

position in the  $\alpha$ -cage to the S2' position inside the  $\beta$ -cage where it interacts with only two waters and becomes  $\text{Ag}^0(\text{A})$ . This model accounts for the inequivalence of the water molecules around  $\text{Ag}^0(\text{C})$  and conversion of  $\text{Ag}^0(\text{C})$  to  $\text{Ag}^0(\text{A})$  in sodium-rich zeolites.

While the location of  $\text{Ag}^0(\text{C})$  in  $\text{Mg}^{2+}$ -rich zeolites is also probably at site S2\* in the  $\alpha$ -cage, the decay product of  $\text{Ag}^0(\text{C})$  is unclear. It should be noted that the possibility of  $\text{Ag}^0(\text{C})$  being inside the  $\beta$ -cages seems ruled out by comparison of its thermal instability with  $\text{Ag}^0(\text{D})$  observed in X and Y zeolites which has been shown<sup>20</sup> to be thermally stable and to interact with four equivalent water molecules inside the  $\beta$ -cage.

In the photochemical water cleavage experiments,<sup>10a</sup> zeolites exchanged with  $\text{Mg}^{2+}$  were found to be most efficient. Isolated or small clusters of silver atoms have been implicated in the water splitting. Since  $\text{Ag}^0(\text{C})$  is enhanced by  $\text{Mg}^{2+}$ , we suggest that it could be the active intermediate in such a reaction.

### Conclusions

The minor species  $\text{Ag}^0(\text{C})$  observed earlier in  $\text{Li}_{12}\text{A}$  and  $\text{Ca}_6\text{A}$  zeolites becomes a major  $\text{Ag}^0$  species by ion exchange of A zeolite

with  $\text{Mg}^{2+}$  prior to doping by  $\text{Ag}^+$ . In A zeolites containing  $\text{Mg}^{2+}$  but still richer in sodium,  $\text{Ag}^0(\text{C})$  decays to  $\text{Ag}^0(\text{A})$  on warming above 100 K. In fully sodium-exchanged A zeolite only  $\text{Ag}^0(\text{A})$  is seen. ESEM analysis indicates that  $\text{Ag}^0(\text{C})$  interacts with two water molecules at an  $\text{Ag}^0\text{-O}_w$  distance of 0.26 nm, which are suggested to be in the  $\alpha$ -cage, and with two more water molecules at an  $\text{Ag}^0\text{-O}_w$  distance of 0.29 nm, which are suggested to be in the  $\beta$ -cage. We suggest that  $\text{Ag}^0(\text{C})$  is located at site S2\* in the  $\alpha$ -cage just above the six-ring window between the  $\alpha$ - and  $\beta$ -cages and moves to S2' sites in the  $\beta$ -cage below the six-ring window to form  $\text{Ag}^0(\text{A})$  when the zeolite contains sufficient numbers of  $\text{Na}^+$  ions.

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Registry No. Ag, 7440-22-4; Mg, 7439-95-4; Na, 7440-23-5.

## Electrochemistry, Spectroelectrochemistry, and Photochemistry of a Series of New Covalently Linked Tris(2,2'-bipyridine)ruthenium(II)/Diquat Complexes

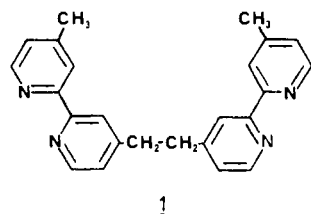
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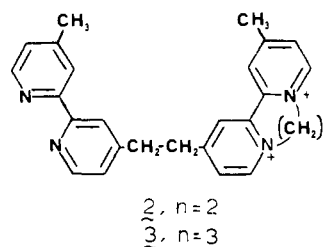
**Abstract:** A method for preparing covalently linked photosensitizer/electron-acceptor complexes using a novel dimer of 4,4'-dimethyl-2,2'-bipyridine has been found. N,N'-Dialkylation of one end of the dimer results in a "diquat"-modified ligand which can be bound to Ru(II) in combination with other substituted or unsubstituted bipyridines. A series of tris(bipyridine)ruthenium/diquat complexes was prepared in which the properties of both the diquat electron acceptor and the ruthenium photosensitizer were varied. The effect of the detailed structure of these linked systems on their electrochemical, spectroelectrochemical, and photophysical properties was investigated.

Photoinduced bimolecular electron-transfer reactions involving a tris(bipyridine)ruthenium photosensitizer and an electron acceptor such as the dipyrindinium salt paraquat have been extensively investigated.<sup>1-4</sup> A few examples of similar unimolecular systems have also been reported.<sup>5-7</sup>

In order to examine the relationships between the detailed structures of both the photosensitizing moiety and electron acceptor, and the photochemical and electrochemical properties of the system, a series of linked tris(bipyridine)ruthenium/electron-acceptor complexes has been prepared. The synthetic method by which an inert, covalent linkage between photosensitizer and acceptor has been accomplished is based on a novel dimer of 4,4'-dimethyl-2,2'-bipyridine, Mebpy-Mebpy, **1**. Conversion of



one of the linked bipyridines of **1** to an N,N'-bridged diquatery salt (diquat) produces an electron acceptor with properties similar to those of paraquat.<sup>4</sup> This conversion yields the ligands Mebpy-*n*DQ<sup>2+</sup>, where *n* is the number of methylene units in the chain linking the pyridine nitrogens (**2**, *n* = 2; **3**, *n* = 3).



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The unmodified bipyridine end of 2 or 3 can then be complexed to ruthenium(II). A series of mixed-ligand complexes of the type  $\text{RuL}_2(\text{Mebpy}-n\text{DQ}^{2+})^{4+}$ , where L = substituted or unsubstituted 2,2'-bipyridine and  $n = 2$  or 3, has been prepared (4-8). Also prepared was the symmetrical tris complex of  $\text{Mebpy}-3\text{DQ}^{2+}$ , 9. The series of complexes is listed as follows: 4,  $\text{Ru}(\text{bpy})_2(\text{Mebpy}-2\text{DQ}^{2+})^{4+}$ ; 5,  $\text{Ru}(\text{bpy})_2(\text{Mebpy}-3\text{DQ}^{2+})^{4+}$ ; 6,  $\text{Ru}(\text{Me}_2\text{bpy})_2(\text{Mebpy}-3\text{DQ}^{2+})^{4+}$ ; 7,  $\text{Ru}(\text{Me}_2\text{bpy})_2(\text{Mebpy}-3\text{DQ}^{2+})^{4+}$ ; 8,  $\text{Ru}[(\text{COOEt})_2\text{bpy}]_2(\text{Mebpy}-3\text{DQ}^{2+})^{4+}$ ; and 9,  $\text{Ru}(\text{Mebpy}-3\text{DQ}^{2+})_3^{8+}$ , where  $\text{bpy} = 2,2'$ -bipyridine,  $\text{Me}_2\text{bpy} = 4,4'$ -dimethyl-2,2'-bipyridine,  $\text{Me}_4\text{bpy} = 4,4',5,5'$ -tetramethyl-2,2'-bipyridine, and  $(\text{COOEt})_2\text{bpy} = 4,4'$ -bis(carboxyethyl)-2,2'-bipyridine.

This synthetic approach has allowed us to vary the properties of the redox system components relatively independently of one another. The reduction potential of the diquat electron acceptor, for example, can be varied by several hundred millivolts by changing the length of the N,N' carbon bridge. Likewise, for the complexes  $\text{RuL}_2\text{Mebpy}-n\text{DQ}^{2+}$ , both the ground-state and excited-state redox properties of the tris(bipyridine)ruthenium center can be altered significantly by changes in substitution on L.<sup>8,9</sup>

The series of complexes described herein thus exhibits a wide range of electrochemical properties. The potentials at which oxidation of the electron donor and reduction of the electron acceptor occur are obviously important considerations in the design of photoredox systems since these factors determine, among other things, the thermodynamic driving force for the electron-transfer quenching process.

Varying the substituents on the tris(bipyridine)ruthenium chromophore would also be expected to result in changes in the detailed nature of the electronically excited state. The excited state of a  $\text{RuL}_3^{2+}$  photosensitizer can be depicted as  $(\text{Ru}^{\text{III}}\text{L}_2\text{L}^-)^{2+}$ .<sup>10,11</sup> It therefore electronically resembles the first reduction product,  $\text{RuL}_3^{1+}$ , in that the highest energy electron presumably is localized in the same ligand-based  $\pi^*$  orbital.<sup>4,11</sup> With the mixed-ligand complexes described here, the relative reduction potentials of the ligands determine which ligand contains the extra electron in the formal  $\text{Ru}^{\text{I}}$ -reduced species and likewise determine the lowest energy location of the electron in the excited state. This type of structural detail is expected to affect electron-transfer rates in both the forward and reverse (recombination) directions.

All the  $\text{RuL}_2(\text{Mebpy}-n\text{DQ}^{2+})^{4+}$  complexes studied, with the exception of the L =  $(\text{COOEt})_2\text{bpy}$  complex, are nonluminescent. Efficient intramolecular electron transfer from the  $\text{Ru}(\text{bpy})_3^{2+}$  excited state to the diquat is responsible for the emission quenching. Irradiation of the  $\text{RuL}_2(\text{Mebpy}-n\text{DQ}^{2+})^{4+}$  complexes with visible light in the presence of large excesses of triethanolamine (TEOA) as a sacrificial electron donor results in an accumulation of the diquat radical cation in solution. Reduction of Ru(III) by TEOA therefore apparently can compete with the back electron transfer from the reduced diquat.

The electrochemical and spectral properties of these linked photosensitizer/acceptor molecules are discussed in greater detail in the following sections. Preliminary studies of their photochemical properties are also included.

## Experimental Section

**Materials.** 4,4'-Dimethyl-2,2'-bipyridine ( $\text{Me}_2\text{bpy}$ ) was supplied by Reilly Tar and Chemical, Indianapolis, IN, and was recrystallized from ethyl acetate before use.

