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Photoinitiated Electron Collection in a Mixed-Metal Trimetallic Complex of the Form $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}(PF_6)_5$ (bpy = 2,2′-Bipyridine and dpb = 2,3-Bis(2-pyridyl)benzoquinoxaline)

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Abstract: Since the synthesis of $[Ru(bpy)_3]^{2+}$ and its subsequent study in excited-state electron-transfer reactions, much attention has focused on the inclusion of multiple ruthenium chromophores into single molecules. Systems of this type are of interest due to their potential for photoinitiated electron collection. This report illustrates the application of a system with two ruthenium polypyridine chromophores to this problem. This represents the first report of photoinitiated electron collection wherein two covalently coupled ruthenium chromophores function within the same molecule to bring about electron collection. The system described herein is of the form $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ (bpy = 2,2′-bipyridine and dpb = 2,3-bis(2-pyridyl)benzoquinoxaline) and is one in a series of mixed-metal trimetallics designed and developed in our laboratory. Photolysis of this complex in the presence of an electron donor, dimethylaniline, leads to the production of the doubly reduced species, $\{[(bpy)_2Ru(dpb^-)]_2IrCl_2\}^{3+}$. Following photolysis, the complex now contains two reduced dpb bridging ligands coordinated to a central iridium core. In a previous study we have shown that the central core, $[Ir(dpb)_2Cl_2]^+$, is able to deliver electrons "stored" on the bridging ligands to a substrate. The details of the photoinitiated electron collection process are described herein.

Introduction

Since the realization that the metal-to-ligand charge-transfer state (MLCT) of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) could undergo excited-state electron transfer, a series of studies have been undertaken to utilize this fact in solar energy conversion schemes.[1] One of the drawbacks of these studies is the desire to produce fuels that involve the transfer of multiple electrons to a substrate. $[Ru(bpy)_3]^{2+}$ can only transfer a single electron to a substrate without the incorporation of a secondary material to function as an electron collector. Consequently, much effort has focused on the development of polymetallic systems which incorporate multiple $Ru^{II}(bpy)_2$ moieties in the same molecule.[2]

The title complex, $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}(PF_6)_5$ (dpb = 2,3-bis(2-pyridyl)benzoquinoxaline), is an example of a new trimetallic species which incorporates two such light-absorbing moieties covalently coupled to a central iridium center.[3] The covalent attachment of two chromophores is designed to allow two separate photoinitiated electron-transfer steps to occur within the same molecule leading to electron collection. This paper describes how this complex performs this function acting as a molecular device for photoinitiated electron collection. The central iridium fragment of the title trimetallic, $[Ir(dpb)_2Cl_2]^+$, has been shown in a previous report from our laboratory to be capable of delivering multiple electrons "stored" on the bridging ligand π^* orbitals to a substrate as it functioned as an electrocatalyst for the reduction of carbon dioxide to formate.[4]

Experimental Section

Materials. The mixed-metal trimetallic, $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}(PF_6)_5$, used in this study was prepared as previously described.[3] The acetonitrile was Burdick and Jackson UV grade and used without further purification. The tetrabutylammonium hexafluorophosphate (TBAH) used in this study was prepared by the metathesis of Bu_4NBr with KPF_6. This was purified by recrystallization and dried under vacuum. All other chemicals were obtained from Aldrich Chemical and used as received.

Electrochemistry. The spectroelectrochemical experiments were carried out in a modified H-cell that uses a 1-cm optical cuvette as the working compartment. This design has been described in detail elsewhere.[3]

Electronic Spectroscopy. All electronic spectroscopy was carried out on acetonitrile solutions at room temperature using a HP 8452A UV–vis diode array spectrophotometer.

