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Polyquinoline-Supported Ruthenium Complex for the Photochemical Reduction of Water

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ABSTRACT: A polyquinoline containing a bipyridyl link in the polymer backbone was coordinated to a ruthenium center to form a tris(bipyridyl)ruthenium complex. The polymer and corresponding model complexes were characterized and then assessed for its photosensitizing ability. The model, 3, and dissolved polymer 4 both sensitized the photoreduction of methyl viologen in a sacrificial system. The polymer was then examined for its suitability as a photosensitizing membrane in a water photolysis cell.

This paper reports the results of the first use of an engineering polymer as a support for a ruthenium photosensitizer for the reduction of water. A coordinating polyquinoline with a bipyridyl link—created during the polymerization—was synthesized, and $Ru(bpy)_2Cl_2$ (bpy = 2,2′-bipyridyl) was reacted with the polymer to create a tris(bipyridyl) type of ruthenium complex. The resulting polymer was then evaluated as a sensitizer and as a membrane in a photolysis cell.

The use of $Ru(bpy)_3$ as a photosensitizer requires an elaborate scheme of cocatalysts and acceptors. These catalysts and reactions generate and "store" electrons (as radical intermediates) until the necessary electrons have been accumulated for a multiple electron transfer to oxidize or reduce water (Figure 1).[1] The cell in Figure 1b produced 0.1 mL/h of O_2 and 0.2 mL/h of H_2 simultaneously.[2,3] The quantum yields for the above cell were poor, apparently because of the lack of selectivity by the relays for their respective cocatalysts. The most severe problem with $[Ru(bpy)_3]^{2+}$ as a sensitizer is that the newly formed $[Ru(bpy)_3]^{3+}$ complex will immediately reoxidize the electron relay in an energy-wasting back-transfer reaction of the electron (eq 1).[4] The excitation energy is then released as heat. When the electron relay (A) is methyl viologen (MV^{2+}), the yield of reduced relay is only 25%.

$$A + Ru(bpy)_3^{+2} \underset{-\Delta}{\overset{h\nu}{\rightleftharpoons}} Ru(bpy)_3^{+3} + A^- \qquad (1)$$

Moving one of the reactants into another phase would limit the amount of contact time of the pair. The phase boundary allows only brief contact of the sensitizer and relay before the ions are quickly separated.[5] Attachment of the sensitizer to a polymer is one strategy used to create a phase boundary. As might be expected because of their ease of synthesis, vinyl polymers with pendant bipyridyl sites have been the only polymers reported to date.[3c]

The quenching efficiency (i.e., sensitizing ability) of a polymer-bound ruthenium center depended on how much consideration was given to neutralizing the additional steric hindrance of the polymer chain. Attachment to styrene and styrene beads generally decreased the sensitizing ability relative to the monomeric $Ru(bpy)_3$.[6,7] However, in an elegant study, a copolymer of acrylic acid and 4-vinyl-4′-methyl-2,2′-bipyridine with coordinated ruthenium centers actually was superior to monomeric $Ru(bpy)_3$ in quenching MV^{2+} (at pH 7). Repulsion of the negative charges on the deprotonated carboxylate groups increases the radius of gyration of the polymer backbone which allows the relays to diffuse in and out of the polymer. In addition, the positively charged MV^{2+} relay is attracted to the polymer by the negative charges. At pH 3, when the carboxylate groups are mostly protonated, the quenching rate is less than that for the monomeric complex.[3c] There have been no observed reports of polymer-supported photosensitizers used for the total photolysis of water; the manner of their application did not address the other issues involved with a homogeneous cell.

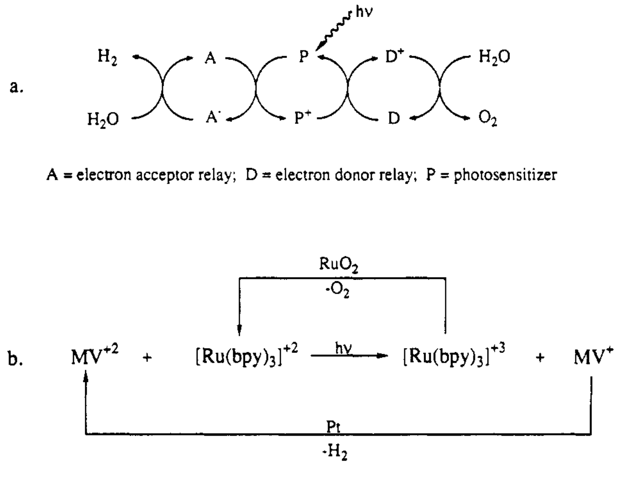

Figure 1. Photolysis scheme (a) and cell (b).