4,4',5,5'-Tetramethyl-2,2'-bipyridine ( $\text{Me}_4\text{bpy}$ ) was prepared by conventional methods from 3,4-lutidine (Aldrich).<sup>12</sup>

4,4'-Bis(carboxyethyl)-2,2'-bipyridine,  $[(\text{COOEt})_2\text{bpy}]$  was prepared as previously described.<sup>13</sup>

*cis*-Dichlorobis(bipyridine)ruthenium ( $\text{Ru}(\text{bpy})_2\text{Cl}_2$ ) was prepared by the method of Meyer et al.<sup>1</sup>

Dichlorotetrakis(dimethyl sulfoxide)ruthenium ( $\text{Ru}(\text{Me}_2\text{SO})_4\text{Cl}_2$ ) was prepared as described elsewhere.<sup>15</sup>

**Preparation of Bipyridine Dimer.** 1,2-Bis[4-(4'-methyl-2,2'-bipyridyl)]ethane ( $\text{Mebpy}-\text{Mebpy}$ ), 1. A solution containing 5 g of  $\text{Me}_2\text{bpy}$  in freshly distilled THF was added dropwise to 1 equiv of lithium diisopropylamide. This addition was conducted under  $\text{N}_2$  at  $-78^\circ\text{C}$ . The resulting dark brown solution was stirred at low temperature for 1-2 h. Five milliliters of 1,2-dibromoethane (Aldrich, 99%) was then added quickly, and reaction mixture was warmed to room temperature. Water was then added, and bipyridine products were extracted from the resulting cloudy yellow solution with ether ( $3 \times 100$  mL). Combined organic phases were evaporated to dryness. The dimer was isolated from the product mixture by column chromatography on silica gel, eluting with acetone/methylene chloride (10% v/v). Recrystallization from ethyl acetate yielded a white crystalline product (yield 1.8-2.2 g, 36-44%).  $\text{Mebpy}-\text{Mebpy}$  was characterized by mass spectrometry and NMR.

**Preparation of Linked Bipyridine-Diquat Ligands.** ( $\text{Mebpy}-2\text{DQ}^{2+}$ )( $\text{PF}_6$ )<sub>2</sub>, 2.  $\text{Mebpy}-\text{Mebpy}$  (0.40 g) was dissolved in 6 mL of hot *o*-dichlorobenzene, and 100  $\mu\text{L}$  of 1,2-dibromoethane (Aldrich, 99%) was added. This mixture was degassed by five freeze-pump-thaw cycles and left under vacuum. The sealed tube was then heated in a paraffin bath maintained at  $170$ - $185^\circ\text{C}$  for 2 days. Resulting dark brown, fine solid was collected by filtration and purified by medium-pressure liquid chromatography on silica gel. Dark, low  $R_f$  impurities were removed by elution with 10% saturated aqueous  $\text{KNO}_3$ , 40% water 50% acetonitrile. A second column, eluted with 5% saturated aqueous  $\text{KNO}_3$ , 45% water 50% acetonitrile, was used for further purifications.  $\text{Mebpy}-2\text{DQ}^{2+}$  eluted as a colorless band near the solvent front. Following evaporation of acetonitrile from the eluent, aqueous  $\text{NH}_4\text{PF}_6$  was added. The precipitated  $\text{PF}_6^-$  salt of  $\text{Mebpy}-2\text{DQ}^{2+}$  was collected by filtration and dried in a vacuum oven at  $45^\circ\text{C}$ . The resulting light-gray powder (0.091 g, 12%) was shown to be pure by TLC and NMR.

( $\text{Mebpy}-3\text{DQ}^{2+}$ )( $\text{PF}_6$ )<sub>2</sub>. This compound was prepared in analogous fashion to ( $\text{Mebpy}-2\text{DQ}^{2+}$ )( $\text{PF}_6$ )<sub>2</sub> by using 1 g of  $\text{Mebpy}-\text{Mebpy}$  and 280  $\mu\text{L}$  of 1,3 dibromopropane (Aldrich, 99%) in 15 mL of *o*-dichlorobenzene. After this mixture was degassed, the sealed tube was immersed in a paraffin bath and temperature was maintained at  $160$ - $170^\circ\text{C}$  for 4 days. Filtration of the hot solution yielded a fine, white solid, ( $\text{Mebpy}-3\text{DQ}^{2+}$ )Br<sub>2</sub>. This salt was dissolved in water and precipitated by the dropwise addition of aqueous  $\text{NH}_4\text{PF}_6$ . ( $\text{Mebpy}-3\text{DQ}^{2+}$ )( $\text{PF}_6$ )<sub>2</sub> was collected by filtration and washed with cold absolute ether. The light pink-gray solid (0.98 g, 51%) was shown to be pure as isolated by TLC and NMR.

**Preparation of Ruthenium(II) Complexes.**  $[\text{Ru}(\text{bpy})_2(\text{Mebpy}-2\text{DQ}^{2+})](\text{PF}_6)_4$ . A mixture of  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (14 mg) in 5 mL of ethylene glycol was heated quickly to boiling and then immersed in a paraffin bath maintained at  $130^\circ\text{C}$ . To the resulting red-orange solution, ( $\text{Mebpy}-2\text{DQ}^{2+}$ )( $\text{PF}_6$ )<sub>2</sub> (20 mg) was added. After 30 min, the reaction mixture was cooled to room temperature, diluted 1:1 with distilled water, and filtered. Aqueous  $\text{NH}_4\text{PF}_6$  was added dropwise, and the resulting orange solid was collected by filtration. Column chromatography on silica gel (eluent: 10% saturated aqueous  $\text{KNO}_3$ /40% water/50% acetonitrile) was used for purification. Acetonitrile was removed by evaporation from those fractions of eluent containing only the desired complex (as determined by TLC). The solution was filtered, and aqueous  $\text{NH}_4\text{PF}_6$  was added to the filtrate.  $[\text{Ru}(\text{bpy})_2(\text{Mebpy}-2\text{DQ}^{2+})](\text{PF}_6)_4$  was collected by filtration (yield 13 mg, 33%). Anal. Calcd for  $\text{RuC}_{46}\text{H}_{42}\text{N}_8\text{P}_4\text{F}_{24}$ : C, 39.81%; H, 3.05%; N, 8.07%. Found: C, 39.58%; H, 3.12%; N, 7.77%.

$[\text{Ru}(\text{bpy})_2(\text{Mebpy}-3\text{DQ}^{2+})](\text{PF}_6)_4$ . This complex was prepared in analogous fashion to the synthesis of  $[\text{Ru}(\text{bpy})_2(\text{Mebpy}-2\text{DQ}^{2+})](\text{PF}_6)_4$ , using  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (69 mg) and ( $\text{Mebpy}-3\text{DQ}^{2+}$ )( $\text{PF}_6$ )<sub>2</sub> (100 mg) in 25 mL of ethylene glycol. Isolation and purification of the complex were carried out by the same methods described above (yield 58 mg, 34%). Anal. Calcd for  $\text{RuC}_{47}\text{H}_{44}\text{N}_8\text{P}_4\text{F}_{24}$ : C, 40.27%; H, 3.16%; N, 7.99%. Found: C, 40.43%; H, 3.39%; N, 8.01%.

$[\text{Ru}(\text{Me}_2\text{bpy})_2(\text{Mebpy}-3\text{DQ}^{2+})](\text{PF}_6)_4$ . A solution of  $\text{Ru}(\text{Me}_2\text{SO})_4\text{Cl}_2$  (38 mg) in 25 mL of ethylene glycol was heated to the boiling point and then immersed in a paraffin bath maintained at  $120^\circ\text{C}$ . A mixture of the two ligands,  $\text{Me}_2\text{bpy}$  (29 mg) and ( $\text{Mebpy}-3\text{DQ}^{2+}$ )( $\text{PF}_6$ )<sub>2</sub> (55 mg), in a 2:1 ratio was added with stirring. After 30 min, the reaction mixture

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was cooled to room temperature and diluted 1:1 with water. Excess aqueous  $\text{NH}_4\text{PF}_6$  was added, and the orange precipitate was collected by filtration. A mixture of complexes was obtained from which the desired mixed-ligand complex was isolated by column chromatography on silica gel. Elution with 10% saturated aqueous  $\text{KNO}_3$ /40% water/50% acetonitrile resulted in good separation of the complexes. Acetonitrile was evaporated from eluent, and aqueous  $\text{NH}_4\text{PF}_6$  was added. The orange precipitate was collected by filtration, recrystallized from acetone/ethanol, and dried under a vacuum at room temperature (yield 15 mg, 13%). Anal. Calcd for  $\text{RuC}_{51}\text{H}_{52}\text{N}_8\text{P}_4\text{F}_{24}$ : C, 42.02%; H, 3.60%; N, 7.69%. Found: C, 41.82%; H, 3.56%; N, 7.48%.

**[Ru(Me<sub>4</sub>bpy)<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)](PF<sub>6</sub>)<sub>4</sub>.** This complex was prepared in analogous fashion to [Ru(Me<sub>2</sub>bpy)<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)](PF<sub>6</sub>)<sub>4</sub>. Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub> (69 mg) was combined with Me<sub>4</sub>bpy (61 mg) and (Mebpy-3DQ<sup>2+</sup>)(PF<sub>6</sub>)<sub>2</sub> (100 mg) in hot ethylene glycol as described above. The resulting mixture of complexes was separated by column chromatography, and the desired complex was isolated and purified by the methods described above (yield 31 mg, 15%). Anal. Calcd for  $\text{RuC}_{55}\text{H}_{60}\text{N}_8\text{P}_4\text{F}_{24}$ : C, 43.63%; H, 3.99%; N, 7.40%. Found: C, 43.37%; H, 4.19%; N, 7.13%.

**[Ru((COOEt)<sub>2</sub>bpy)<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)](PF<sub>6</sub>)<sub>4</sub>.** This complex was prepared according to the method described for [Ru(Me<sub>2</sub>bpy)<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)](PF<sub>6</sub>)<sub>4</sub>. Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub> (69 mg) was combined with (COOEt)<sub>2</sub>bpy (86 mg) and (Mebpy-3DQ<sup>2+</sup>)(PF<sub>6</sub>)<sub>2</sub> (100 mg) in 25 mL of hot ethylene glycol as described above. The mixture of complexes was separated by column chromatography. Elution with acetonitrile removed Ru[(COOEt)<sub>2</sub>bpy]<sub>3</sub><sup>3+</sup> from the column. Eluent was changed to 10% aqueous  $\text{KNO}_3$ /40% water/50% acetonitrile, to elute the desired mixed-ligand complex. Isolation from the eluent and purification of the complex were accomplished by methods described above (yield 45 mg, 19%). Anal. Calcd for  $\text{RuC}_{59}\text{H}_{60}\text{N}_8\text{O}_8\text{P}_4\text{F}_{24}$ : C, 41.93%; H, 3.58%; N, 6.63%. Found: C, 41.65%; H, 3.45%; N, 6.75%.

