can improve the efficiency somewhat [53-56]. Early studies [57] and further developments with this type of system have been reported [58]. In another variation, the inner compartment contained the water soluble sensitizer $Ru(bpy)_3^{2+}$ and EDTA, a water insoluble viologen relay (**3**, $R = R' = C_{10}H_{21}$, $C_{14}H_{29}$ or $C_{18}H_{37}$) was embedded in the lipid membrane and the outer solution contained $Fe(CN)_6^{3-}$. On illumination electron transfer from excited $Ru(bpy)_3^{2+}$ to $Fe(CN)_6^{3-}$ was achieved [59,60] with quantum yields greater than for systems where a photoactive sensitizer is incorporated in the membrane rather than in the inner compartment. Further developments have been reported [61-64]. While bilayer membranes are good model systems charge separation of the primary redox pair is difficult to achieve with high efficiency in the viscous environments of these systems [31,44]. In other related publications alkyl viologens (e.g. **3**, $R = R' = CH_3$, C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_{13} , C_7H_{15} , C_8H_{17} , $C_{10}H_{21}$, benzyl) and (**3**, $R = CH_3$, $R' = C_{14}H_{29}$) were found to quench the excited state of chlorophyll a incorporated in the phospholipid vesicles. They are more effective as quenchers as they become less water soluble since they are more likely to be incorporated in the membrane. However, the efficiency of radical cation formation then decreases and the rate of reverse electron transfer increases. For the chlorophyll a and viologen radical cations to separate efficiently the viologen radical has to be able to diffuse from the membrane to the water phase at a rate that competes effectively with the reverse electron transfer [65]. The exit rate constant from the vesicles decreases as the chain length increases [66]. In

other studies electron transfer kinetics with the viologens (**3**, R = R' = CH₃, C₃H₇, C₁₂H₂₅, C₁₄H₂₉, C₁₆H₃₃, C₁₈H₃₇ and (CH₃)₃N⁺.CH₂.CH₂.CH₂) in various phospholipid membranes and with Ru(bpy)₃²⁺ as sensitizer have been reported [67] and an electron spin resonance study of the photoionization yields of various alkylmethyl viologens in phospholipid vesicles has been described [42].

Some work has been reported involving solvents other than water. Microemulsions (water-in-oil and oil-in-water) in particular have been studied. These offer hydrophilic-hydrophobic two phase systems. Following on from earlier work using (**3**, R = R' = C₁₆H₃₃) [68] it has been shown that in a water-in-oil (toluene) system in the presence of surfactant using Ru(bpy)₃²⁺ as sensitizer, an ammonium salt of EDTA as electron donor and the electron relays (**3**, R = R' = CH₃, C₄H₉, C₆H₁₃, C₈H₁₇, C₁₄H₂₉, C₁₈H₃₇) the photoproducts C_nV^{•+} and Ru(bpy)₃³⁺ were stabilized against recombination when the alkyl groups were hexyl or higher. This was attributed to the function of the oil-water interface in extraction of the amphiphilic photoproducts C_nV^{•+} [69]. Other work on similar microemulsions has been reported [70,71]. In a two phase system using water and cyclohexane, hydrogen has been generated by irradiation of the aqueous phase incorporating EDTA, Ru(bpy)₃²⁺ and octyl viologen (**3**, R = R' = C₈H₁₇) and used to hydrogenate acetylenes dissolved in the organic phase which also contained the platinum or palladium catalyst [72]. In a three phase liquid system an ethylene dichloride organic phase was placed between two aqueous phases. ZnTPPS⁴⁻, cetyltrimethylammonium bromide, the viologen (**3**, R = R' = C₆H₁₃) and an electron donor such as Na₂S₂O₃ were placed in the first aqueous phase. In the second aqueous phase an electron acceptor such as flavin mononucleotide was present. On illumination of the first aqueous phase an electron was transported across the organic phase and reduced FMNH was formed [73].

Reverse micelles have also been studied. For example, water can be readily dispersed in an organic medium such as isooctane using Aerosol OT (sodium 2-ethylhexylsulfosuccinate) as dispersant. AOT possesses a hydrophilic head which in the presence of water leads to the formation of aggregates of colloid dimensions in non-polar solvents. They constitute reverse micelles. Using the water insoluble sensitizer magnesium tetraphenylporphyrin it has been confirmed that photoelectron transfer occurs across the interface with viologens including heptyl viologen (**3**, R = R' = C₇H₁₅) [74]. Other work on reverse micelles has been reported [46]. A good review of the background to microemulsions, micelles and vesicles is available [75]. Further recent work in oil-in-water and water-in-oil micelles and microemulsions has been reported [76].

In a study in mixed organic-water solvents involving the viologens (**3**, R = R' = C₂H₅, C₄H₉, C₆H₁₃, C₇H₁₅, C₈H₁₇,

C₁₀H₂₁, C₁₂H₂₅, C₁₄H₂₉, C₁₆H₃₃, and C₁₈H₃₇) and using the water insoluble zinc *meso*-tetraphenylporphyrin as the sensitizer it was found that one of the best systems for light induced redox reactions involved dodecyl viologen stabilized by a cationic surfactant such as hexadecyltrimethylammonium chloride with 6% dimethyl formamide or dimethyl sulfoxide. If the organic solvent content rose above 20% reduction decreased dramatically. Some hydrogen bubbles were evolved on addition of EDTA and platinum catalyst [77].

Polyelectrolytes have also been used as media for quenching reactions [e.g. 78]. As a specific example the rate of quenching of Ru(phen)₃²⁺ by benzyl viologen (**3**, R = R' = benzyl) in polyvinylsulfate solution was enhanced compared with that in water. This is attributed to the sensitizer and the relay being concentrated into the anionic polymer domain due to electrostatic and/or hydrophobic interaction [79].