The deployment of the photosensitizer as a polymer-supported complex can also remedy the other problems associated with the homogeneous photolysis cell in Figure 1b. A difficulty with a homogeneous cell is that the oxidation and reduction cycles run concurrently. The relays in each cycle must react selectively with the proper cocatalyst, or else, if the relay reacts with the wrong cocatalyst, then that cycle is actually reversed. For example, if the function of the ruthenium oxide cocatalyst is to accumulate positive charge, then reaction of that cocatalyst with a reducing relay such as MV^+ would cause the ruthenium particle to be reduced in charge. If a polymer-supported sensitizer were used as a *membrane to separate the half-reactions*, then the problem of selectivity is moot because it would be impossible to have cross-reactions. Even though polymer-supported sensitizers are generally quenched less efficiently than their homogeneous counterparts, the loss would be balanced by the improved efficiency in the relays. The membrane would be in contact with both solutions, so it would not be necessary to use a sacrificial system (Figure 2). Other advantages of using

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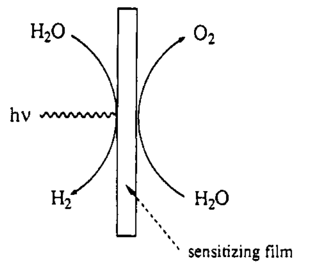
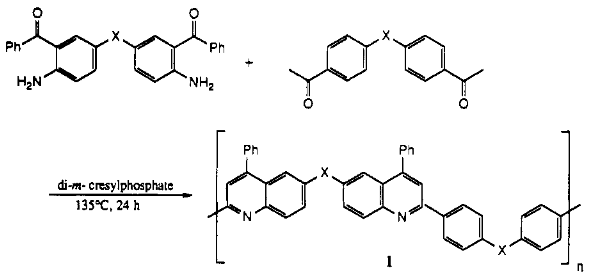


Figure 2. Photosensitizing membrane/photolysis cell.

a polymer-supported sensitizer as a membrane are the ease of deployment and recovery of the catalysts, separation of the evolved gases, and the scale of deployment that can be used.

To support the sensitizer in a membrane application, the polymer backbone needs to be fairly robust. The conditions in the solar cell will subject that polymer to irradiation, heat, and chemical attack by hydrogen and oxygen in the presence of activated redox catalysts and possibly acidic (corrosive) conditions. Obviously, the vinyl polymers previously considered are not going to be able to withstand these conditions for prolonged use as a membrane. Modern engineering polymers are designed to withstand harsh environments, and their heterocyclic structures lend themselves to the coordination of transition-metal catalysts. Polyquinolines are an example of engineering polymers. Made by the acid-catalyzed Friedlander condensation, polyquinolines have been synthesized with a wide variety of linkages (X) in the backbone and substituents on the chain (eq 2).[8] If X = oxygen, a flexible amorphous polymer soluble in common organic solvents such as chloroform and tetrahydrofuran (THF) is produced. This polymer can be cast from chloroform or tetrachloroethane to give a tough transparent film having a T_g of approximately 250 °C. If the aromatic rings are linked directly together (X = nil), the resulting rigid-rod polymer is crystalline, with $T_m > 500$ °C. This material has excellent mechanical properties and is insoluble in common solvents. As a class, polyquinolines offer excellent chemical resistance and thermal stability. The lifetime of a film of polymer 1, X = oxygen, has been estimated to be greater than 10 years at 200 °C.[8] Polyquinolines have also been evaluated as matrix resins in high-performance composites and have been found to maintain their mechanical properties past 200 h at 316 °C *in air*.[8b]



(2)

We were able to take advantage of the heterocyclic ring formation in the polymerization to form a coordinating polymer. The use of a 2-acetylpyridine monomer in the polymerization formed a copolymer having a bipyridyl site in the polyquinoline backbone. This bipyridyl site was then used to coordinate a ruthenium complex to the polymer (Figure 3). This bidentate coordination site allowed secure attachment of the ruthenium center to the polymer. The use of the metallopolymer as a sensitizing film was pursued as a means of eliminating the crossover reactions of the relays observed in homogeneous photolysis cells.