**[Ru(Mebpy-3DQ<sup>2+</sup>)<sub>3</sub>](PF<sub>6</sub>)<sub>8</sub>.** Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub> (23 mg) was added to 10 mL of ethylene glycol. The solution was heated quickly to reflux and then immersed in a paraffin bath maintained at 120 °C. Three equivalents of (Mebpy-3DQ<sup>2+</sup>)(PF<sub>6</sub>)<sub>2</sub> (100 mg) was added; heating and stirring were continued for 40 min. After cooling to room temperature, the complex was precipitated by addition of water and aqueous  $\text{NH}_4\text{PF}_6$ . The dark-orange solid was collected by filtration, recrystallized from acetone/ethanol, and dried at room temperature under vacuum (yield 55 mg, 46%).

**[Ru((COOEt)<sub>2</sub>bpy)<sub>2</sub>(Me<sub>2</sub>bpy)](PF<sub>6</sub>)<sub>2</sub>.** One hundred milligrams of Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub> and 10 mL of ethylene glycol were heated near reflux until the Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub> went into solution. (COOEt)<sub>2</sub>bpy (120 mg, 2 equiv) was added and heating continued for approximately 5 min until the solution became deep reddish brown. Approximately 0.1 g of LiCl and an additional 10 mL of ethylene glycol were then added with continued heating until the LiCl dissolved (approximately 3 min). The cooled solution was extracted with  $\text{CH}_2\text{Cl}_2$  to isolate the Ru[(COOEt)<sub>2</sub>bpy]<sub>2</sub>Cl<sub>2</sub>. The  $\text{CH}_2\text{Cl}_2$  was removed by rotary evaporation and the residue redissolved in ethylene glycol containing 36.7 mg of Me<sub>2</sub>bpy. The solution was heated until it turned deep orange. The complex was precipitated as the PF<sub>6</sub><sup>-</sup> salt by the addition of aqueous  $\text{NH}_4\text{PF}_6$  to the cooled ethylene glycol solution. Anal. Calcd for  $\text{RuC}_{44}\text{H}_{44}\text{N}_6\text{O}_4\text{P}_2\text{F}_{12}$ : C, 44.6%; H, 3.75%; N, 7.10%. Found: C, 44.43; H, 3.89; N, 7.44.

**Cyclic Voltammetry.** The equipment and cells for cyclic voltammetry experiments have been described elsewhere.<sup>8,16</sup> Ruthenium complex oxidations were carried out in acetonitrile (Burdick & Jackson, "Distilled in Glass") with a platinum electrode. Ligand and ruthenium complex reduction potentials were measured in dimethylformamide (Burdick & Jackson, "Distilled in Glass") with a glassy carbon electrode. In both solvents, tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. All potentials were measured relative to SCE. Cyclic voltammograms were recorded after addition of the ligand or complex to a previously degassed solution of supporting electrolyte in the working electrode compartment of the cell. This was necessary due to the instability of these compounds in DMF in the presence of O<sub>2</sub> and light.<sup>17</sup>

**Spectroelectrochemistry.** The equipment and optically transparent thin-layer electrochemical (OTTLE) cell have been described previously.<sup>8,16</sup> Spectra were recorded on a Perkin-Elmer 552A UV-vis spectro-

Table I. Reduction<sup>a</sup> of Diquats and Diquat/bpy Ligands

compound	DQ <sup>2+/1+</sup>		DQ <sup>1+/0</sup>		bpy <sup>0/1-</sup> E <sub>1/2</sub>
	E <sub>1/2</sub>	ΔE <sub>p</sub>	E <sub>1/2</sub>	ΔE <sub>p</sub>	
2DQ <sup>2+</sup> <sup>b</sup>	-0.38	0.74	-0.78	0.79	
3DQ <sup>2+</sup> <sup>b</sup>	-0.58		-0.80		
Me <sub>2</sub> -2DQ <sup>2+</sup>	-0.48	0.65	-0.89	0.67	
Me <sub>2</sub> -3DQ <sup>2+</sup>	-0.67	0.61	-0.91	0.62	
Mebpy-2DQ <sup>2+</sup>	-0.47	0.61	-0.88	0.62	-2.19
Mebpy-3DQ <sup>2+</sup>	-0.65	0.60	-0.89	0.63	-2.19

<sup>a</sup> Potentials vs. SCE in DMF/0.10 M TBAPF<sub>6</sub>. <sup>b</sup> Obtained from ref 9.

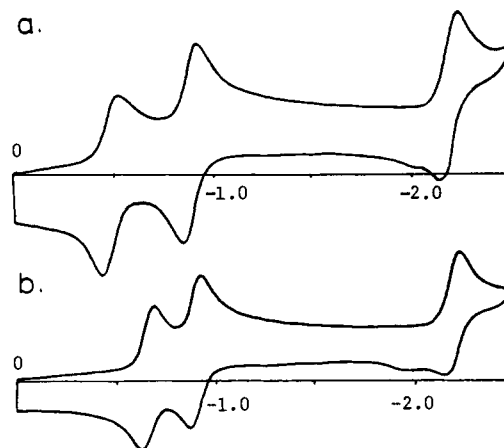


Figure 1. Cyclic voltammograms of (a) (Mebpy-2DQ)(PF<sub>6</sub>)<sub>2</sub> and (b) (Mebpy-3DQ)(PF<sub>6</sub>)<sub>2</sub> in DMF/0.10 M TBAPF<sub>6</sub> on glassy carbon (potentials vs. SCE).

photometer and a Perkin-Elmer 561 recorder. The cell path length was  $5.1 \times 10^{-3}$  cm. DMF was used as the solvent, and tetrabutylammonium hexafluorophosphate (0.1 M) was used as supporting electrolyte in all cases. Solutions of the ligands ( $3.0 \times 10^{-3}$  M) and ruthenium complexes ( $1.5 \times 10^{-3}$  M) were prepared immediately before addition to the cell and were purged with N<sub>2</sub> for 15 min before use. Electronic absorption spectra in the wavelength range 315–900 nm of the reduced species were recorded after drawing new solution into the OTTLE cell, applying the desired potential to the gold minigrad electrode, and waiting until minimal current was being passed (1–5 min). A spectrum was recorded following reoxidation of the solution to check the chemical reversibility at each potential step.

**Emission.** Relative emission intensities and wavelength maxima were measured on a Perkin-Elmer MPF-44B fluorescence spectrophotometer. Solutions of the ruthenium bipyridine-diquat complexes, and the appropriate diquat-free tris(bipyridine)ruthenium complexes (i.e., Mebpy-*n*DQ<sup>2+</sup> replaced by Me<sub>2</sub>bpy) to which they were compared, were prepared such that they exhibited the same absorption at the wavelengths corresponding to their absorption maxima. The emission spectra of these solutions were recorded with the same instrumental conditions. The excitation wavelengths used were the wavelengths of maximum absorption for each complex.

**Photochemistry.** Dilute solutions of the [RuL<sub>2</sub>(Mebpy-*n*DQ<sup>2+</sup>)]<sup>4+</sup> complexes in 1:2:7 triethanolamine/acetonitrile/water were prepared and degassed by nitrogen purge in the dark. Initial spectra were then recorded. Visible irradiation of the solutions was carried out with a slide projector lamp. Spectra were recorded at various irradiation times. For comparison, a spectrum of the same solution following addition of 1 drop of aqueous sodium hydrosulfite, a chemical reducing agent, was recorded. Also, irradiation of identical TEOA-containing solutions of Mebpy-*n*DQ<sup>2+</sup> was also carried out to determine if any direct photoreduction of diquat occurred. No DQ<sup>+</sup> products were observed for the uncomplexed ligand.<sup>7</sup>

## Results and Discussion

**Electrochemistry.** Diquat species (*n*DQ<sup>2+</sup>) undergo two reversible, one-electron reductions in roughly the same range of potentials as do alkyl viologens. The reduction potentials of several diquat species are given in Table I. The first reduction potential is seen to shift by 200 mV upon increasing *n*, the length of the alkyl chain bridging the quaternary nitrogens, from 2 to 3, a consequence of the increased dihedral angle and therefore reduced

(16) Elliott, C. M.; Hershenhart, E.; Finke, R. G.; Smith, B. L. *J. Am. Chem. Soc.* **1981**, *103*, 5558.

(17) In dimethylformamide, rapid photodecomposition of the RuL<sub>2</sub>(Mebpy-*n*DQ<sup>2+</sup>) complexes is observed when oxygen is present. This photooxidation process involves at least two steps. Cyclic voltammetry of the photooxidation product shows the disappearance of the diquat reductions, while the ligand-based tris(bipyridine)Ru(II) reductions are unchanged.

**Table II.** Redox Potentials for Various RuL<sub>3</sub> and RuL<sub>2</sub>L-DQ<sup>2+</sup> Complexes

entry	complex	Ru <sup>3+/2+</sup>	DQ <sup>2+/1+</sup>	DQ <sup>1+/0</sup>	Ru <sup>2+/1+</sup>	Ru <sup>1+/0</sup>	Ru <sup>0/1-</sup>	Ru <sup>1-/2-</sup>	Ru <sup>2-/3-</sup>	Ru <sup>3+/2+*</sup>	Ru <sup>1+/2+*</sup>
1	Ru(bpy) <sub>2</sub> (Mebpy-2DQ <sup>2+</sup> )	+1.24	-0.44	-0.84	-1.29	-1.47	-1.74				
2	Ru(bpy) <sub>2</sub> (Mebpy-3DQ <sup>2+</sup> )	+1.24	-0.63	-0.86	-1.29	-1.47	-1.75				
3	Ru(Me <sub>2</sub> bpy) <sub>2</sub> (Mebpy-3DQ <sup>2+</sup> )	+1.12	-0.62	-0.85	-1.35	-1.53	-1.79				
4	Ru(Me <sub>2</sub> bpy) <sub>2</sub> (Mebpy-3DQ <sup>2+</sup> )	+1.06	-0.62	-0.85	-1.39	-1.62	-1.92				
5	Ru[(COOEt) <sub>2</sub> bpy] <sub>2</sub> (Mebpy-3DQ <sup>2+</sup> )	+1.43	-0.62	-0.86	-0.86	-1.04	-1.51	-1.70	-2.06		
6	Ru(Mebpy-3DQ <sup>2+</sup> ) <sub>3</sub>	+1.15	-0.62	-0.85	-1.37	-1.55	-1.81				
7	Ru(bpy) <sub>3</sub> <sup>c</sup>	+1.24			-1.27	-1.46	-1.70			-0.79	+0.76
8	Ru(Me <sub>2</sub> bpy) <sub>3</sub> <sup>c</sup>	+1.13			-1.37	-1.54	-1.80			-0.85	+0.67
9	Ru(Me <sub>4</sub> bpy) <sub>3</sub>	+1.06			-1.49	-1.70	-1.99			-0.99	+0.56
10	Ru[(COOEt) <sub>2</sub> bpy] <sub>3</sub> <sup>c</sup>	+1.54			-0.89	-1.01	-1.19	-1.63	-1.83	-0.42	+1.07
11	Ru[(COOEt) <sub>2</sub> bpy] <sub>2</sub> (Me <sub>2</sub> bpy)	+1.44			-0.88	-1.11	-1.52	-1.73	-2.05	-0.44	+1.01