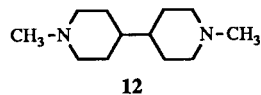
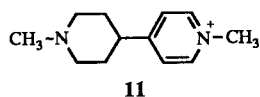
Miscellaneous items worthy of note include the following. Photoexcited carbazole covalently attached to anionic polymer latex particles such as sodium *p*-styrenesulfonate was quenched in aqueous solution with the viologens (**3**, R = R' = CH₃, C₂H₅, C₄H₉ and C₆H₁₃), the quenching being more efficient as the chain length increased due to the viologen entering the more hydrophobic region [80]. Quenching of excited Ru(bpy)₃²⁺ by viologens (**3**, R = R' = CH₃, C₂H₅, C₄H₉ and C₈H₁₇) in various environments including a polystyrenesulfonate polyelectrolyte and a polystyrene latex, not surprisingly, changed drastically depending on reaction environment [81]. Miscellaneous electron transfer quenchings by various viologens including quenching of rhodamine B in solid polymer films [82] and monolayers [83], quenching of ruthenium-arachidic acid assemblies [84] and indigo derivatives [85] have been described. Several viologens, for example, **3** (R = R' = C₁₂H₂₅) and **3** (R = CH₃, R' = C₁₄H₂₉) have been

useful in studying quenching rates and back reactions with various new ruthenium sensitizers [2]. The asymmetry of quenching in an asymmetrically sensitized photoreaction involving a 1-methyl-1'-pinanyl derivative of 4,4'-bipyridine and enantiomers of Ru(bpy)₃²⁺ as sensitizers has been reported [86]. Bolaform amphiphiles with viologen head groups form vesicles but the polyene bixin chromophore is unstable [87]. On a pessimistic note, although excellent for developing optimum conditions, the four component system of electron donor, sensitizer, electron relay and catalyst for the photoreduction of water is not really suitable for practical solar energy devices due to the presence of the sacrificial electron donor. It is necessary to replace the sacrificial electron donor with a system capable of oxidizing water to oxygen. This is very difficult to achieve using a viologen as a relay [88]. A solar to electricity conversion device employing triethanolamine

as electron donor, $\text{Ru}(\text{bpy})_3^{2+}$ as sensitizer and **3** ($\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_{18}\text{H}_{37}$) confined within an anodic aluminium oxide film as electron relay has been constructed on a gold electrode [89].

Some work involving viologens has been reported on the use of TiO_2 and CdS as photosensitizers or semiconductors. Hydrogenases immobilized on TiO_2 or CdS powders gave an irradiation in the presence of EDTA and the viologens **3** ($\text{R} = \text{R}' = \text{CH}_3$ or C_7H_{15}) and **3** ($\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_{14}\text{H}_{29}$) yields of hydrogen comparable to the platinum catalysed reaction [90]. Hydrogen is also generated by illumination of ultrafine TiO_2 particles in alkaline medium in the presence of **3** ($\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_{14}\text{H}_{29}$) and platinum [91]. Photosensitized CdS transfers an electron to **3** ($\text{R} = \text{R}' = \text{C}_7\text{H}_{15}$) in non-aqueous media [92].

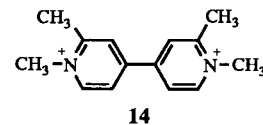
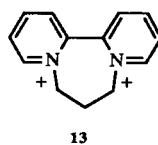
As well as the problem of needing to retard the back electron transfer from reduced R^- to the oxidized photosensitizer P^* the use of viologens as relays causes difficulties due to the fact that they themselves can react with hydrogen to form hydrogenated derivatives such as **11** and **12** which no longer can participate as electron relays. The viologen is thus slowly removed from the system. In an effort to circumvent this difficulty it has been found that cyclodextrin inclusion complexes of viologens with hydrophobic tails such as **3** ($\text{R} = \text{C}_2\text{H}_5$, $\text{R}' = \text{C}_{12}\text{H}_{25}$) greatly increased the ability of the viologen to resist hydrogenation [93] and resulted in enhanced hydrogen yields per viologen consumed. Others have confirmed the usefulness of cyclodextrins [94]. When an anionic zinc porphyrin was used as sensitizer the viologens (**3**, $\text{R} = \text{R}' = \text{C}_8\text{H}_{17}$ or benzyl) were photoreduced in the presence of β -cyclodextrin to their respective radical cations, the inclusion complexes between the viologen and cyclodextrin preventing the viologen from forming unreactive ion-pairs with the anionic photosensitizer.



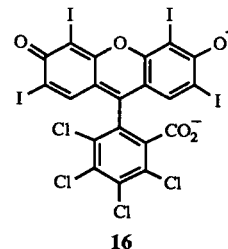
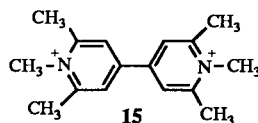
III. Diquaternary Salts of 4,4'-Bipyridine Containing Ring Substituents.

An extensive study of several methyl, ethyl and phenyl ring substituted derivatives of **3** ($\text{R} = \text{R}' = \text{CH}_3$, C_2H_5 and benzyl) as well as some ring substituted derivatives of diquat (**5**) and its trimethylene analogue (**13**) has been described [96]. In homogeneous aqueous solution using EDTA as electron donor, $\text{Ru}(\text{bpy})_3^{2+}$ as sensitizer and platinum as catalyst it was found that the yields of hydrogen at pH values of 5.0 and 7.0 were best with compounds with reversible reduction potentials (E_0) near -0.5 and -0.7 V respectively provided they were stable. Kinetic measurements showed that the rate of quenching of excited

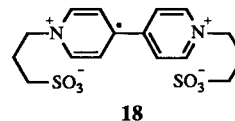
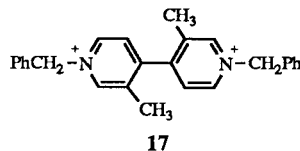
$\text{Ru}(\text{bpy})_3^{2+}$ decreased and the rate of the catalyzed reduction of water increased as the potential became more



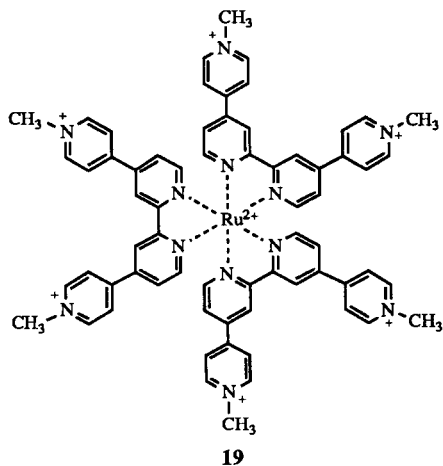
negative. The main loss of the diquaternary bipyridinium compounds during irradiation is caused by catalytic hydrogenation. Therefore compounds that are more resistant to hydrogenation than methyl viologen are more effective in the production of hydrogen provided their potentials fall within the required range. In practical terms the methyl ring substituted analogues **14** and **15** were more effective than methyl viologen. The addition of sulfur compounds such as glutathione to the reaction mixture suppressed unwanted side reactions and gave improved yields and rate of formation of hydrogen especially using **15** [97]. Other work with methyl substituted derivatives of methyl viologen has been reported [98].