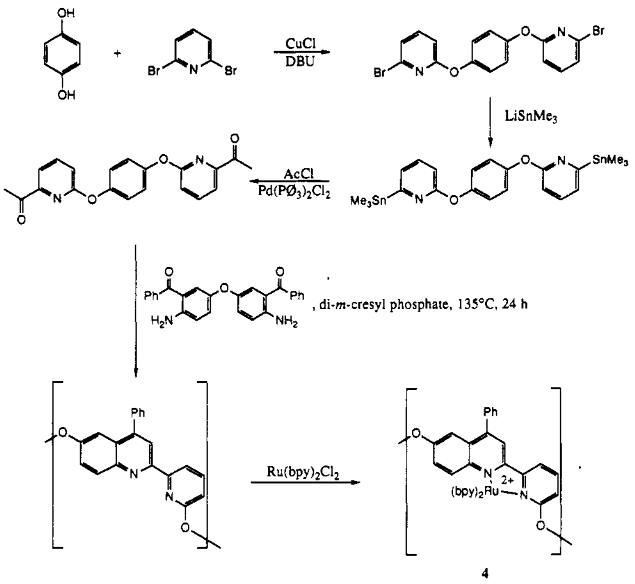
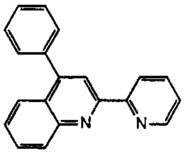


Figure 3. Synthesis of coordinating polyquinolines.

Results and Discussion

Polymer Synthesis. The synthesis of monomer, model ligand, and coordinating polymer has been previously described.[9] For convenience, the synthesis is outlined in Figure 3. The model ligand, 4-phenyl-2-(2-pyridyl)quinoline, hereafter denoted as qpy, was prepared in 54% yield by reaction of *o*-aminobenzophenone with 2-acetylpyridine at 135 °C with either di-*m*-cresylphosphate or P_2O_5/*m*-cresol as catalyst.



qpy

Ruthenium Complexes. In a procedure analogous to those used to prepare $\mathrm{Ru(bpy)_3Cl_2}$,[10,11] $[\mathrm{Ru(qpy)_3}]^{2+}$ (**2**) was prepared in 39% yield (eq 3). The product was a black, microcrystalline solid that was purified by chromatography. Unlike $[\mathrm{Ru(bpy)_3}]^{2+}$, the qpy complex was not soluble in water.

$$\mathrm{RuCl_3} + 3\,\mathrm{qpy} \xrightarrow[\text{2. NH}_4\text{PF}_6]{\text{1. EtOH, Et}_3\text{N}} \underset{\mathbf{2}}{[\mathrm{Ru(qpy)_3}](\mathrm{PF_6})_2} \tag{3}$$

The model ruthenium complex, **3**, was synthesized by rapidly heating to reflux a mixture of $\mathrm{Ru(bpy)_2Cl_2}$ and the qpy ligand in ethylene glycol (eq 4). When the reaction

$$\mathrm{Ru(bpy)_2Cl_2} + \mathrm{qpy} \xrightarrow[\substack{\text{2. 120°C, 24h} \\ \text{3. NH}_4\text{PF}_6}]{\text{1. HOCH}_2\text{CH}_2\text{OH}} \underset{\mathbf{3}}{[\mathrm{Ru(bpy)_2\,qpy}](\mathrm{PF_6})_2} \tag{4}$$

was finished, the mixture was diluted with water, and the product was precipitated as the hexafluorophosphate salt. The complex was purified by chromatography to yield a brownish-orange solid in 58% yield. The model was soluble in ethanol and dichloromethane, slightly soluble in acetone, and insoluble in water.

Preparation of the polymer complex was carried out in a similar manner except *m*-cresol was added to the reaction to dissolve the polymer, and also the polymer was added

Table I
Visible Absorptions of Tris(bipyridyl) Complexes[a]

complex	λ, nm (ε, M^{-1} cm^{-1})
$[Ru(bpy)_3](PF_6)_2$	451 (6100)
$[Ru(bpy)_2qpy](PF_6)_2$	450 (7520), 485 (7330)
$[Ru(bpy)_2polym]Cl_2$	450, 485
$[Ru(qpy)_3](PF_6)_2$	491 (17 000)

[a] Measured in CH_2Cl_2.