<sup>a</sup>Ru(II/III) potentials were measured in acetonitrile/0.10 M TBAPF<sub>6</sub> at glassy carbon. All other potentials were obtained in DMF/0.10 M TBAPF<sub>6</sub>. <sup>b</sup>These potentials were calculated as suggested in ref 19. The λ<sub>max</sub> for the emission in H<sub>2</sub>O/acetonitrile (1:1) was used to calculate the difference in excited-state potential. These values should therefore be considered as rough approximations. <sup>c</sup>Obtained from ref 9.

conjugation of the 3DQ<sup>2+</sup>. The second reduction potential is shifted only slightly cathodically. The addition of alkyl substituents to the pyridinium rings in the 4 and 4' positions shifts the reduction potential ~100 mV in the negative direction relative to unsubstituted nDQ<sup>2+</sup>.

*E*<sub>1/2</sub> potentials of the Mebpy-nDQ<sup>2+</sup> ligands are also listed in Table I, and the cyclic voltammograms are shown in Figure 1. These compounds exhibit redox properties quite similar to those of the corresponding Me<sub>2</sub>-n(diquats) but are slightly more easily reduced (by 10–20 mV). The Mebpy-nDQ<sup>2+</sup> ligands also exhibit a third one-electron wave corresponding to reduction of the unmodified bipyridine. This process (as for simple bipyridines) is not completely reversible; the shape of the wave and its scan rate dependence indicate that an irreversible chemical process follows the reduction of the bipyridine. The *E*<sub>1/2</sub> value agrees closely with values previously reported for reduction of 4,4'-dimethyl-2,2'-bipyridine.<sup>8</sup>

When Mebpy-nDQ<sup>2+</sup> ligands are incorporated into tris(bipyridine)ruthenium complexes, the electrochemistry observed is qualitatively the simple superposition of the DQ<sup>2+</sup> and RuL<sub>3</sub> electrochemistries. There are, however, subtle differences. For example, the DQ<sup>2+/1+</sup> and DQ<sup>1+/0</sup> couples are shifted anodically by 20–40 mV relative to the free ligand, ostensibly due to electrostatic effects.

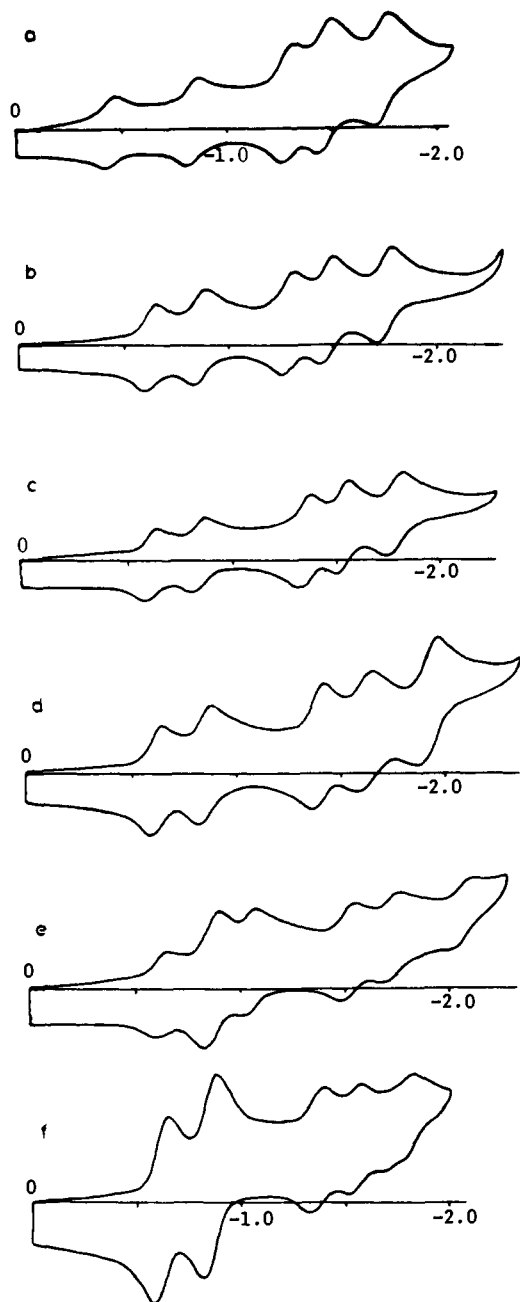
The electrochemistry associated with the RuL<sub>3</sub> center in these complexes is typical of other tris(bipyridine)ruthenium complexes. There is a primarily metal-centered oxidation (+1.0 to +1.5 V) and a series of three or more ligand-based reductions (<0.0 V), the potentials of which vary in a predictable way with ring substitution on the ligand.<sup>8</sup> Electron-donating groups make the ruthenium complex both easier to oxidize and harder to reduce. Likewise, electron-withdrawing groups produce opposite shifts in potential. For the ligands employed in this study, the relative *E*<sub>1/2</sub> values are (COOEt)<sub>2</sub>bpy >> bpy > Me<sub>2</sub>bpy = Mebpy-nDQ<sup>0</sup> > Me<sub>4</sub>bpy. This range of ligand reduction potentials allows several features of the RuL<sub>3</sub> moiety to be varied independently of the DQ<sup>2+</sup>. First, by changing the two non-diquat-containing bipyridine ligands, one can shift the potential of the RuL<sub>3</sub>-based redox processes relative to those of the DQ<sup>2+</sup>. Second, for the initial ligand-based reduction, the spacial location of the highest energy electron relative to the position of the diquat can be controlled. This second consideration is especially important in so much as the same spacial arrangement of electron and DQ<sup>2+</sup> electron acceptor should exist in the excited state and could, thereby, influence rates of intramolecular electron transfer. These ideas are considered in more detail below.

The data in Table II confirm the expectation that the -CH<sub>2</sub>CH<sub>2</sub>DQ<sup>0</sup> substituent on the bipyridine is electronically equivalent to a methyl group for both the complexed and uncomplexed ligand. The respective RuL<sub>3</sub>-based redox processes (i.e., non-diquat) for Ru(Me<sub>2</sub>bpy)<sub>3</sub><sup>2+</sup>, Ru(Mebpy-3DQ<sup>2+</sup>)<sub>3</sub><sup>8+</sup>, and Ru(Me<sub>2</sub>bpy)<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)<sup>4+</sup> thus all occur within 20 mV of each other (cf. Table II). In each of the complexes there are basically three degenerate LUMO's, in which an added electron could choose to reside, one associated with each bipyridine. Similarly, the same arguments could be presented for the excited

state. In contrast, for mixed-ligand complexes, this energetic degeneracy is not, in general, the case.

Based on the data in Table II for the symmetrical tris complexes with unsubstituted and alkyl-substituted bipyridines (entries 7–9), one can predict the details of the electrochemistry of the mixed complexes (entries 1, 2, and 4). For a given formal redox couple (e.g., RuL<sub>3</sub><sup>1+/0</sup>), the potential of that process in the mixed complex corresponds closely to the potential of the analogous process (i.e., 1+/0 couple) in the symmetrical tris complex containing the type of ligand undergoing the redox change. For example, in Ru(bpy)<sub>2</sub>(Mebpy-3DQ<sup>0</sup>)<sup>2+</sup>, **5** (Figure 2), bpy is easier to reduce than Mebpy-3DQ<sup>0</sup> (-1.99 vs. 2.19 V). The first ligand-based reduction in **5** occurs at -1.29 V (Table II, entry 2) which corresponds closely with the first reduction of Ru(bpy)<sub>3</sub> at -1.27 V (Table II, entry 7). Likewise, the second reduction in **5** occurs also on a bpy ligand (-1.47 vs. -1.46 V, entries 2 and 7, Table II, respectively). The next reduction, however (-1.75 V), occurs in the Mebpy-3DQ<sup>0</sup> ligand, and the potential corresponds to the third reduction of Ru(Me<sub>2</sub>bpy)<sub>3</sub> (-1.80 V; Table II, entry 8). In general, for complexes 4–7, the prediction made from consideration of relative potentials of corresponding redox processes are consistent with the redox data in Table II and the spectroelectrochemistry presented later. The cyclic voltammograms of Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)<sup>4+</sup> and their interpretation are somewhat more complicated than those of the other mixed-ligand complexes due to an increase in the number of observable reductions. Six one-electron reductions are observed for Ru-[(COOEt)<sub>2</sub>bpy]<sub>3</sub><sup>2+</sup>. Due to the stabilizing effect of the electron-withdrawing carboxyethyl groups, each ligand is capable of being reduced by two electrons within the potential window of the solvent. The cyclic voltammogram of Ru[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)<sup>4+</sup> indicates that five non-diquat reductions are possible. The first two reductions occur at similar potentials to those of the [(COOEt)<sub>2</sub>bpy]<sub>3</sub> complex (the first reduction is superimposed on the DQ<sup>1+/0</sup> peak in the voltammogram). Due to the low *E*<sub>1/2</sub> value of the third reduction, and on the basis of the similarity of the absorption spectrum of the resulting reduced species to that of Ru[(COOEt)<sub>2</sub>bpy]<sub>3</sub><sup>2-</sup> (vide infra), it appears that the third non-diquat reduction corresponds to a second electron being placed into an already reduced (COOEt)<sub>2</sub>bpy ligand. The last two reduction waves result from reduction of the Mebpy-3DQ<sup>0</sup> ligand and a second reduction of the other (COOEt)<sub>2</sub>bpy ligand, but it is not clear which of these processes occurs first.