Photochemistry. The steady-state photolysis system consisted of an Oriel 1000-W xenon arc lamp source mounted to the beginning of the optical rail. The light beam was passed through an IR filter followed by

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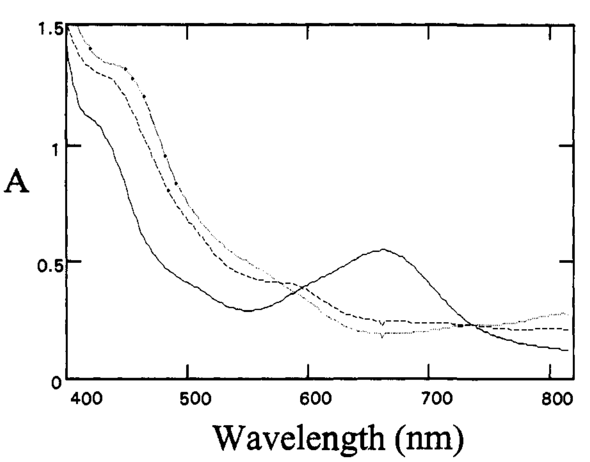


Figure 1. Electronic spectroscopy in acetonitrile: (—) original $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ solution (2.4×10^{-5} M) with added dimethylaniline (0.035 M) containing 0.1 M Bu_4NPF_6 in acetonitrile; (···) after electrochemical generation of oxidized dimethylaniline and reduced trimetallic, $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{3+}$; (- - -) after photolysis for 30 min at 650 nm to photochemically generate $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{3+}$.

a broad band (50-nm band-pass) interference filter for wavelength selection. The filter centered at 650 nm. The light was focused on a 1-cm cylindrical cell which contained the photolysis solution. The solution was thermostated at 25 °C and bubbled with acetonitrile-saturated argon during the course of the photolysis. Each solution was deoxygenated for 30 min prior to the onset of the photochemical experiment. The progress of the photochemical experiment was monitored spectroscopically. Dark controls showed no observable change in the electronic absorption spectrum over the time frame of the photolysis. Photolysis of the trimetallic complex in the absence of dimethylaniline did not result in a change in the electronic spectrum. Only the photolyses of the trimetallic carried out in the presence of dimethylaniline gave rise to an observable spectroscopic change.

Analysis of the spectroscopic data was as follows. Chemical actinometry of the light intensity was performed using Reinecke's salt. Quantum efficiencies for disappearance of reactant were calculated by plotting Φ_{apparent} as a function of photolysis time and extrapolating to zero time. Monitoring formation of product follows a similar trend, although quantification of this species is less accurate. The electronic spectroscopy obtained during the photochemical experiment was used to obtain ΔA (660 nm) for each time interval. These ΔA values were utilized to calculate the moles of product produced. This can be related to ΔA by the known ϵ for the $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ and $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{4+}$ species. The $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{3+}$ species is not considered since this method is only applied at early photolysis times. At these early times any $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{3+}$ that is produced would comproportionate with the large excess of $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ to produce primarily the $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{4+}$ species. The moles of product obtained in this manner are used to calculate apparent quantum yields using the initial absorbance of the solution and the incident light intensity. Plots of Φ_{apparent} versus photolysis time are linear at short times. The apparent quantum yield decreases with photolysis time. This is consistent with the decrease in the absorbance of the photolysis solution at the wavelength of irradiation as the photoreaction progresses. Φ_{limiting} is obtained by extrapolating to zero time using data obtained at <10% conversion.

Exhaustive photolysis in the presence of dimethylaniline leads to the formation of products of the oxidation of dimethylaniline that exhibit absorbances in the visible region of the spectrum. Complete quantitative correction for these products is difficult; therefore, a qualitative approach has been taken to address the contribution from dimethylaniline oxidation products to the spectroscopy observed. Oxidative electrolysis of dimethylaniline in acetonitrile leads to increases in absorbance at 480 nm. The data illustrated in Figure 1 were obtained as follows. A solution of 2.6×10^{-5} M dimethylaniline was electrolyzed at +1.20 V vs SCE to yield the oxidation product of the dimethylaniline. Next, solid $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}(PF_6)_5$ was added to obtain a concentration of 1.6×10^{-5} M. Next, the trimetallic was electrochemically reduced by two electrons. This electrochemical result is plotted with the result of the exhaustive photolysis at 650 nm of a solution of the trimetallic that contained 0.035 M dimethylaniline scaled to the initial concentrations of the trimetallic. The two solutions should differ in that the photolysis solution by necessity contains a large excess of dimethylaniline. This gives rise to some of the spectroscopic differences observed. These are discussed in the Results and Discussion section below.