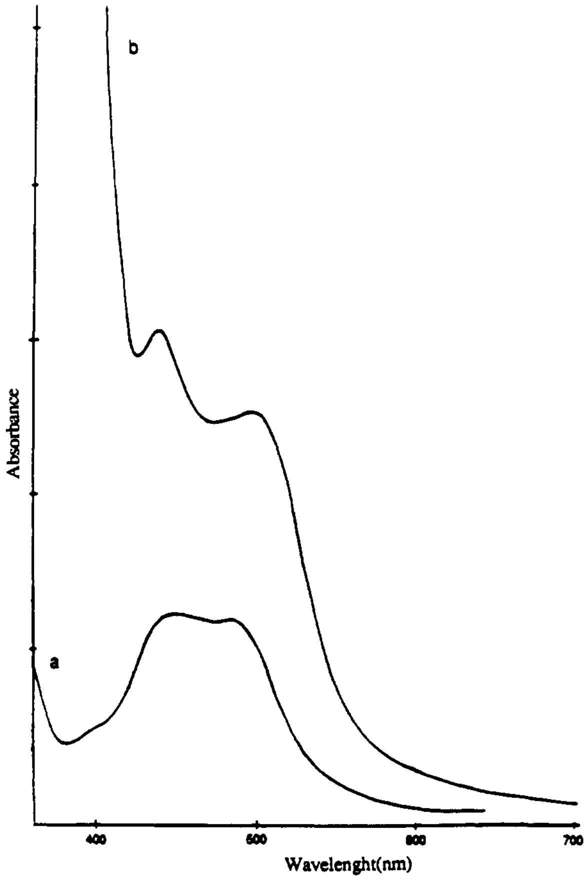


Figure 4. Visible spectra of model and polymer complexes: (a) 6.5×10^{-5} M $[Ru(bpy)_2qpy]Cl_2$ in CH_2Cl_2; (b) $[Ru(bpy)_2polym]Cl_2$, 4 mg in 10 mL of $CHCl_3$. Absorbance scales are independent for each complex.

after the reflux period. The polymer did not withstand the conditions of *m*-cresol and ethylene glycol at reflux, and the molecular weight of the polymer fell from M_w = 110 000 to 7000. By adding the polymer after the reflux period, the degradation was avoided. The polymer was isolated from the reaction solvents by precipitation in 10% triethylamine/ether solution. Polymer 4 was purified by reprecipitation from chloroform and copious washings of ethanol. The dried polymer had T_g = 273 °C. The polymer was soluble in chloroform and could be cast from solution to form tough, transparent, orange films.

Characterization. Table I shows the visible absorptions of the ruthenium complexes. The effect of coordinating a qpy ligand is a red shift of approximately 30 nm in the d–π* transition to 485 nm. This is in excellent agreement with the reported 484 nm adsorption for the coordination of 2-(2-pyridyl)quinoline.[12,13] The emergence of two bands in the visible spectrum, one band for each type of ligand, is also in agreement with the behavior of 2-(2-pyridyl)quinoline and other mixed pyridyl complexes. The visible spectrum of metallopolymer 4 is nearly identical to that of the model complex 3 (Figure 4). The polymer spectrum is broadened, and the visible cutoff at 400 nm prevents resolution of the bpy band at 450 nm.

Table II
Far-IR Spectra of Ruthenium Bipyridine Complexes[a,b]

	bpy	qpy	Ru–N (bpy)	Ru–N (qpy)
$[Ru(bpy)_3](PF_6)_2$	423		358, 339	
$[Ru(qpy)_3](PF_6)_2$		457, 405		348, 338
$[Ru(bpy)_2qpy](PF_6)_2$	423	450, 410	348[b]	
$[Ru(bpy)_2qpy]Cl_2$			337	344
$[Ru(bpy)_2polym]Cl_2$	421 (sh)	450, 410	not seen well	

[a] bpy and qpy bands are out-of-plane deformations. [b] Ru–N bands are stretches.

Table III
$E_{1/2}$ of Tris(bipyridyl)ruthenium Complexes[a]

	3+/2+	2+/1+	+1/0
$[Ru(bpy)_3](PF_6)_2$	+1.24	−1.27	−1.46
$[Ru(bpy)_2qpy](PF_6)_2$	+1.31	−1.11	−1.51
$[Ru(bpy)_2polym]Cl_2$	+1.33	−1.06	−1.49

[a] All values are in volts and are reported vs SCE. Measured in 0.1 M *n*-Bu_4NPF_6/CH_3CN.

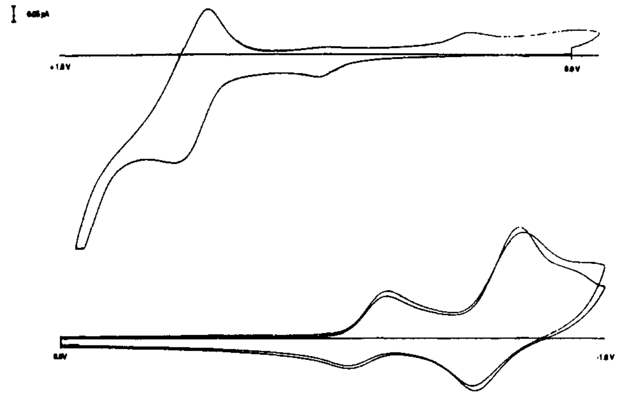


Figure 5. Cyclic voltammagram of $[Ru(bpy)_2polym]Cl_2$. Taken as a thin film on a platinum disk electrode in 0.1 M *n*-Bu_4NPF_6/CH_3CN, sweep rate = 50 mV/s.