The data presented in Tables I and II and Figure 1 confirm that a large degree of variation in the redox potentials of the components of the system is possible. The reduction potential of the attached diquat electron acceptor can be shifted by almost 200 mV (without affecting electrochemical properties of the Ru complex) by changing the length of the diquaternary N,N'-bridging group. A range of potentials from +1.06 to +1.43 for the oxidation of the tris(bipyridine)ruthenium electron donor is obtained by varying the substituents on the bipyridine rings. In addition, a very wide range of ligand-based reduction potentials can be obtained by changing ligand substitution. With the series described here, Ru<sup>2+/1+</sup> potentials between -0.86 and -1.39 were



**Figure 2.** Cyclic voltammograms of (a)  $[\text{Ru}(\text{bpy})_2(\text{Mebpy}-2\text{DQ})](\text{PF}_6)_4$ , (b)  $[\text{Ru}(\text{bpy})_2(\text{Mebpy}-3\text{DQ})](\text{PF}_6)_4$ , (c)  $[\text{Ru}(\text{Me}_2\text{bpy})_2(\text{Mebpy}-3\text{DQ})](\text{PF}_6)_4$ , (d)  $[\text{Ru}(\text{Me}_4\text{bpy})_2(\text{Mebpy}-3\text{DQ})](\text{PF}_6)_4$ , (e)  $[\text{Ru}[(\text{COOEt})_2\text{bpy}]_2(\text{Mebpy}-3\text{DQ})](\text{PF}_6)_4$ , and (f)  $[\text{Ru}(\text{Mebpy}-3\text{DQ})_3](\text{PF}_6)_8$  all in DMF/0.10 M TBAPF<sub>6</sub> on glassy carbon.

measured. These potentials are important because of the electronic similarity between this electrochemically reduced species, which can be written as  $\text{Ru}^{\text{II}}(\text{L})_2(\text{L}^-)$  and the photochemically excited triplet state of the complex, a MLCT state which can be depicted as  $\text{Ru}^{\text{III}}(\text{L})_2(\text{L}^-)$ . In both cases, the same ligand based  $\pi^*$  orbital is presumably occupied by a lone electron.

**Spectroelectrochemistry.** Figure 3 shows the visible absorption spectra of the electrochemically reduced forms of the linked bipyridine-diquat ligands. At 0.0 V vs. SCE, solutions of  $\text{Mebpy}-2\text{DQ}^{2+}$  and  $\text{Mebpy}-3\text{DQ}^{2+}$  do not absorb in the visible region. Diquat species typically exhibit strong absorption in the UV, with absorption maxima at approximately 300 nm. Values for the absorption band maxima of  $\text{Mebpy}-n\text{DQ}^{1+}$  and  $\text{Mebpy}-n\text{DQ}^0$  and the potentials at which the spectra were recorded are given in Table III. The radical cation form of both of these ligands is characterized by a sharp, intense absorption at 380–390 nm, an additional, less intense peak (or peaks) in the region 430–540 nm,

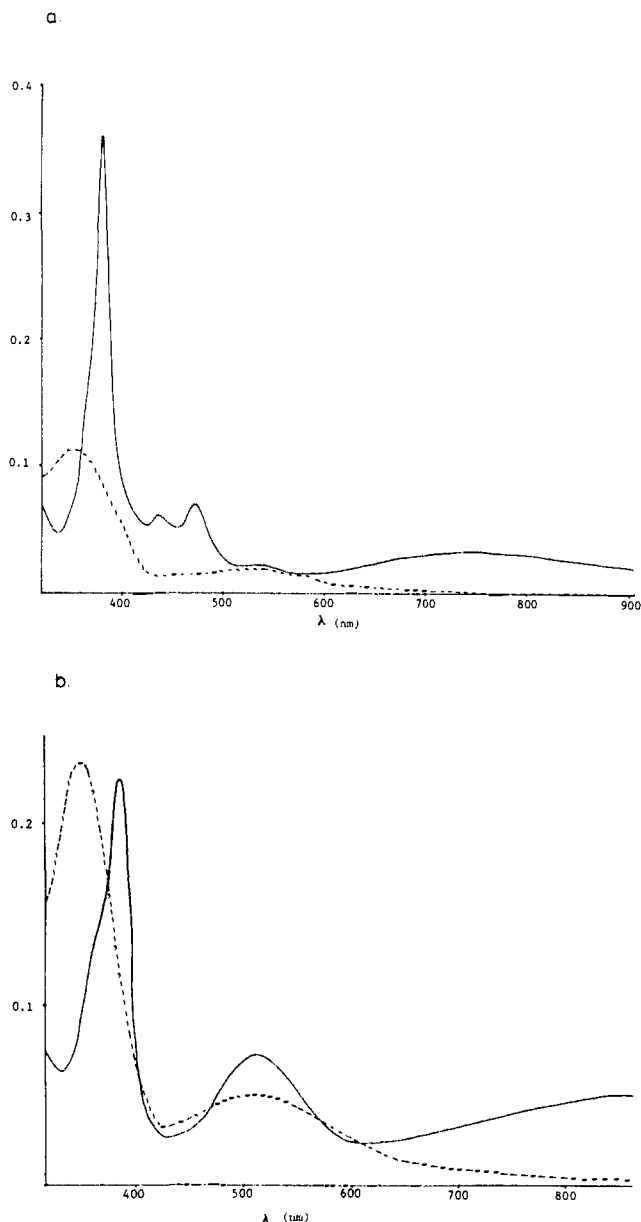
**Table III.** Spectroelectrochemical Data for bpy-DQ Ligands and Complexes

$\text{Ru}^n\text{DQ}^m$	potential	$\lambda_{\text{max}}$ ( $\epsilon$ ) <sup>b</sup>
<b>Mebpy-2DQ</b>		
$\text{DQ}^{1+}$	-0.60	380 (23 600), 435 (4200), 452 (4700), 535 (1500), 760 (2100)
$\text{DQ}^0$	-1.00	349 (7 400), 534 (1 300)
<b>Mebpy-3DQ</b>		
$\text{DQ}^{1+}$	-0.75	387 (14 500), 514 (4400), 880 (3100)
$\text{DQ}^0$	-1.40	351 (14 800), 515 (3000)
<b><math>\text{Ru}(\text{bpy})_2(\text{Mebpy}-2\text{DQ})</math></b>		
$\text{Ru}^{2+}\text{DQ}^{2+}$	0.00	434 (10 100), 455 (12 200)
$\text{Ru}^{2+}\text{DQ}^{1+}$	-0.60	380 (27 900), 437 (15 100), 452 (15 800), 464 (15 600), 760 (2900)
$\text{Ru}^{2+}\text{DQ}^0$	-1.00	348 (18 300), 434 (11 200), 454 (13 300)
$\text{Ru}^{1+}\text{DQ}^0$	-1.38	340 (28 600), 464 (11 300), 495 (13 800), 520 (13 900)
$\text{Ru}^0\text{DQ}^0$	-1.61	343 (30 300), 506 (16 600), 538 (18 200)
<b><math>\text{Ru}(\text{bpy})_2(\text{Mebpy}-3\text{DQ})</math></b>		
$\text{Ru}^{2+}\text{DQ}^{2+}$	0.00	400 (7300), 426 (12 300), 456 (15 600)
$\text{Ru}^{2+}\text{DQ}^{1+}$	-0.75	359 (12 900), 374 (14 400), 423 (13 200), 455 (16 900), 525 (5700)
$\text{Ru}^{2+}\text{DQ}^0$	-1.08	353 (20 900), 423 (13 500), 455 (17 000)
$\text{Ru}^{1+}\text{DQ}^0$	-1.38	346 (32 300), 459 (14 400), 492 (17 700), 519 (17 600)
$\text{Ru}^0\text{DQ}^0$	-1.64	348 (52 300), 506 (20 900), 539 (22 500)
<b><math>\text{Ru}(\text{Me}_4\text{bpy})_2(\text{Mebpy}-3\text{DQ})</math></b>		
$\text{Ru}^{2+}\text{DQ}^{2+}$	0.00	364 (6400), 399 (6800), 423 (10 300), 452 (12 500)
$\text{Ru}^{2+}\text{DQ}^{1+}$	-0.73	364 (12 700), 388 (16 900), 422 (11 400), 453 (13 900), 518 (4400), 850 (1800)
$\text{Ru}^{2+}\text{DQ}^0$	-1.20	350 (18 700), 422 (11 600), 453 (14 400)
$\text{Ru}^{1+}\text{DQ}^0$	-1.51	347 (30 500), 362 (29 500), 468 (14 400), 502 (17 800), 542 (12 000)
$\text{Ru}^0\text{DQ}^0$	-1.77	351 (28 500), 361 (28 200), 518 (18 000), 545 (17 900)
<b><math>\text{Ru}[(\text{COOEt})_2\text{bpy}]_2(\text{Mebpy}-3\text{DQ})</math></b>		
$\text{Ru}^{2+}\text{DQ}^{2+}$	0.00	367 (13 900), 401 (11 100), 445 (14 400), 486 (17 400)
$\text{Ru}^{2+}\text{DQ}^{1+}$	-0.75	368 (21 100), 386 (22 800), 445 (15 500), 488 (20 300), 520 (7800), 850 (2500)
$\text{Ru}^{1+}\text{DQ}^0$	-0.97	350 (34 500), 442 (16 300), 506 (17 100), 531 (17 500)
$\text{Ru}^0\text{DQ}^0$	-1.15	350 (45 700), 448 (19 000), 504 (19 600), 539 (16 000)
$\text{Ru}^{2-}\text{DQ}^0$	-1.60	363 (48 400), 494 (27 800)
$\text{Ru}^{3-}\text{DQ}^0$	-1.80	362 (51 100), 468 (32 300)
<b><math>\text{Ru}(\text{Mebpy}-3\text{DQ})_3</math></b>		
$\text{Ru}^{2+}(\text{DQ}^{2+})_3$	0.00	364 (9800), 436 (14 600), 459 (15 900)
$\text{Ru}^{2+}(\text{DQ}^{1+})_3$	-0.73	366 (39 200), 388 (59 900), 436 (19 800), 473 (23 200), 530 (17 700), 860 (11 800)
$\text{Ru}^{2+}(\text{DQ}^0)_3$	-1.00	350 (58 900), 435 (21 100), 463 (23 900)
$\text{Ru}^{1+}(\text{DQ}^0)_3$	-1.46	348 (79 500), 474 (26 100), 507 (30 300), 534 (29 500)
$\text{Ru}^0(\text{DQ}^0)_3$	-1.65	350 (90 300), 517 (34 500), 545 (33 700)

<sup>a</sup> Obtained at an Au minigrad in DMF/0.10 M TBAPF<sub>6</sub>. <sup>b</sup> In all cases where  $\text{DQ}^{1+}$  is present, a very broad peak is observed with a  $\lambda_{\text{max}}$  > 850 nm. In cases where the peak is too broad and weak to establish  $\lambda_{\text{max}}$  these values have been omitted from the table (see Figure 4).

and a broad weak absorption at long wavelengths. The neutral species exhibit an absorption at 350 nm, and a second, weaker absorption at > 500 nm. Both the 1+ and 0 oxidation states are reversible. However, reduction at -2.30 V (bipyridine reduction) is not reversible; a spectrum of the same solution upon reoxidation to the 1+ oxidation state revealed that the diquat group had been destroyed.