The tetramethyl ring substituted analogue **15** of methyl viologen has also been found to be an excellent electron relay in the production of hydrogen in a system using triethanolamine as donor, the xanthene dye Rose Bengal (**16**) as sensitizer and platinum as catalyst at a pH value of 9.0. The photostability of the dye was enhanced when it was bound to a poly(vinyl-pyrrolidone) polymer [99]. The ring substituted derivative **17** is an effective electron relay



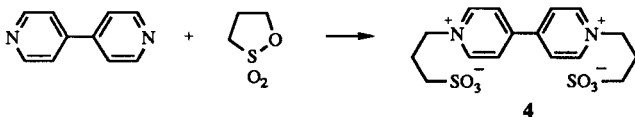
for the production of hydrogen using another xanthene dye, eosin, as sensitizer, triethanolamine as donor and platinum as catalyst. Colloid particles of SiO_2 assisted the separation of the primary redox products [100]. Methyl ring substituted analogues **14** and **15** have been used in a study of the production of hydrogen with the new photosensitizer $\text{Ru}(\text{bpyz})_3^{2+}$, where bpyz stands for 2,2'-bipyrazine [101,102].



In a very interesting recent development working at pH 7.0 and using triethanolamine as donor, the new ruthenium complex (**19**) from a terpyridine as sensitizer, **14** as electron relay and platinum as catalyst, hydrogen was obtained on irradiation in quantum yields claimed to be the best so far with ruthenium complexes. Interestingly hydrogen was liberated without the presence of **14** but not in as good yield [103].

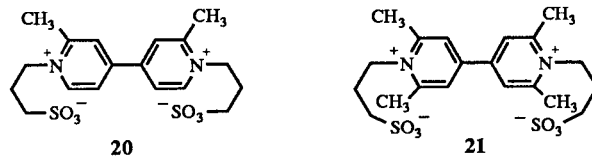
IV. Zwitterion Diquaternary Salts of 4,4'-Bipyridine.

A development which has generated considerable interest is the use of zwitterionic viologens such as **4** as electron relays instead of methyl viologen analogues. The zwitterionic viologen **4**, abbreviated as PVS, has a reduction potential (E_o) of $-0.37V$ which is slightly higher than that of methyl viologen. On one electron reduction it forms reversibly a radical anion **18** unlike the situation with methyl viologen which on one electron reduction gives the methyl viologen radical cation **2**. This charge difference on one electron reduction creates great ramifications in the use of **4** as an electron relay for the photoreduction water. Compound **4** is synthesized by reaction of 4,4'-bipyridine with 1,3-propanesultone [104].

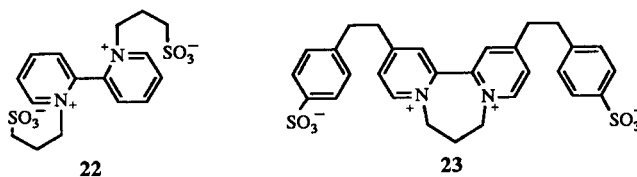


In particular much research has been conducted with systems using **4** in the presence of negatively charged SiO_2 colloids. With $Ru(bpy)_3^{2+}$ as sensitizer it was found that the quenching of $Ru(bpy)_3^{2+}$ by **4** was not affected by the negatively charged SiO_2 particles but the back electron transfer between the oxidized photosensitizer $Ru(bpy)_3^{3+}$ and $PVS^{\cdot-}$ was substantially retarded in the presence of the SiO_2 colloids. This retardation is attributed to electrostatic repulsion of the radical anion $PVS^{\cdot-}$ from the oxidized sensitizer $Ru(bpy)_3^{3+}$ which is adsorbed on the negatively charged SiO_2 particles. The importance of the

surface potential of the SiO_2 colloids in retarding the back reaction was demonstrated by varying the ionic strength and pH of the medium [105]. Illumination of $Ru(bpy)_3^{2+}$ or $ZnTMPyP^{4+}$ in the presence of an electron donor and SiO_2 suspensions thus leads to rapid formation of the radical anion $PVS^{\cdot-}$ in a quantum yield of 0.37. In the absence of SiO_2 the quantum yield of $PVS^{\cdot-}$ was only 0.038 [53, 106]. The SiO_2 colloids thus provide an especially effective solid-liquid interface with a very high negative surface charge density that can retard back reactions while allowing the forward reaction with a neutral electron acceptor to proceed. Replacement of the positively charged sensitizers by the anionic zinc *meso*-tetraphenylporphyrin-tetrasulfonate ($ZnTPP_4^{4-}$) as expected resulted in a low quantum yield (0.016) of $PVS^{\cdot-}$. Thus repulsion of the two negatively charged photoproducts by the SiO_2 particles allows a recombination rate similar to that observed in the homogeneous reaction (0.012) in the absence of SiO_2 colloids. It has been confirmed that colloidal SiO_2 can retard the reverse electron transfer in a system using triethanolamine as donor, $Ru(bpy)_3^{2+}$ as sensitizer and **4** as electron relay. Interestingly alkyl ring substituted analogues of **4** such as **20** and **21**, the latter having an E_o value of $-0.54V$, were more effective than **4** for the production of hydrogen



due to their lower reduction potential and greater stability against hydrogenation [107]. In basic solution (pH 9-10) using the same donor and sensitizer, PVS is too weak a reductant to produce hydrogen but the use of the zwitterionic derivative from 2,2'-bipyridine **22** which has a low redox potential ($E_o = -0.75 V$) enabled hydrogen to be produced in the presence of platinum catalyst and SiO_2 colloids [108,109]. No hydrogen was obtained in the absence of SiO_2 . Hydrogen is also produced in aqueous systems (pH 9.8) with semi-conductor TiO_2 modified SiO_2 colloids using **22** as electron relay in uv light or with the addition of $Ru(bpy)_3^{2+}$ in visible light. Platinum was the catalyst [110].



A new zwitterion bridged 2,2'-bipyridinium salt (**23**) which has an E_o value of $-0.65 V$ is superior to **22** for the production of hydrogen at pH 8-9.2 using $Ru(bpy)_3^{2+}$ as sensitizer, triethanolamine as donor and platinum as

catalyst both in homogeneous solution and in the presence of SiO₂ colloids. The salt **23** shows completely reversible redox behaviour whereas **22** does not [111].

In miscellaneous items PVS (**4**) in the presence of SiO₂ colloids has been used as a mediatory electron acceptor in the photoinduced reduction of anthraquinone sulfonates using Ru(bpy)₃²⁺ as sensitizer and triethanolamine as electron donor [112].