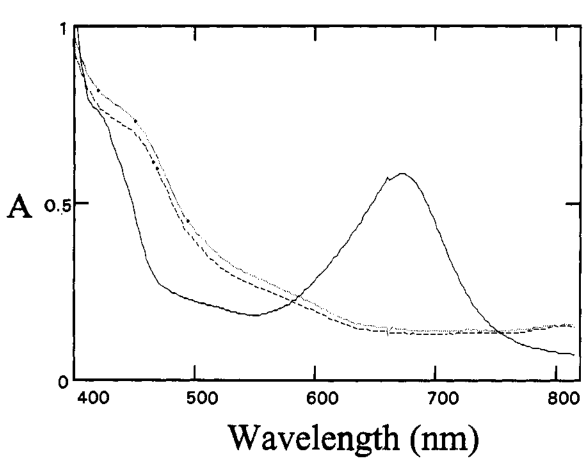


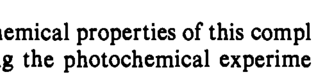
Figure 2. Electronic spectroscopy in acetonitrile: (—) original $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ solution (2.8×10^{-5} M) with added triphenylamine (1.4×10^{-2} M) containing 0.1 M Bu_4NPF_6 in acetonitrile; (···) after electrochemical generation of $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{3+}$; (- - -) after photolysis for 30 min to photochemically generate $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{3+}$.

Photolysis of the trimetallic in the presence of triphenylamine also leads to production of the two-electron-reduced complex. Due to the low solubility of triphenylamine in acetonitrile, higher light intensities are needed. Photolysis of a solution of the trimetallic in a saturated solution of triphenylamine using light with $\lambda > 340$ nm is shown in Figure 2. This yields a much cleaner match with the electrochemical result since we do not observe any contributions to the visible spectrum from the oxidation product of the triphenylamine. Subsequent electrolysis of the photolysis product is possible to regenerate the synthesized oxidation state, $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$.

Results and Discussion

This trimetallic species is prepared in 95% yield by using an $[Ir(dpb)_2Cl_2]^+$ metal complex as a "bridging ligand" in our building block approach to couple two ruthenium bis(bipyridine) moieties together as outline in Scheme 1. This title trimetallic complex is one in a series of such systems recently prepared in our laboratory of the general form $\{[(bpy)_2Ru(BL)]_2MCl_2\}^{n+}$ (BL = 2,3-bis(2-pyridyl)pyrazine, 2,3-bis(2-pyridyl)quinoxaline, or 2,3-bis(2-pyridyl)benzoquinoxaline and M = Ir^{III}, Rh^{III}, and Os^{II}), and the details of their preparation and characterization appear elsewhere.[3,5,6]

Our interest in these complexes arises from their ability to covalently couple two light-absorbing fragments to a central metal core. This forms the basis for a photochemical molecular device for photoinitiated electron collection.[2p] Photolysis of $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ in the presence of an added sacrificial electron donor leads to the formation of the doubly reduced species, $\{[(bpy)_2Ru(dpb^-)]_2IrCl_2\}^{3+}$, in which both bridging ligands coordinated to the central iridium metal center have been photoreduced by one electron (LA = ruthenium light absorber, BL = dpb, CAT = central iridium metal center):



The electrochemical properties of this complex are important in understanding the photochemical experiment. This mixed-metal trimetallic complex has numerous electroactive moieties and shows two reversible oxidations and a series of six reversible