Spectra of the reduced ruthenium complexes,  $\text{RuL}_2(\text{Mebpy}-n\text{DQ})^{n+}$  and  $\text{Ru}(\text{Mebpy}-3\text{DQ})_3^{n+}$ , are given in Figure 4. Absorption data and the potentials at which the spectra were obtained are listed in Table III. The oxidation states of the diquat and ruthenium species at each potential are also indicated. Spectra taken at 0.0 V following each potential step indicate that the diquat



**Figure 3.** Electronic absorption spectra of reduced diquat ligands (a) Mebpy-2DQ<sup>n+</sup> [(—) *n* = 1; (---) *n* = 0] and (b) Mebpy-3DQ<sup>n+</sup> [(—) *n* = 1; (---) *n* = 0] obtained in DMF/0.10 M TBAPF<sub>6</sub> at a gold minigrad optically transparent thin-layer electrode.

reductions are completely reversible. Following the first and second ruthenium reductions, slight changes in the spectrum of the reoxidized Ru<sup>2+</sup>-DQ<sup>2+</sup> species were observed, indicating some slight chemical decomposition. The third reduction, in general, was not chemically reversible. Therefore, spectral data for this oxidation state are not included.

Comparison of the spectra presented in Figure 4a-c with spectra for analogues symmetrical tris(bipyridine)ruthenium complexes<sup>8,9</sup> indicate that the model used for assigning redox orbital "locations" based on potentials (vide supra) is consistent with the spectroelectrochemical results. In general, spectra at potentials corresponding to the Ru<sup>2+</sup>-DQ<sup>1+</sup> and Ru<sup>2+</sup>-DQ<sup>0</sup> species can be described as a superposition of the initial 0.0 V spectrum of the ruthenium complex with the absorption bands characteristic of the reduced diquat species described above. In the case of the L = (COOEt)<sub>2</sub>bpy, complex **8** (Figure 4d), stepping the potential to -0.97 V results in simultaneous reduction of DQ<sup>1+</sup> to DQ<sup>0</sup> and Ru<sup>2+</sup> to Ru<sup>1+</sup>. The spectrum at this potential therefore shows both the neutral diquat absorption and the absorption pattern resulting from reduction of one bound (COOEt)<sub>2</sub>bpy ligand. Both the formal Ru<sup>1+</sup> and Ru<sup>0</sup> states of **8** exhibit spectra which are quite similar to spectra of Ru[(COOEt)<sub>2</sub>bpy]<sub>3</sub> in its 1+ and 0

oxidation states (with the addition of the bands attributable to the DQ<sup>0</sup>). Following the third reduction to the formal Ru<sup>1+</sup> species at a potential of -1.15 V, however, the spectrum closely resembles that of Ru[(COOEt)<sub>2</sub>bpy]<sub>3</sub><sup>2-</sup>, in which one of the three ligands is doubly reduced. This implies that this third non-diquat reduction corresponds to a second reduction of one of the (COOEt)<sub>2</sub>bpy ligands rather than reduction of the Mebpy-3DQ<sup>0</sup> ligand. Likewise, the spectrum of Ru[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Mebpy-3DQ<sup>0</sup>)<sup>2-</sup> recorded at a potential of -1.60 is very similar to that of Ru-[(COOEt)<sub>2</sub>bpy]<sub>3</sub><sup>3-</sup>. This reduction product is not completely chemically stable, however, and therefore the spectral data may not represent the spectrum of the intact complex. Although it cannot be stated with complete certainty, it appears that both (COOEt)<sub>2</sub>bpy ligands are doubly reduced at this potential and that not until the fifth reduction (at *E*<sub>1/2</sub> = -2.06) is the Mebpy-3DQ<sup>0</sup> ligand reduced.

**Photochemistry.** In general, a variation in the potential at which the first ligand is reduced produces a qualitatively similar variation in excited-state properties. Using the emission maxima for the analogous diquat-free complexes (e.g., Ru(Me<sub>2</sub>bpy)<sub>3</sub><sup>2+</sup>) and the solution electrochemical data, it is possible to roughly estimate the redox potentials of the excited state.<sup>20</sup> These estimates are included in the last two columns of Table II. It should be noted that for three of the species (compare Table II, entries 2, 3, and 4 with 7, 8, and 9), the excited state is predicted to be a sufficiently strong reducing agent to be able to quench by directly reducing the attached diquat. For the fourth complex, Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>), the excited state should not be able to reduce the diquat (compare Table II entries 5 and 11). These predictions are entirely consistent with the luminescence data below.

The linked RuL<sub>2</sub>(Mebpy-*n*DQ<sup>2+</sup>) complexes are nonluminescent when L is an unsubstituted or alkyl-substituted bipyridine (4-7 and 9). The corresponding symmetrical RuL<sub>3</sub><sup>2+</sup> complexes are highly luminescent, exhibiting emission maxima in the range of 600-640 nm. Intramolecular electron transfer between the MLCT excited state and the attached diquat electron acceptor accounts for the emission quenching in the linked complexes. A very weak emission with a lifetime similar to that of Ru(bpy)<sub>3</sub><sup>2+</sup> can be observed for these complexes by laser flash photolysis. This luminescence is attributable to minute traces of a complex in which there is no attached diquat, which may be initially present as an impurity or may be produced as a result of laser irradiation. The back electron transfer between Ru(III) and the diquat radical cation is sufficiently fast that these species cannot be detected by transient absorption measurements (time scale <5 ns). In contrast to the L = bpy, Me<sub>2</sub>bpy, and Me<sub>4</sub>bpy complexes, Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)<sup>4+</sup> is luminescent. Comparison of the luminescence intensity of this compound with Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>Me<sub>2</sub>bpy<sup>2+</sup> indicates that within experimental error, there is no quenching of the fluorescence by the attached diquat. The aforementioned excited-state redox potential estimates (Table II) are entirely consistent with these results. The direct intramolecular electron transfer for Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)<sup>4+</sup> is predicted to be endothermic by >0.2 V and thus does not compete with emission. In the other compounds, the electron transfer is exothermic in every case by at least 0.2 V. Thus, in these complexes, the excited state is very efficiently quenched by intramolecular electron transfer.

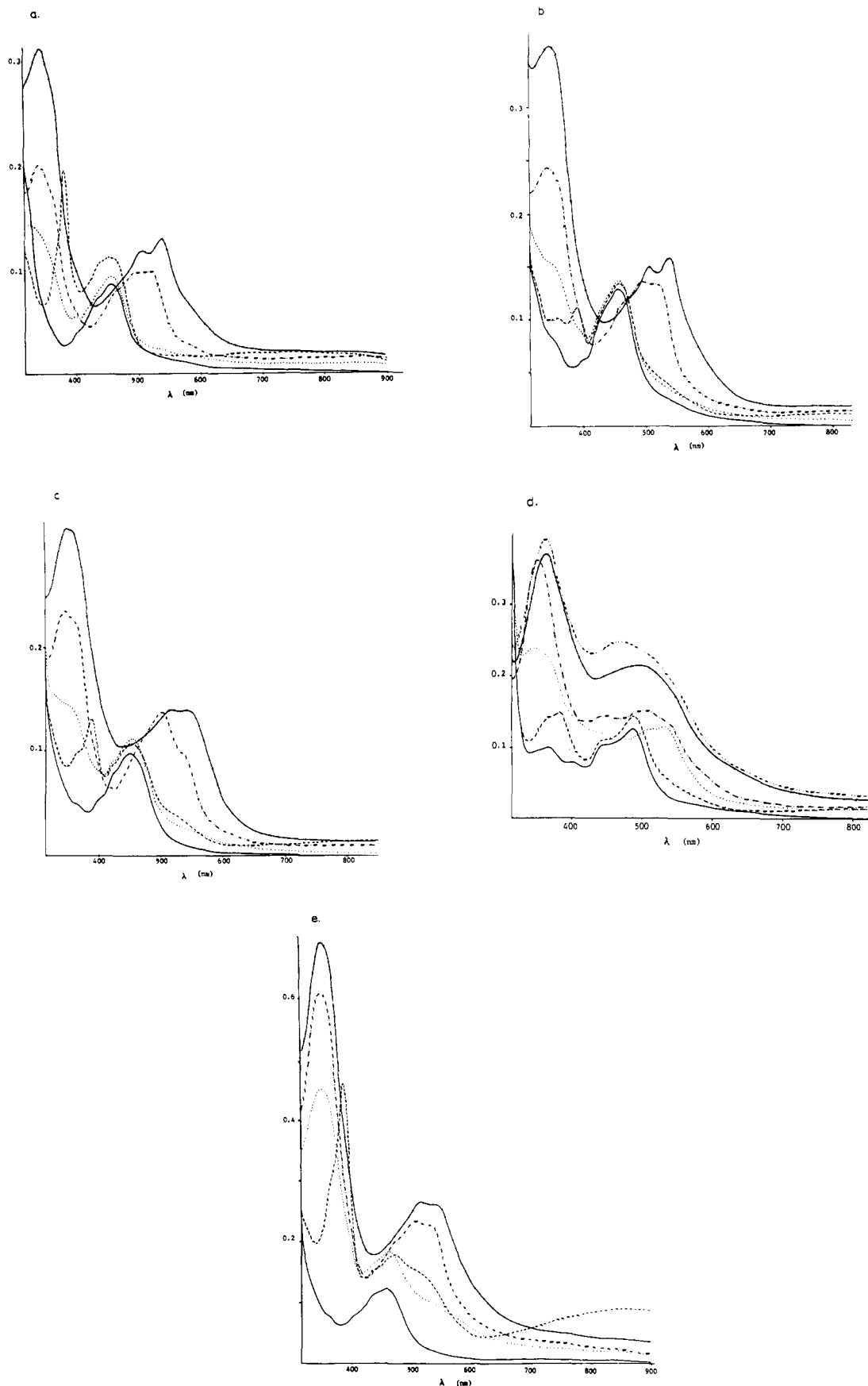
In 1:1 acetonitrile/water, the linked donor/acceptor complexes are fairly photostable; no spectral changes are observed over a period of several hours for solutions exposed to room light. After several days, however, the emission intensity is seen to increase, indicating that the diquat moiety is no longer intact in some fraction of the molecules.