In the near-IR, a five-band series centered at 769 cm^{-1} was identified as the ring-adjacent hydrogen deformations resulting from coordinated qpy. Bipyridine has a sharp band occurring at 759 cm^{-1}.[14] In the far-IR, assuming the bands for qpy would be in close proximity to the bpy bands,[14,15] bands occurring at 457 and 405 cm^{-1} were assigned as qpy out-of-plane deformations. The band at 405 cm^{-1} is very broad, and it is as unmistakable for qpy as the presence of the band at 421 cm^{-1} is for bpy. Weak bands at 345 and 338 cm^{-1} were assigned as Ru–N stretches (Table II).[15]

The electrochemistry of the model and polymer complexes was very clean, and both materials behaved as the parent $[Ru(bpy)_3]^{2+}$ did. The free qpy ligand undergoes a reversible reduction at −1.8 V.[10] The 3+/2+ couple potential for 3 was +1.31V (Table III) which is in good agreement with the predicted +1.37 V from a free-energy relationship between the reduction potential for the free ligand and 3+/2+ or 2+/1+ couples in the coordinated complex.[16] A reduction potential of the uncoordinated polyquinoline could not be obtained, but 4 spin-coated on a platinum disk electrode (the polymer was not electroactive while in solution) gave a very clean cyclic voltammogram with the 3+/2+ couple occurring at +1.33 V (Figure 5), in good agreement with the result from the model complex. These results show that the metallopolymer has a discrete ruthenium entity similar to the model complex, that the polyquinoline-supported complexes are (and can be) electrochemically active and that the polymer complexes undergo redox behavior.

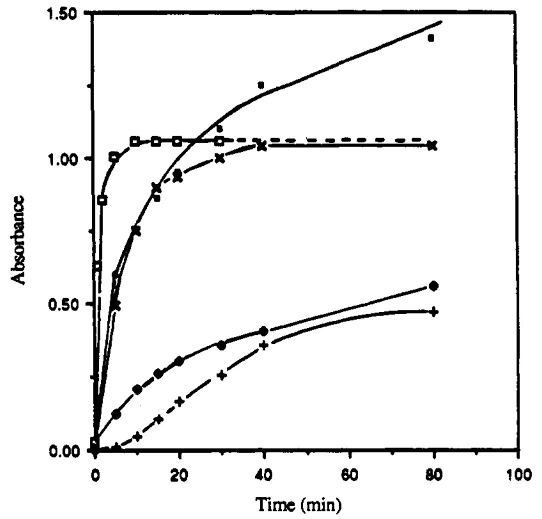


Figure 6. Sacrificial system study. Performed in 9:1 DMF/water: (×) [Ru(bpy)$_2$polym]Cl$_2$ with sodium anthracene-9-carboxylate; (+) [Ru(bpy)$_2$polym]Cl$_2$; (□) [Ru(bpy)$_2$qpy]Cl$_2$ with sodium anthracene-9-carboxylate; (♦) [Ru(bpy)$_2$qpy]Cl$_2$; (■) [Ru(bpy)$_3$]Cl$_2$.

Water Reduction. To determine whether the metallopolymer could act as a photosensitizer for the photolysis of water, the interaction of the model and the polymer complexes with MV^{2+} to generate MV$^+$ in a sacrificial system was tested. The amount of MV$^+$ produced was followed by measuring the adsorption of the reduced relay at 602 nm with increasing irradiation time. The results are shown in Figure 6. The model complex does cause the production of MV$^+$, and therefore it is capable of acting as a photosensitizer. A low molecular weight sample (M_w ~7000) of 4 that was soluble in DMF also sensitized the reaction, and it worked nearly as well as the model. A control reaction with no ruthenium present showed no formation of MV$^+$. The addition of sodium anthracene-9-carboxylate accelerated the reaction dramatically.[19] These results show that [Ru(bpy)$_2$qpy]$^{2+}$ and 4 have sufficiently long excited-state lifetimes that they can react with MV^{2+} and act as sensitizers, but the steric hindrance of the qpy and polymer ligands causes the model and polymer complexes to be quenched less efficiently than [Ru(bpy)$_3$]$^{2+}$.

One objective of this work was to use 4 as a membrane in a photolysis cell. To that end, a photolysis cell was constructed from two pieces of 1 in. diameter glass tubing sealed on one end with flat glass disks and two small sampling ports attached on the sides. The halves were mated in the center with two flanges of flat ground-glass surfaces. The polymer film was then clamped between the two glass pieces as to serve as a barrier between the cell halves. The total volume of the cell was 50 mL, and the cell was constructed of Pyrex glass to eliminate deep UV light.