A number of investigations with zwitterionic diquaternary salts of 4,4'-bipyridine in the absence of SiO₂ colloids have also been described. The rate of quenching of ZnTPPS₃³⁻ with PVS was less than that with methyl viologen but the back electron transfer rate was also less due to repulsion of the negatively charged PVS⁻ by the oxidized ZnTPPS₃³⁻ [113]. Somewhat similar results were achieved with a polymeric anionic sensitizer. Here, PVS⁻ accumulated three times faster than the methyl viologen radical cation due to retardation of the back reaction. With a polymeric cationic sensitizer, however, there was no significant accumulation of PVS⁻ at all since the back electron transfer was enhanced due to the electrostatic attraction between PVS⁻ and the polycation [114,115]. Other related studies have been described [116-118].

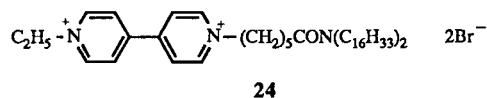
In other items the association constant for PVS with the anionic sensitizer ZnTPPS₃³⁻, as expected, was less than with methyl viologen, the positively charged methyl viologen favoring association [119]. As a result the reduction rate of PVS was larger than with methyl viologen [120]. In the presence of 2-mercaptoethanol as donor and hydrogenase as catalyst hydrogen was evolved, with the zwitterionic derivative of 2,2'-bipyridine **22** being better than PVS or methyl viologen due, in part, to its lower reduction potential (E₀ = -0.75 V) [121], but the situation

is complicated. If the ZnTPPS₃³⁻ concentration is increased the determining step for hydrogen evolution is changed from the photoreduction of the bipyridinium salt to reaction of the reduced salt with the catalyst. In these circumstances methyl viologen was best since it is a better substrate for hydrogenase [122].

Some work has been reported with cationic micelles and bilayer membranes. Thus, in the system triethanolamine, Ru(bpy)₃²⁺ and PVS, the addition of a cationic surfactant such as cetyltrimethylammonium chloride (CTAC) or the bilayer membrane forming didodecyldimethylammonium bromide increased the efficiency of the photoreduction of PVS. This was attributed to the electrostatic field of positively charged surfactant assemblies trapping the radical anions of the reduced viologen and thereby retarding the back electron transfer to the oxidized sensitizer Ru(bpy)₃³⁺ [44,123]. Similar results have been obtained using ZnTMPyP⁴⁺ as sensitizer [35]. Experiments using the reduced nicotinamide NADPH as electron donor, a hematoporphyrin dissolved by cetyltrimethylammonium

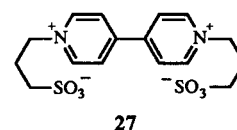
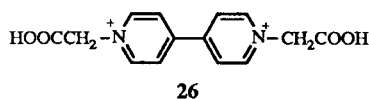
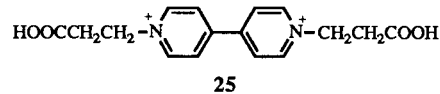
bromide as sensitizer and PVS as electron relay have also been described [124].

An interesting result has been reported using cationic bilayer membranes formed from 1-ethyl-1'-[5-(*N,N*-dihexadecylcarbamoyl)pentyl]-4,4'-bipyridinium dibromide, abbreviated to LEV²⁺ (**24**). Using triethanolamine as donor, Ru(bpy)₃²⁺ or ZnTMPyP⁴⁺ as sensitizer and PVS as electron relay charge separation of the photogenerated ion pairs was achieved in nearly quantitative yield (quantum yield 0.80) in the presence of LEV²⁺. The primary step in the reaction is the oxidative quenching of the sensitizer by PVS. The electron was transferred to the bilayer membrane of LEV²⁺ by PVS⁻. The reduction potential of LEV²⁺ is slightly more positive than that of PVS. The zwitterionic viologen was thus confirmed to shuttle as an efficient electron relay between the bulk aqueous solution and interface of the bilayer membrane with successive electron transfer to the surface of the viologen bilayer which enables temporary storage of the captured electron. The back electron transfer was suppressed 500-fold attributed to electrostatic repulsion between the oxidized sensitizer and the positively charged interface of the bilayer membrane [125,126].



Work has also been reported with anionic micelles. In the presence of anionic sodium dodecylsulfate (SDS) micelles, the oxidized sensitizer ZnTMPyP⁵⁺ is adsorbed on the micelles and the back reaction with the anionic PVS⁻ is retarded due to electrostatic repulsion [35]. The use of SDS micelles, however, is fourfold less efficient in the formation of PVS⁻ compared with SiO₂ colloids due to the surface potential of the sodium laurylsulfate system being much less than that of SiO₂ colloids [53,127]. Nonetheless several zwitterionic analogues of methyl viologen, PVS (**4**), **25**, **26** and **27** produce hydrogen two-fold better than methyl viologen using ZnTPPS₄⁴⁻ as sensitizer, *N*-phenylglycine as donor and platinum as catalyst in the presence of sodium laurylsulfate micelles. Further enhancement is achieved using an amphiphilic Ru(bpy)₃²⁺ derivative as sensitizer solubilized in sodium tetradecyl-di-

Block 16



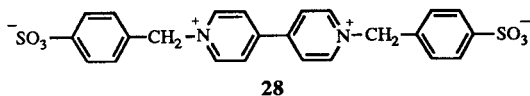
oxyethylene sulfate anionic micelle assemblies and **27** as electron relay [128]. The photoreduction of PVS by phthalocyanine sensitizers in anionic micelles has also been reported [129].

In work in negatively charged membranes consisting of phosphatidyl-glycerol or phosphatidic acid, the photosensitized oxidation of a manganese(III) porphyrin by ZnTMPyP⁴⁺ which is confined to the membrane has been described with PVS being reduced in the aqueous phase [130] and further work on related systems has been described [131].

In experiments using illuminated chloroplasts hydrogen evolution rates were better with both PVS and **26** than methyl viologen in the presence of either platinum or a hydrogenase catalyst [132].

Work has also been reported with PVS in reverse micelles using isooctane as the organic medium and Aerosol OT as dispersant with magnesium tetraphenylporphyrin [74], ZnTPP or ZnTMPyP⁴⁺ as sensitizer [133].