The photochemistry of Ru(bpy)<sub>2</sub>(Mebpy-2DQ<sup>2+</sup>)<sup>4+</sup> and Ru-(bpy)<sub>2</sub>(Mebpy-3DQ<sup>2+</sup>)<sup>4+</sup> in the presence of excess triethanolamine (TEOA) as a sacrificial electron donor has been investigated in

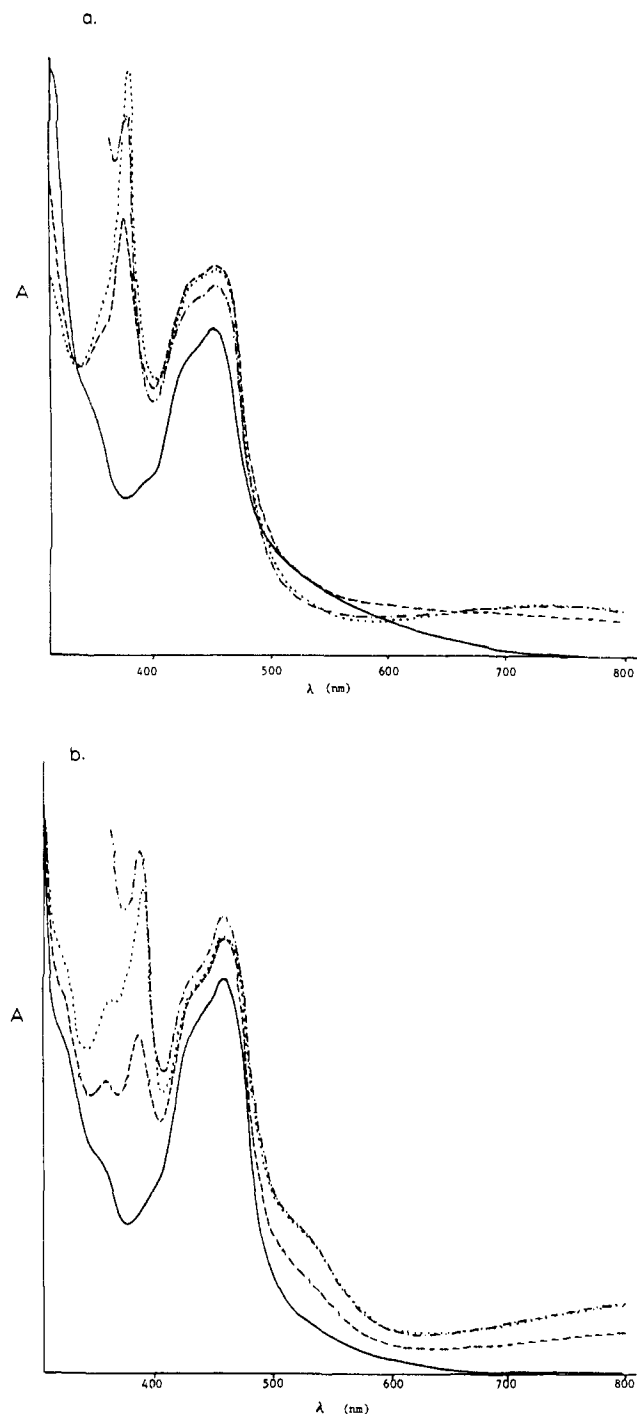
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**Figure 4.** Electronic absorption spectra of the linked tris(bipyridine)Ru/diaquat complexes in various oxidation states (DMF, 0.10 M TBAPF<sub>6</sub>). (a) Ru<sup>m+</sup>(bpy)<sub>2</sub>(Mebpy-2DQ<sup>n+</sup>): (—)  $m = 2, n = 2$ ; (---)  $m = 2, n = 1$ ; (...)  $m = 2, n = 0$ ; (-·-·-)  $m = 1, n = 0$ ; (+++)  $m = 0, n = 0$ . (b) Ru<sup>m+</sup>(bpy)<sub>2</sub>(Mebpy-3DQ<sup>n+</sup>): (—)  $m = 2, n = 2$ ; (---)  $m = 2, n = 1$ ; (...)  $m = 2, n = 0$ ; (-·-·-)  $m = 1, n = 0$ ; (+++)  $m = 0, n = 0$ . (c) Ru<sup>m+</sup>(Me<sub>4</sub>bpy)<sub>2</sub>(Mebpy-3DQ<sup>n+</sup>): (—)  $m = 2, n = 2$ ; (---)  $m = 2, n = 1$ ; (...)  $m = 2, n = 0$ ; (-·-·-)  $m = 1, n = 0$ ; (+++)  $m = 0, n = 0$ . (d) Ru<sup>m+</sup>[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Mebpy-3DQ<sup>n+</sup>): (—)  $m = 2, n = 2$ ; (---)  $m = 2, n = 1$ ; (...)  $m = 1, n = 0$ ; (-·-·-)  $m = 0, n = 0$ ; (+++)  $m = -1, n = 0$ ; (-·-·-·-)  $m = -2, n = 0$ . (e) Ru<sup>m+</sup>(Mebpy-3DQ<sup>n+</sup>)<sub>3</sub>: (—)  $m = 2, n = 2$ ; (---)  $m = 2, n = 1$ ; (...)  $m = 2, n = 0$ ; (-·-·-)  $m = 1, n = 0$ ; (+++)  $m = 0, n = 0$ .

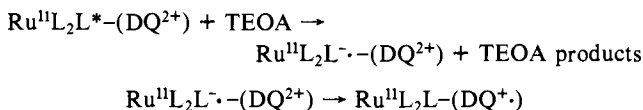


**Figure 5.** Photochemistry of (a)  $\text{Ru}(\text{bpy})_2(\text{Mepby-2DQ}^{2+})^{4+}$  and (b)  $\text{Ru}(\text{bpy})_2(\text{Mepby-3DQ}^{2+})^{4+}$  in the presence of triethanolamine: (—) initial spectrum, (---) after 1-min exposure to projector lamp, (...) after 4 min, (-·-·-) spectrum of same concentration solution after reduction with  $\text{Na}_2\text{S}_2\text{O}_4/\text{NH}_3$ .

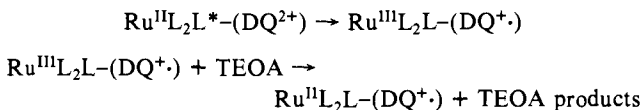
a qualitative way. Solutions of these complexes in acetonitrile/water containing TEOA (10% by volume) were prepared and purged with nitrogen in the dark. Irradiation with visible light was followed spectrophotometrically. Spectral changes corresponding to a buildup of the reduced diquat were observed (Figure 5). It is thus evident that reduction of Ru(III) by TEOA can effectively compete with the back electron transfer process, trapping the diquat radical cation produced by photoinduced electron transfer. The reduced diquat species accumulated until it reached a maximum concentration. At this point, the spectrum in the wavelength range 370–800 nm is quite similar to that obtained following chemical reduction of the  $\text{Ru}(\text{bpy})_2(\text{Mepby-}n\text{DQ}^{2+})^{4+}$  complex to  $\text{Ru}(\text{bpy})_2(\text{Mepby-}n\text{DQ}^{1+})^{3+}$  with sodium

hydrosulfite (Figure 5). Further irradiation results in a gradual decrease in the absorption of the peaks corresponding to the  $n\text{DQ}^{1+}$  species. Upon exposure of the irradiated sample to air, the diquat radical cation peaks disappear, and the spectrum of the resulting solution is different from that of the solution prior to irradiation. Also, following irradiation and exposure to oxygen, the complex is then luminescent. The diquat groups apparently are modified in such a way that emission quenching by electron transfer can no longer take place. Finally, irradiation of  $\text{Mebpy-3DQ}^{2+}$  under identical solution conditions produced no evidence of  $\text{Mebpy-3DQ}^{1+}$  product.

Irradiation of the  $\text{Ru}[(\text{COOEt})_2\text{bpy}]_2(\text{Mebpy-3DQ}^{2+})^{4+}$  complex in the presence of excess TEOA was also carried out. Despite the fact that the excited state is not adequately energetic to reduce the diquat directly, the diquat radical cation was detected spectrophotometrically in somewhat smaller quantities than observed for other complexes. A consideration of the emission behavior of the diquat-free analogue complexes provides an explanation for these results. The intensity of  $\text{Ru}(\text{Me}_2\text{bpy})_3^{2+}$  emission in either acetonitrile/water or in the same solvent containing 10% TEOA is within experimental error, the same. However, in an analogous experiment employing  $\text{Ru}[(\text{COOEt})_2\text{bpy}]_2(\text{Me}_2\text{bpy})^{2+}$ , the relative emission intensity is decreased by 35% with the addition of TEOA. The excited state of the latter complex is a better oxidizing agent than is the former by approximately 0.3 V. Apparently the initial step for the photochemical reaction of the excited state of  $\text{Ru}[(\text{COOEt})_2\text{bpy}]_2(\text{Mebpy-3DQ}^{2+})^{4+}$  is the oxidation of the TEOA followed by the intramolecular reduction of the diquat.



Similarly, the almost total lack of fluorescence for the other three diquat-containing complexes (even in the absence of TEOA) and the lack of fluorescence quenching by TEOA under these conditions in the diquat-free analogue complexes implies the reverse mechanistic order for electron transfers.