To establish the effect of the polymer membrane on each "half-reaction", it was planned to study each half with a sacrificial system, and then the total photolysis would be studied. The hydrogen reaction was studied first. To be sure that polyquinolines did not inhibit this reaction, a control reaction using [Ru(bpy)$_3$]$^{2+}$ as the sensitizer was run in the presence of a ether–ether polyquinoline film (where X = O), 1, in the photolysis cell. There was no inhibition, and hydrogen was visibly evolved. A similar reaction was run with [Ru(bpy)$_2$qpy]$^{2+}$ as the sensitizer[17,18] using a variety of relays. Only in the presence of sodium anthracene-9-carboxylate was hydrogen evolution visible (Table IV). Unfortunately, the use of 4 in a film did not sensitize the reduction of water under any conditions. The analysis of the reaction mixtures for dissolved hydrogen by gas chromatography showed not even trace amounts of hydrogen were produced.[19] When it is remembered that dissolved 4 could sensitize the reduction of MV^{2+}, that 4 is electroactive and can do redox chemistry, and that 4 adsorbs visible light, it is clear that the failure of the polyquinoline membrane to sensitize the reduction of water is due to the hydrophobicity of the polymer. Undoubtedly, the aqueous relays were not able to diffuse into the polymer to the ruthenium centers. The excited complexes then lost their excitation energy through nonproductive processes.[20] With the failure of the hydrogen half-reaction, the total photolysis of water was abandoned.

Table IV
Rates of Hydrogen Production

system	volume,[a] mL/h/25 mL of solution
Ru(bpy)$_3$$^{2+}$/MV^{2+}/Pt sol[b]	5
Ru(bpy)$_2$qpy/MV^{2+}/AA$^-$/Pt sol[b]	2
Ru(bpy)$_2$qpy/MV^{2+}/Pt sol[b]	0
Ru(bpy)$_2$qpy/Co(sep)/Pt sol[b]	0
Ru(bpy)$_2$polym/MV^{2+}/AA$^-$/Pt sol[c]	0

[a] Volumes not corrected for altitude. Reactions run at pH 5 (acetate buffer), [Ru] = 1×10^{-4} M, [MV^{2+}] = 5×10^{-3} M, [Pt] = 0.05 M, [EDTA] = [TEOA] = 0.1 M, [AA$^-$] = 5×10^{-3} M. [b] Experiment conducted in the presence of an ether–ether polyquinoline film, 1. [c] Polymer deployed as a film in the photolysis cell.

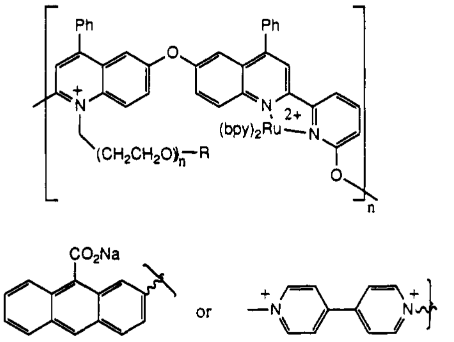


Figure 7. Quaternized polyquinolines with pendent relays.

Conclusions

It has been shown that polyquinoline and quinolyl type ruthenium complexes can be used as photosenitizers for the reduction of water. These materials absorb visible light at the proper wavelength, have sufficient excited-state lifetimes to allow reactions with an electron relay, and have a clean redox chemistry with sufficient potential to reduce methyl viologen. A sacrificial system with [Ru(bpy)$_2$qpy]$^{2+}$ as the photosensitizer did produce hydrogen upon irradiation with visible light. The use of the metallopolymer as a sensitizing film failed most likely because the hydrophobic polymer backbone prevents the relay's access to the ruthenium centers in the film.

The polymer could be modified to reduce its hydrophobicity and yet still act as a membrane. One way to do this would be to quaternize the surface of the polymer film to make it more hydrophilic by charging the polymer backbone. The relays could also be attached to the polymer chain with long hydrophilic chains that could extend into the solution but still be held in close proximity to the ruthenium center (Figure 7). A much longer lived organic relay could be substituted on the 4 position of the quinoline unit if a suitable monomer were synthesized (Figure 8). Finally, with the excellent chemical resistance

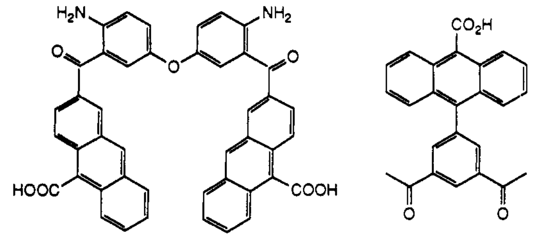


Figure 8. Possible comonomers to provide attached relays.

of polyquinolines, the metallopolymer could be used to coat an electrode or semiconductor surface.[3c] This would stop corrosion of the semiconductor surface (no small problem), and since the polymer would be in intimate contact with the electron relay, the polymer's performance would also be raised.