The effect of polyelectrolytes has been investigated by studying the effect of anionic and cationic polyelectrolytes on the photoinduced electron transfer between ZnTMPyP⁴⁺ and PVS. They decrease both the forward and back electron transfer rates. The effect of the anionic polyelectrolyte is due to the hydrophobic envelopment of the sensitizer by the polyelectrolyte hindering approach of reactants and thus reducing all bimolecular reaction rates between the sensitizer and species in solution. The cationic polyelectrolyte decreases the back electron transfer due to the binding of PVS⁻ to the polyelectrolyte which then repels the oxidized porphyrin electrostatically [134]. On the other hand with the new zwitterionic derivative **28** of benzyl viologen, abbreviated to BSV, which was used to quench the excited state of Ru(bpy)₃²⁺ it was found that addition of the polyelectrolyte polyvinyl sulfate enhanced the rate of quenching and retarded the decay of the electron transfer products Ru(bpy)₃³⁺ and BSV⁻ [135,136].



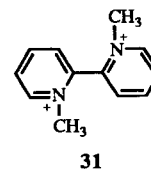
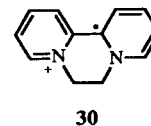
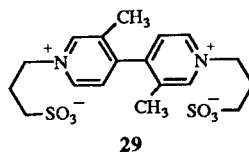
In further work with Rose Bengal, PVS and the 2,2'-bipyridine zwitterion salt **22** do not form complexes with Rose Bengal as readily as methyl viologen and they quench the excited state of the dye but the major problem in using Rose Bengal, namely photodegradation of the dye remains [137].

In miscellaneous items the rate of formation of PVS⁻ was found to be greater using Ru(bpy)₃²⁺ as sensitizer than a new complex ruthenium polymer sensitizer [138]. Other work involving PVS and potential new polymeric ruthenium sensitizers has been described [139,140]. In an

interesting experiment a polymer bound ruthenium sensitizer was packed in a column with silica gel and irradiated with visible light. When PVS or methyl viologen and triethanolamine in aqueous solution were passed down the column reduced viologen was continuously separated [141]. PVS makes it possible to achieve good photoredox charge separation in a system using a zinc tetrasulfonated phthalocyanine sensitizer [142,143]. Zwitterionic viologens have also been used in a study of the catalytic platinum reaction [144], in an investigation of photophysical properties of pyrene covalently bound to polyelectrolytes [145] and in the quenching of copolymers of methacrylic acid and vinylperylene [146].

Some work has been reported involving PVS with the photochemistry of CdS [147,148] and with hydrogen production from montmorillonite clay modified electrodes [149].

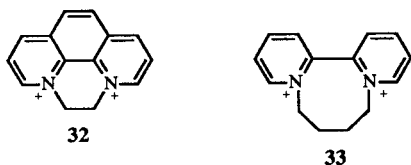
As well as the photoreduction of water the photoreduction of carbon dioxide to methane and higher hydrocarbons has been accomplished in aqueous solution using triethanolamine as donor, Ru(bpy)₃²⁺ or Ru(phen)₃²⁺ as sensitizer and the zwitterionic viologen **29** or a diquaternary salt of 2,2'-bipyridine, for example **13**, as electron relay in the presence of ruthenium or osmium colloid catalysts. Hydrogen was produced as well. The reduction potential (E₀) of **29** is about -0.79V which is substantially lower than that of PVS and this lower potential is necessary for the reduction of CO₂ to occur [150,151].



V. Diquaternary Salts of 2,2'-Bipyridine.

As well as diquaternary salts of 4,4'-bipyridine several diquaternary salts of 2,2'-bipyridine have been investigated as electron relays for the photolysis of water, a few of which have already been mentioned. The bridged diquaternary salt of 2,2'-bipyridine, compound **5** is the well-known herbicide diquat. It is reversibly reduced in aqueous solution by a one electron transfer to a stable radical cation **30** but at a slightly higher potential, E₀ = -0.35 V, than that of paraquat. As well as bridged diquaternary salts of 2,2'-bipyridine, the 1,1'-dimethyl diquaternary salt **31**, which has an E₀ value of -0.72 V, and its

relatives have also received attention. In addition bridged diquatery salts of 1,10-phenanthroline (e.g. **32**) have been studied.



In homogeneous aqueous systems at pH 6-7 using EDTA as electron donor, Ru(bpy)₃²⁺ as sensitizer and colloidal platinum as catalyst compound **13**, which has an E₀ value of -0.55 V and a dimethyl ring substituted derivative were effective in producing hydrogen on illumination but were not superior to methyl viologen. A series of bridged diquatery salts of 1,10-phenanthroline such as **32** were not as good due to their poor electrochemical reversibility [152]. Very similar conclusions were reached in other studies which included diquat **5** and **31**. The redox potential of the most efficient electron relays is about -0.45 V and none was better than methyl viologen [1,15]. Earlier related studies have been reported [7,13,153]. Other studies involving quenching of various ruthenium (and other metal) ligand sensitizers by diquat and its relatives have been reported [17] including studies with **31** in acetonitrile [154].

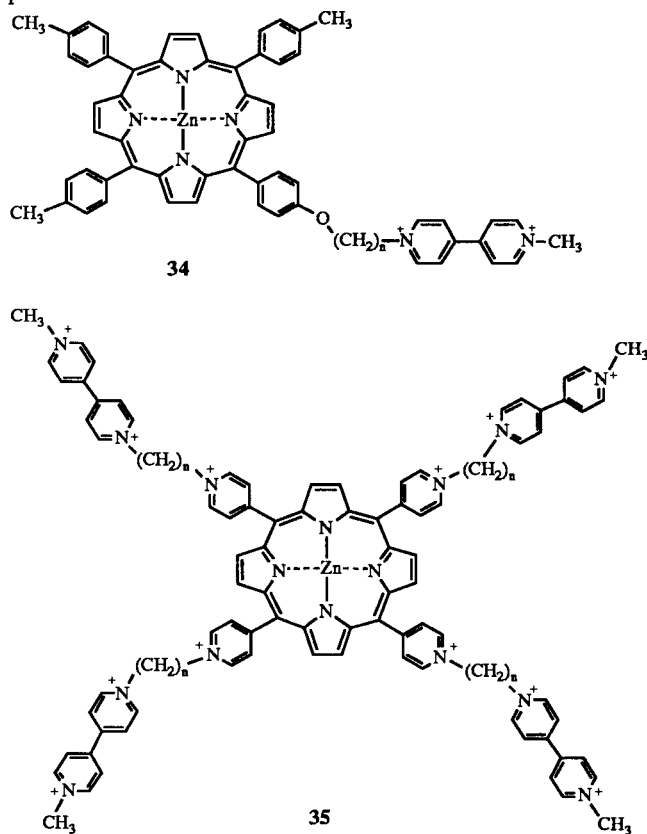
On the other hand working with the system using 2-mercaptoethanol as donor, zinc tetraphenylporphyrintrisulfonate (ZnTPPS₃³⁻) as sensitizer and hydrogenase as catalyst it was found that on illumination hydrogen evolution rates were better with the salts **31**, **13** and **33**, all of which have reduction potentials (E₀) between -0.55 and -0.72 V, than with methyl viologen. This was attributed to differences in the association constants of the viologens with the anionic sensitizer since, as noted earlier, complexes between the viologen and sensitizer usually do not take part readily in the photoreduction and also to rate differences in the separation of electron transfer from the sensitizer to the bipyridinium salts [98,121,155]. The situation is complicated however. If the concentration of the sensitizer is increased, the rate determining step for hydrogen evolution is changed from photoreduction of the bipyridinium salt to hydrogen evolution by the reduced bipyridinium salt. In that case methyl viologen was best since it is a better substrate for hydrogenase [122]. In the presence of anionic (SDS) micelles an increase in the accumulation of the reduced bipyridinium salts **31**, **13** and **33** was observed due to the electrostatic effects between the micellar surfaces, the oxidized ZnTPPS₃²⁻ and the reduced viologen. When platinum catalyst was used hydrogen evolution was better with all three 2,2'-bipyridinium diquatery salts than with methyl viologen [156,157]. The presence of SDS inhibited the effectiveness