**Summary.** The detailed nature of the mechanism of photoinduced electron-transfer reactions and associated recombination reactions are dependent on the detailed structure of the various system components. By combining these components into a single molecular unit, one can control and/or eliminate the diffusional aspects necessary in bimolecular reactions. It is also, to a degree, possible to enforce certain orientational aspects that are difficult or impossible to control for bimolecular reactions. The synthetic approach taken to generate the compounds reported herein is very general and affords great flexibility with respect to (1) controlling the optical properties of the ruthenium chromophore, (2) controlling the redox potentials for the excited state, (3) controlling the redox potential of the electron acceptor, and (4) controlling the preferred orientation of the  $\text{L}^{\cdot-}$  in the excited state relative to the  $\text{DQ}^{2+}$  acceptor (i.e., whether in the excited state, the arrangement is  $\text{L}'_2\text{RuL}^{\cdot-}-\text{DQ}^{2+}$  as in 7 or  $\text{L}'\text{L}'^{\cdot-}\text{RuL}-\text{DQ}^{2+}$  as in 5). By slight modifications of the synthetic route, it is possible to vary the alkyl chain length connecting the bpy and  $\text{DQ}^{2+}$  and also to vary the position of substitution on the bipyridine (e.g., to the 5 position). Complexes generated from such ligand modifications will be the subject of subsequent reports.

Presently, measurements of fluorescence lifetimes and transient absorption spectra have not been possible because of instrumental limitations. We can, at present, give only upper limits. Assuming dynamic quenching, the excited state must be virtually totally quenched in less than 200 ps and recombination must be complete in less than 5 ns for each of the complexes reported which are nonfluorescent (complexes 4–7 and 9).



Finally, while the electron-transfer products have lifetimes of <5 ns, we have shown that it is possible to compete with recombination by using TEOA as a sacrificial donor. We are presently studying complexes in which we have incorporated both diquat-modified ligands and electron donor species (e.g., phenothiazine) into a tris(bipyridine)ruthenium chromophore.

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**Registry No. 1,** 96897-04-0; **2**(PF<sub>6</sub>)<sub>2</sub>, 96897-06-2; **2<sup>+</sup>**, 96897-13-1; **2** (neutral), 96897-14-2; **2<sup>-</sup>**, 96947-74-9; **3**(PF<sub>6</sub>)<sub>2</sub>, 96897-08-4; **3<sup>+</sup>**, 96897-15-3; **3** (neutral), 96897-16-4; **3<sup>-</sup>**, 96947-75-0; **4**(PF<sub>6</sub>)<sub>4</sub>, 96897-18-6; **4<sup>5+</sup>**, 96897-30-2; **4<sup>3+</sup>**, 96897-37-9; **4<sup>2+</sup>**, 96897-43-7; **4<sup>+</sup>**, 96913-25-6; **4** (neutral), 96897-56-2; **4<sup>-</sup>**, 96913-27-8; **5**(PF<sub>6</sub>)<sub>4</sub>, 96897-19-7; **5<sup>5+</sup>**, 96410-78-5; **5<sup>3+</sup>**, 96897-38-0; **5<sup>2+</sup>**, 96897-44-8; **5<sup>+</sup>**, 96897-49-3; **5** (neutral), 96897-

57-3; **5<sup>-</sup>**, 96897-63-1; **6**(PF<sub>6</sub>)<sub>4</sub>, 96897-21-1; **6<sup>5+</sup>**, 96897-31-3; **6<sup>3+</sup>**, 96897-39-1; **6<sup>2+</sup>**, 96897-45-9; **6<sup>+</sup>**, 96897-50-6; **6** (neutral), 96897-58-4; **6<sup>-</sup>**, 96897-64-2; **7**(PF<sub>6</sub>)<sub>4</sub>, 96897-23-3; **7<sup>5+</sup>**, 96897-32-4; **7<sup>3+</sup>**, 96897-40-4; **7<sup>2+</sup>**, 96897-46-0; **7<sup>+</sup>**, 96897-51-7; **7** (neutral), 96897-59-5; **7<sup>-</sup>**, 96897-66-4; **8**(PF<sub>6</sub>)<sub>4</sub>, 96897-25-5; **8<sup>5+</sup>**, 96897-33-5; **8<sup>3+</sup>**, 96897-41-5; **8<sup>2+</sup>**, 96897-47-1; **8<sup>+</sup>**, 96897-52-8; **8** (neutral), 96897-60-8; **8<sup>-</sup>**, 96897-65-3; **8<sup>2-</sup>**, 96897-70-0; **8<sup>3-</sup>**, 96897-72-2; **9**(PF<sub>6</sub>)<sub>4</sub>, 96897-27-7; **9<sup>5+</sup>**, 96897-34-6; **9<sup>3+</sup>**, 96897-42-6; **9<sup>2+</sup>**, 96897-48-2; **9<sup>+</sup>**, 96897-53-9; **9** (neutral), 96913-26-7; **9<sup>-</sup>**, 96897-67-5; [Ru(Me<sub>4</sub>bpy)<sub>3</sub>]<sup>3+</sup>, 96897-35-7; [Ru(Me<sub>4</sub>bpy)<sub>3</sub>]<sup>+</sup>, 96897-54-0; [Ru(Me<sub>4</sub>bpy)<sub>3</sub>]<sup>-</sup>, 96897-61-9; [Ru(Me<sub>4</sub>bpy)<sub>3</sub>]<sup>-</sup>, 96897-68-6; [Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>3+</sup>, 96897-36-8; [Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Me<sub>2</sub>bpy)](PF<sub>6</sub>)<sub>2</sub>, 96897-29-9; [Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>+</sup>, 96897-55-1; [Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Me<sub>2</sub>bpy)], 96897-62-0; [Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>-</sup>, 96897-69-7; [Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>2-</sup>, 96897-71-1; [Ru-[(COOEt)<sub>2</sub>bpy]<sub>2</sub>(Me<sub>2</sub>bpy)]<sup>3-</sup>, 96897-73-3; Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, 15746-57-3; Ru(Me<sub>2</sub>SO)<sub>4</sub>Cl<sub>2</sub>, 11070-19-2; Me<sub>2</sub>bpy, 1134-35-6; Me<sub>2</sub>-2DQ<sup>2+</sup>, 96913-23-4; Me<sub>2</sub>-2DQ<sup>+</sup>, 96897-09-5; Me<sub>2</sub>-2DQ, 96913-24-5; Me<sub>2</sub>-3DQ<sup>2+</sup>, 96897-10-8; Me<sub>2</sub>-3DQ<sup>+</sup>, 96897-11-9; Me<sub>2</sub>-3DQ, 96897-12-0; 1,2-dibromoethane, 106-93-4; 1,3-dibromopropane, 109-64-8.

## Fluorescence Study of Pyrene and Naphthalene in Cyclodextrin-Amphiphile Complex Systems

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**Abstract:** Amphiphilic molecules are shown to interact with pyrene- $\beta$ -cyclodextrin (Py- $\beta$ -CD) complexes leading to an extremely hydrophobic environment for pyrene (Py) in aqueous solution. The three-component systems give rise to a 1:1:1 complex of Py,  $\beta$ -CD, and the surfactant. The binding constant of Py and  $\beta$ -CD increases significantly in the presence of the surfactants, which suggests an improvement in the solubility of Py in aqueous  $\beta$ -CD systems. Larger binding constants of Py and  $\beta$ -CD were obtained in the presence of shorter chain amphiphiles between C<sub>4</sub> and C<sub>16</sub> surfactants. Fluorescence quenching of Py in Py- $\beta$ -CD-pyridinium surfactants (C<sub>n</sub>Pd<sup>+</sup>X<sup>-</sup>) systems obeyed first-order kinetics, which were independent of the concentration of C<sub>n</sub>Pd<sup>+</sup>X<sup>-</sup> above a certain concentration, while the quenching rate constant was markedly affected by the chain length of the pyridinium surfactants. Smaller rate constants are obtained for longer chain surfactants. The observed kinetics are explained in terms of a 1:1:1 complex formation of Py,  $\beta$ -CD, and C<sub>n</sub>Pd<sup>+</sup>X<sup>-</sup>, and the chain-length-dependent rate constants are interpreted by assuming a "diffusion-controlled reaction within limited space". On the other hand, Stern-Volmer kinetics were observed for Py fluorescence quenching in the Py- $\beta$ -CD-C<sub>16</sub>C<sub>2</sub>V<sup>2+</sup> (1-ethyl-1'-hexadecyl-4,4'-bipyridinium ion) system. This is ascribed to the long-range nature of the reaction in Py(S<sub>1</sub>)-viologen group systems compared with that in Py(S<sub>1</sub>)-pyridinium group systems. In the naphthalene- $\beta$ -CD (N- $\beta$ -CD) system, reduced association constants were observed in the presence of surfactants, which is markedly different from that observed in the Py- $\beta$ -CD system. A determination of the dynamic parameters of the equilibrium showed that the entry rate constant of naphthalene into  $\beta$ -CD was reduced in the presence of surfactants, while the exit rate constant was unchanged. The exit rate was appreciably reduced in the Py- $\beta$ -CD system on addition of surfactants. Quenchers such as oxygen, nitromethane, copper(II) ion, thallium(I) ion, etc., which reside in the aqueous phase also quench excited Py in  $\beta$ -CD. The influence of CD with and without surfactant on the rate depends on the nature of the quenching reaction, and on the degree of screening by the host system on the guest molecule. It is demonstrated in the present study that the introduction of amphiphilic molecules into the Py- $\beta$ -CD complex system improves the organization of the system and simplifies the reaction mechanism. The unique types of reaction kinetics observed are due to the selective organization of reactants in the CD system.

The past decade has witnessed an ever-increasing interest in the effects of organized assemblies on photochemical reactions.<sup>1</sup> Reactants accommodated in molecular assemblies, i.e., micelles, microemulsions, vesicles, etc., often achieve a greater degree of organization compared to homogeneous solution, a feature which may promote unique reaction features, features which may mimic reactions in biosystems and also may have an application for energy storage. Photophysical and photochemical properties of

organic molecules included in the cavity of cyclodextrins (CD's) have also been studied from a similar standpoint.<sup>2</sup> The cavity of CD's can provide a hydrophobic environment for a guest molecule while still in aqueous solution. Earlier studies indicate substantial binding constants for many organic molecules with CD's.<sup>3</sup> However, complicated behavior of formation of the in-

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