Experimental Section

All solvents were distilled from calcium hydride just prior to use. *m*-Cresol was fractionally distilled. Absolute ethanol (Midwest Solvents) was always USP grade and was used as obtained unless specified otherwise. Electrochemical solvents (Burdick and Jackson) were used as obtained except water, which was triply-distilled from potassium permanganate. Water and dimethylformamide (DMF) were degassed by using three freeze–thaw cycles. All reagents were used as obtained from commercial suppliers unless otherwise noted. Alumina (Aldrich) used for chromatography was neutral Brockmann I, 150 mesh, CAMAG 507C-I. Silica chromatography utilized Absorbenzien Woelm (Universal Scientific), 32–63 silica gel. Gas chromatography (GC) was performed on a Varian 3700 gas chromatograph with a 80/100-mesh 5-Å molecular sieve column (2 m × 0.125 in.) fitted with a precolumn (0.5 m × 0.125 in.) packed with the same material. Both near- and far-IR were recorded on a Nicolet SX-60 interferometer or a Beckman 4240 using potassium bromide (1% concentration) for near-IR and cesium iodide (50% concentration) for far-IR as solvents unless otherwise noted. UV/vis spectra were recorded on a Perkin-Elmer 552A spectrophotometer or Varian Techtron 635. Dilute viscosities were measured in chloroform at 25 °C using a Cannon size 50 Ubbelohde viscometer at concentrations of 0.50, 0.40, 0.31, and 0.25 g/dL. The electrochemical apparatus have been previously described.[21] Irradiations were performed with a 300 W Multi-Mirror GE projection lamp at a distance of 5 in. from the cells. Melting points were obtained on a Mel-Temp melting apparatus and are uncorrected. Elemental analyses were preformed by Atlantic Microlab, Atlanta, GA.

Tris(2,2′-bipyridyl)ruthenium bis(hexafluorophosphate)[10] and tetrakis(dimethyl sulfoxide)ruthenium dichloride[22] were prepared by literature procedures.

Bis(2,2′-bipyridyl)ruthenium(II) Dichloride. Under an Ar atmosphere, 0.048 g (0.10 mmol) of $Ru(DMSO)_4Cl_2$, 0.031 g (0.20 mmol) of 2,2′-bipyridine, and 2 mL of distilled, degassed tetrachloroethane were combined, and the resulting mixture was heated to reflux for 30 min. The reaction was allowed to cool to room temperature, and the resulting solid was filtered and washed with chloroform. The black solid was allowed to dry overnight to yield 0.033 g (68%) of product: UV/vis was identical to literature.[11]

[4-Phenyl-2-(2-pyridyl)quinolyl]bis(2,2′-bipyridyl)ruthenium Dichloride (3). A mixture of 0.073 g (0.26 mmol) of 4-phenyl-2-(2-pyridyl)quinoline, 0.12 g (0.26 mmol) of bis(2,2′-bipyridyl)ruthenium dichloride, and 10 mL of ethylene glycol was quickly heated to reflux in a 220 °C sandbath and then placed in a 120 °C oil bath for 30 min. The reaction was allowed to cool and then was poured into 250 mL of dichloromethane. The mixture was extracted with 2 × 250 mL of brine. The organic phase was dried over K_2CO_3, and the solvent was removed under reduced pressure. The residue was dissolved in a small amount of dichloromethane and eluted through a 5.5 cm × 2.5 cm slug of neutral alumina with 10% 2-propanol/dichloromethane until the starting material eluted and then with 50% acetone/methanol. The bright orange band was collected, and the solvent was removed under reduced pressure to yield 0.114 g of a dark solid. The yield was 66% based on the converted starting material. UV/vis (CH_2Cl_2): 485 nm (ϵ = 7330 cm^{-1} M^{-1}), 445 (7520), 310 (20 400), 298 (26 200). An analytical sample was prepared by dissolving the material in a mixture of water and alcohol and then precipitating the complex as the bis(hexafluorophosphate salt). Anal. Calcd for the dihydrate $C_{40}H_{34}F_{12}N_6O_2P_2Ru$: C, 47.02; H, 3.35; N, 8.22. Found: C, 46.80; H, 3.40; N, 8.19.