of hydrogenase as catalyst. Association constants between ZnTPPS₃³⁻ and the salts **5**, **13**, **31** and **33** have been determined. The constants are smaller than for methyl viologen [158,159].

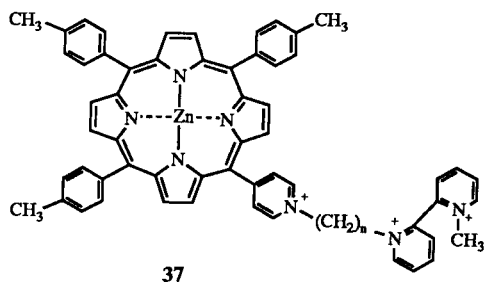
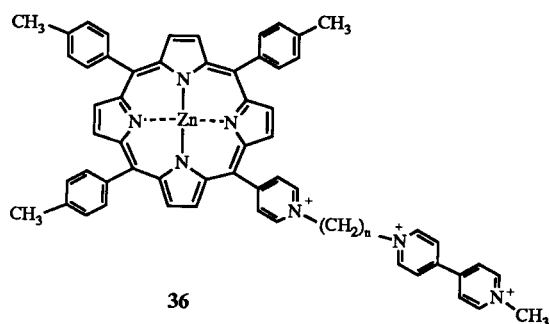
Work has also been reported on hydrogen production with **13** using new tin and ruthenium porphyrin sensitizers [16]. Working with a tin *meso*-tetraanilineporphyrin as sensitizer, platinum as catalyst and EDTA as electron donor, the yield of hydrogen was best with **13** as electron relay, being superior to both methyl and benzyl viologens and other bridged 2,2'-bipyridinium salts [160]. Hydrogen has also been obtained on illumination of a system using triethanolamine as donor, a copper complex of 2,9-diphenyl-1,10-phenanthroline as sensitizer with anthracene-9-carboxylate as auxiliary, **13** as electron relay and titanium dioxide supported platinum as catalyst [161]. A theoretical paper on a kinetic model for cyclic water cleavage involving **13** and **33** has been published [162] and **13** has been used in a photoelectrical cell for production of hydrogen and hydrogen peroxide by photoredox reactions [163].

Viologens Linked to Porphyrins.

Some interesting work has been reported on compounds containing viologens covalently linked to porphyrins. Some of these are able to combine the properties of sensitizer and electron carrier in the one molecule for the photoreduction of water.



Following on from some earlier work on fluorescence quenching of viologen linked porphyrins such as compounds of type **34** [164-166] it was found that using NADPH as electron donor, hydrogenase as catalyst and the water soluble viologen linked porphyrins of structure **35** ($n = 2-5$) as combined sensitizer and electron relay hydrogen was generated on irradiation. The hydrogen evolution rate decreased with increasing chain length from $n = 2$ to $n = 4$ but when $n = 5$, the hydrogen evolution rate was best possibly due to conformational changes and direct transfer of an electron from porphyrin to viologen [167]. Addition of Triton X-100 surfactant greatly enhanced hydrogen evolution [168]. Further work with these compounds and extensions thereof have been described [169]. In the series containing only one covalently linked viologen group **36**, however, only the compound with $n = 2$ acted as photosensitizer and electron relay for the production of hydrogen. The compounds with $n = 3-6$ were inactive. Platinum was found to be better than hydrogenase as catalyst [170]. In a later paper the evolution of hydrogen with **36** ($n = 2$) was confirmed and the experiments extended to show that a 2,2'-bipyridine analogue (**37**, $n = 5$) also was effective as both sensitizer and electron relay for the production of hydrogen. In the latter series when $n = 2-4$ the compounds were inefficient for photoinduced hydrogen evolution [171]. Further work on related series has been described [172,173] and patented [174]. A proton nmr conformational study of metal free **36** has been published [175].



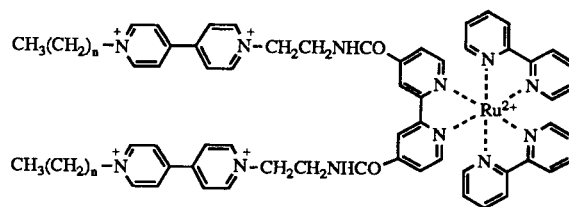
Also worthy of note are studies in non-aqueous polar solvents such as DMSO of the photoinduced formation of long-lived intramolecular radical ion pairs from molecules

containing porphyrins and viologens covalently combined where the viologens contain long flexible chains [176]. Further evidence for intramolecular electron transfer quenching from related metal free excited porphyrins to covalently linked long-chained viologens in acetonitrile [177] and DMSO [178] has been obtained. Other related studies have been carried out [179-181] and extended to include studies in aqueous DMF with zinc phthalocyanines containing covalently bonded long-chained viologens [182]. Photoelectron transfer in a complex porphyrin-viologen-quinone triad molecule has been studied where a benzyl viologen is covalently attached to a zinc porphyrin [183] and another triad where the porphyrin is replaced by pyrene has been described [184]. The effect of an external magnetic field on the lifetime of ion pair states in viologen linked porphyrins has recently been the subject of much study [185-187] including work with reversed micelles [188,189].

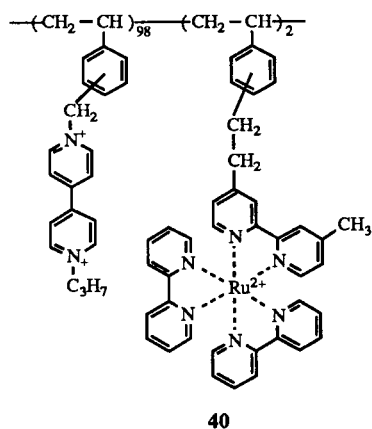
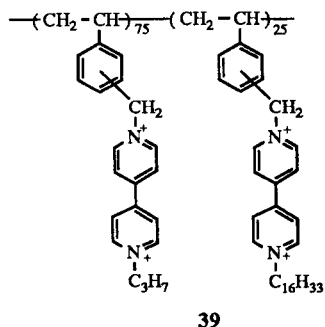
VII. Viologen Polymers and Pendant Viologens on Polymers.

As well as research on viologens covalently linked to porphyrin sensitizers some work has been reported on viologens covalently linked to ruthenium ligand sensitizers. This latter area, however, has often been associated with the use of pendant viologens on polymers and will be dealt with in that context. The rationale for work with viologens pendant on polymers is to attempt to find means of separating the photogenerated primary redox pairs other than by using the viscous environments associated with membranes or vesicles where charge separation depends on molecular diffusion.

In a system using EDTA as electron donor it was found that with the viologen linked ruthenium complex (**38**, $n = 3$) the quantum yield of the photoinduced reduction of the viologen units was only 1-2% of that of the free $\text{Ru}(\text{bpy})_3^{2+}$ and methyl viologen in aqueous solution. However, the quantum yield of photoreduction of viologen units rose considerably when the longer chained **38** ($n = 15$) was used in conjunction with the pendant viologen polymer **39** and the quantum yield was even better when the ruthenium photoreactive centre was directly attached to the electron relay system in the polymer chain as in **40**. These



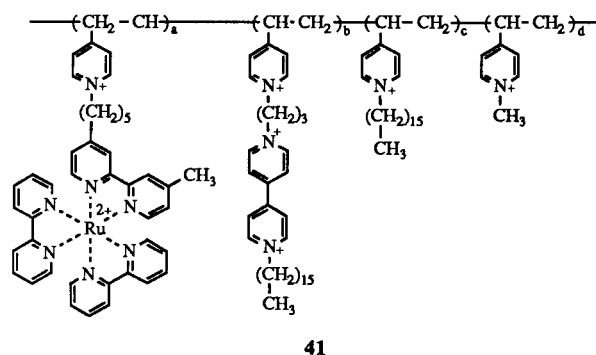
results were attributed to the enhancement of charge separation of the photoproducted primary ion pair due to electron injection from the photoreaction centres into the electron relay system and succeeding electron migration among the viologen units in the relay system [190]. Further developments in related systems using in addition bilayer molecular membranes from didodecylmethyl ammonium bromide have been reported [44] and extensions to various analogues of **38** in the presence of micelles and bilayer membranes have been investigated [191]. Hydrogen has actually been photogenerated in aqueous solution



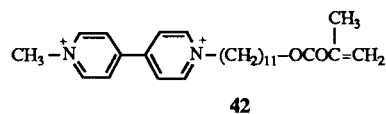
using a polymer of type **39** as electron relay with EDTA as donor, $\text{Ru}(\text{bpy})_3^{2+}$ as sensitizer and colloidal platinum as catalyst [44] although with an efficiency less than that of the $\text{Ru}(\text{bpy})_3^{2+}$ and methyl viologen system mainly due to the decreased probability of encounter between photosensitizer and electron mediator [192]. Very similar results were obtained by other groups using closely related pendant viologen systems [193,194]. Likewise the yields of hydrogen were lower than with methyl viologen using a pendant viologen derived from 1-methyl-4,4'-bipyridinium chloride and polyvinylbenzyl chloride as electron relay, ZnTMPyP^{4+} sensitizer and colloidal platinum in the presence of an electron donor [195]. Further studies of electron transfer quenching of related pendant viologens in non-aqueous media have been reported [196].

In subsequent work using triethanolamine as donor and $\text{Ru}(\text{bpy})_3^{2+}$ as sensitizer it has been found that particularly long lived reduced viologens were generated by electron transfer from the zwitterionic 4,4'-bipyridinium salt **4** to viologen polymers of type **39** [197] and polymers such as **39** can act as electron store when the salt **4** is used as electron relay and electron shuttle [198].

Further interesting work has been reported with polymers related to **40** where the ruthenium photoactive centre is directly attached to the electron relay system in the polymer chain. Working with EDTA as electron donor, the combined sensitizer and relay polymers of type **41** and platinumized TiO_2 as photocatalyst hydrogen evolution was obtained on visible light illumination. Addition of methyl viologen usually improved the yield of hydrogen but not in the case of **41** ($a = 7, b = 7, c = 0, d = 86$) which gave on its own just about the best yield of hydrogen [199].



Intramolecular and energy transfer processes have been studied in molecular assemblies consisting of ruthenium bipyridine complexes covalently linked to a diquat analogue and a phenothiazine derivative [200,201]. As well as viologens linked to ruthenium sensitizers a viologen has been covalently attached to the sensitizer dye eosine and the photoinduced and intramolecular electron transfer reactions of the complex were studied [202].

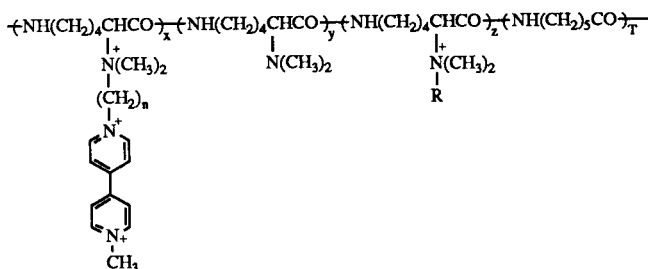


In other work polymerization of the salt **42** gives aggregates whose electron transfer properties using $\text{Ru}(\text{bpy})_3^{2+}$ as sensitizer have been compared with those of methyl viologen [203] and the photoreduction properties of polymers derived from, for example, 1-methyl-1'-(*p*-vinylbenzyl)-4,4'-bipyridinium salts have been investigated [204]. Polymerisation of viologens with long chained quaternizing groups containing acetylenic linkages have been reported and their possible usefulness as electron carriers mentioned [205]. Intramolecular photochemical electron transfer has also been observed in viologens link-

ed to pyrene [206] and light induced charge separation has been achieved in a zeolite framework with an N,N' -dialkyl 2,2'-bipyridinium salt covalently bound to a $Ru(bpy)_3^{2+}$ type sensitizer [207]. Experiments designed to obtain information on the redox potential of pendant viologens on polymers have been described [208].