Poly[2,2′-[6,6′-(1,4-bisoxyphenylene)pyridine]-6,6′-bis-(4-phenylquinolinyl) ether bis[bis(2,2′-bipyridyl)ruthenium(II) dichloride]] (4). Under a static nitrogen atmosphere were combined 0.064 g (0.13 mmol) of bis(2,2′-bipyridyl)ruthenium dichloride and 2.5 mL of ethylene glycol, and the mixture was heated to 245 °C for 2.5 h. To the reaction was added 0.20 g (0.066 mmol) of coordinating polyquinoline[9] in 20 mL of *m*-cresol, and the reaction was then placed in a 120 °C oil bath and heating was continued for another 18 h. The reaction was allowed to cool and then poured into 150 mL of ether. The resulting precipitate was filtered and washed with 95% ethanol until the washings were colorless. The solid was then washed with ether and dried under reduced pressure at 100 °C overnight to yield 0.19 g (73%) of a brownish powder. UV/vis ($CHCl_3$): 500 nm; IR (film): 1595, 1240, 1210, 761, 731 (w) cm^{-1} T_g (DSC): 273 °C. Anal. Calcd for $C_{254}H_{164}Cl_4N_{20}O_{11}Ru_2$: C, 75.96; H, 4.12; N, 6.98. Found: C, 77.38; H, 4.42; N, 5.77.

Tris[4-phenyl-2-(2-pyridyl)quinolyl]ruthenium(II) Bis-(hexafluorophosphate) (3). Under a static nitrogen atmosphere, 0.10 g (0.38 mmol) of ruthenium trichloride trihydrate, 0.325 g (1.15 mmol) of 4-phenyl-2-(2-pyridyl)quinoline, 1.0 mL (17 mmol) of triethylamine, and 10 mL of absolute ethanol were heated to reflux for 24 h. The reaction was allowed to cool, and the solvent was evaporated to a volume of approximately 2.5 mL. To this solution was added 2 mL of a saturated NH_4PF_6 ethanol solution, and the mixture was placed in the refrigerator overnight. The reaction was filtered, and the resulting solid was washed with water until the washings were colorless. The solid was then washed with 150 mL of ether and dried in air. The solid was dissolved in a small amount of dichloromethane and eluted down a 15 cm × 2.5 cm column of neutral alumina with 2-propanol/dichloromethane. The fractions were separated by color. The orange fraction was collected, and the solvent was removed under reduced pressure to yield 0.19 g (39%) of an orange solid. UV/vis (CH_2Cl_2): 495 nm. IR (CsI): 457, 405, 348, 338 cm^{-1}. Anal. Calcd for $C_{60}H_{48}F_{12}N_6O_3P_2Ru$: C, 55.72; H, 3.74; N, 6.50. Found: C, 55.63; H, 3.92; N, 6.06.

Platinum Sol. To a solution of 0.0288 g (0.0592 mmol) of K_2PtCl_6 and 1.0 g of poly(ethylene glycol), MW = 900 000, in 100 mL of triply-distilled water was added 0.0051 g (0.135 mmol) of sodium borohydride. The solution was allowed to stir overnight. Anal. Calcd: Pt, 114 ppm. Found: Pt, 110 ppm.

Sacrificial System Study. A solution of 0.66 mL (50 mmol) of triethanolamine, 0.026 g (0.10 mmol) of methyl viologen dichloride monohydrate, 1.0 × 10^{-3} mol of ruthenium complex, and, if necessary, 0.012 g (0.05 mmol) of sodium anthracene-9-carboxylate in 90.00 mL of degassed DMF and 10.00 mL of degassed triply-distilled water was prepared, and 0.45 mL of the solution was charged to a 1 mm path-length quartz UV cell that was sealed with a septum and then had been purged with argon. The cell was irradiated through a Pyrex filter at a distance of 5 in. with a 300 W slide projector. The absorption at 602 nm was then measured at intervals of 1, 2, 5, 10, 15, 20, 30, 40, and 80 min.

Water Reduction. Polyquinoline films were cast from ca. 20 wt % chloroform solutions. Photolysis solutions consisted of 1.25 mL of 0.010 M methyl viologen solution, 2.5 mmol of triethanolamine or disodium ethylenediaminetetracarboxylic acid, 0.0050 mmol of ruthenium complex (1 mL of absolute ethanol was added to $[Ru(bpy)_2(qpy)](PF_6)_2$ solutions to dissolve the complex), 10 mL of the platinum sol solution, and, if necessary, 0.003 g (1 mmol) of sodium anthracene-9-carboxylate diluted to 25.00 mL with an acetate buffer (pH 5) prepared with degassed triply-distilled water. The solution was cannulated into the argon-purged photolysis cell and irradiated at a distance of 5 in. with a 300 W slide projector.

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References and Notes

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Registry No. EDTA, 60-00-4; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy)_2(qpy)^{2+}$, 137728-68-8; $Ru(qpy)_3^{2+}$, 138898-81-4; $MV^{2+}\cdot 2Cl^-$, 1910-42-5; H_2, 1333-74-0; Pt, 7440-06-4; $[HO(CH_2)_2]_3N$, 102-71-6; sodium anthracene-9-carboxylate, 16336-69-9.