Pendant viologens have also been incorporated as coating layers on graphite electrodes [209] and electrodes modified to contain polymers of a ruthenium chromophore linked to a viologen acceptor have been described [210].

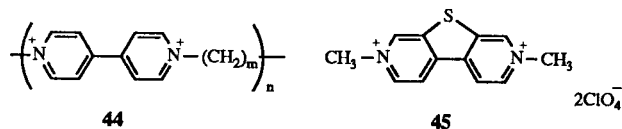
In another type of pendant viologen a paper has described investigations with viologens attached to nylon polymers of type **43**. In the presence of triethanolamine as donor and $ZnTMPyP^{4+}$, for example, as sensitizer the quantum yield for the photoinduced reduction of the viologen groups was variable depending on a number of factors such as the fraction of pendant viologen, the concentration of electron donor and ionic strength of the solution. By laser flash photolysis the reaction rates for electron transfer from the excited porphyrin to the viologen group in the polymer and for the back electron transfer to oxidized porphyrin were measured. It was found that the cationic and/or hydrophobic polymer environment retards the back electron transfer which increases the quantum yields of viologen cation radicals [211,212]. A pendant viologen attached to a similar nylon polymer was also found to be effective in stabilizing colloidal platinum catalyst in an aqueous system using triethanolamine as donor, $ZnTMPyP^{4+}$ as sensitizer and methyl viologen as electron relay and by its use quantum yields of hydrogen were increased on irradiation [213]. Stabilization of colloidal CdS and platinum photocatalyst has also been noted with the pendant viologen [214]. Viologens have also been attached to polypeptide matrices to provide an electroactive polymer [215].



43

Several papers have appeared involving polyviologens of structure **44** and related types as electron carriers in aqueous systems using EDTA as electron donor, $Ru(bpy)_3^{2+}$ or various dyes as sensitizer and a platinum containing catalyst. On irradiation hydrogen is produced but the results are variable [216-218] although some claims

to improvement over methyl viologen have been made. However, various polyviologens have been investigated as quenchers of $Ru(bpy)_3^{2+}$ and related sensitizers but the back electron transfer rates were usually fast [219]. Polyviologens have also been used in polymer complexes in various film coated electrodes [220-223].

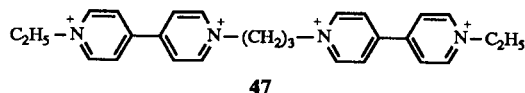
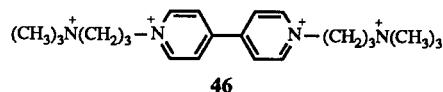


Lastly polymeric membranes cross-linked with viologens have been described and electron transport in the membranes studied. Their application to the photodecomposition of water by irradiation is envisaged [224].

VIII. Miscellaneous Viologens.

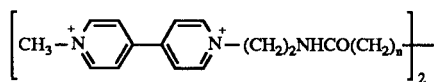
A sulfur containing analogue of methyl viologen, 2,7-dimethylthieno[2,3-c:5,4-c']dipyridinium bisperchlorate (**45**) has been synthesised [225]. It has been found to act both as photosensitizer and electron relay for the photo-reduction of water. In experiments in aqueous solution using EDTA as electron donor, colloidal platinum as catalyst and **45** as combined photosensitizer and electron relay hydrogen was evolved on irradiation [226]. An X-ray crystallographic analysis of **45** has recently been published [227].

A series of viologens ranging from neutral zwitterionic salts to tetraquateryary salts of type **46** have been compared with respect to their ability to quench $Ru(bpy)_3^{2+}$ [228] and to effect hydrogen evolution from water in homogeneous and vesicular systems [229]. The association coupling constants of various viologens with the sensitizers eosin, $ZnTMPyP^{4+}$ and $ZnTPPS^{4-}$ have been determined [230]. In the photoreduction of carbon dioxide to formic acid electron transfer from excited $Ru(bpy)_3^{2+}$ to the tetraquateryary salt **47** was not as efficient as with methyl and benzyl viologens. Triethanolamine was the electron donor and formate dehydrogenase the catalyst [231].



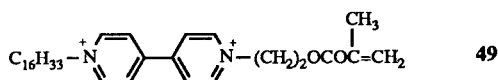
Membrane vesicles containing redox active bipyridinium groups are formed from compounds such as **48** [232]. A number of other redox active surfactant vesicles from

4,4'-bipyridinium diquatery salts have been synthesised [233]. The salts all contain ethylenic linkages and some can be polymerised by an initiation or by uv irradiation across either their bilayers or their head groups depending on the position of the double bond. Typical monomer

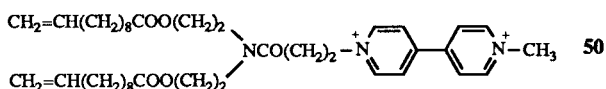


48

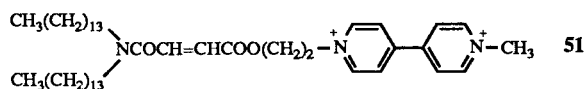
structures include **49**, **50** and **51**. Some of these polymerized vesicles give good charge separation using $\text{Ru}(\text{bpy})_3^{2+}$ as photosensitizer and result in long lived reduced viologens [234,235]. Electron transport membranes have also been constructed from polypeptides containing covalently attached viologen moieties and redox reaction across the membranes have been demonstrated whereby substrates were reduced without coming into contact with the reducing agent [236].



49

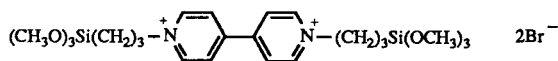


50



51

To complete the review the silyl diquatery salt of 4,4'-bipyridine (**52**) has been used to derivatize various surfaces including glass [237], silicon [238-242] and indium tin oxides [243] by hydrolysis of the $\text{Si}(\text{OCH}_3)_3$ bonds and attachment of the bipyridinium moiety to the surface to give a redox polysiloxane network. In conjunction with platinum, palladium or rhodium catalysts and appropriate photoelectrodes evolution of hydrogen from water was achieved. A related procedure to attach a silanized 4,4'-bipyridinium salt to TiO_2 particles has been accomplished and light induced evolution of hydrogen was achieved in the presence of a hydrogenase [244]. Attachment of 4,4'-bipyridinium diquatery salts containing long alkyl chains to gold electrodes has also been accomplished through a sulfide linkage and the redox behaviour of the assembled layers has been studied [245, 246].



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