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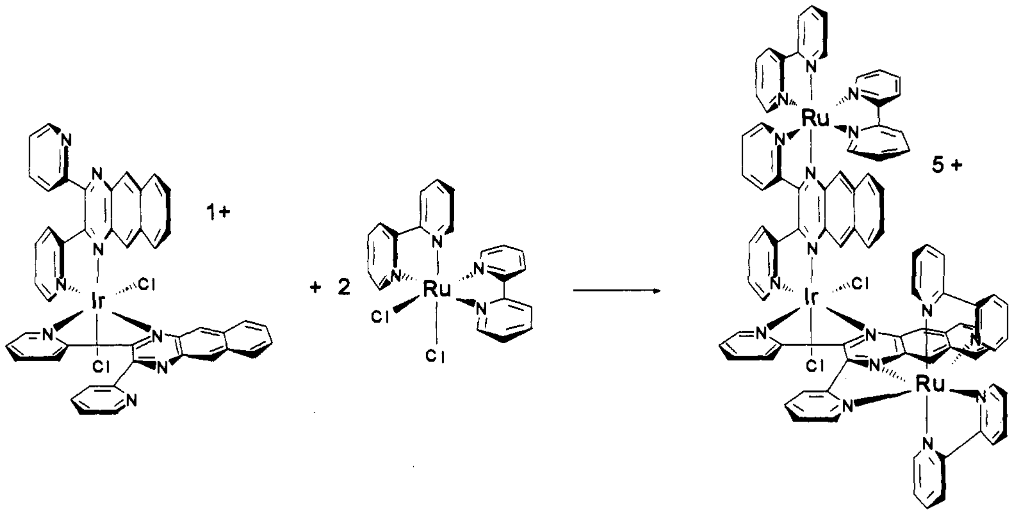
Scheme 1



reductions on the cyclic voltammetric time scale. The two equivalent dpb ligands reduce at different potentials, 0.03 and −0.12 V vs $Ag^+/AgCl$. This indicates a stabilization of the species with one dpb reduced, $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{4+}$. The $\Delta E_{1/2}$ gives a measure of the energetics of the comproportionation reaction ($K_{com} = e^{\Delta E_{1/2}\,(mV)/25.69}$ at T = 298 K).[7]

$$\text{dpb}^-,\text{dpb}^- + \text{dpb},\text{dpb} \overset{K_{com}}{\rightleftarrows} 2\text{dpb}^-,\text{dpb}$$

For $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$, the comproportionation constant is 340. This indicates that a mixture of the doubly and unreduced trimetallic would comproportionate to yield largely the singly reduced species. The oxidative wave represents the nearly simultaneous oxidation of the two equivalent terminal ruthenium centers. This gives rise to a molecule with a highest occupied molecular orbital that is based on either of the two equivalent ruthenium centers. The lowest unoccupied molecular orbital in this system is based on either of the two equivalent dpb bridging ligands. Hence, the lowest lying excited state in this complex is $Ru(d\pi) \rightarrow dpb(\pi^*)$ MLCT in nature involving either of the two equivalent terminal chromophoric units. It is the nature of this MLCT that directs the collected electrons toward the central iridium core in this molecule.

Bulk electrolysis to generate the one-, two-, three-, and four-electron-reduced species as well as the two-electron-oxidized species has been achieved with greater than 95% reversibility. The electronic spectroscopy of the synthesized oxidation state, as well as the two-electron-reduced species obtained through spectroelectrochemical studies, is shown in Figure 1.[3] The electronic spectrum of the singly reduced complex is intermediate between that obtained for the doubly reduced complex and the synthesized oxidation state. The absorbance at 660 nm for the 4+ complex is one-half that of the 5+ species. It is this wavelength that is utilized to monitor the photochemistry. A previous report describing the spectroelectrochemistry of a series of such trimetallics has been published.[3,5] The figure presented here shows spectroelectrochemistry conducted in the presence of 2 equiv of oxidized dimethylaniline to make comparison to the photochemical experiment more valid. The UV region of the photochemical experiment is obscured by the dimethylaniline, and thus only the visible spectroscopy is reported. Many characteristic changes are observed in the electronic spectroscopy of the species with two reduced bridging ligands, $\{[(bpy)_2Ru(dpb^-)]_2IrCl_2\}^{3+}$. Most notably a loss of the lowest lying $Ru(d\pi) \rightarrow dpb(\pi^*)$ MLCT transition at 666 nm is observed. This is consistent with electrochemical occupation of this dpb-based π^* orbital, giving rise to a large shift in energy of this transition. In addition, the $Ru(d\pi) \rightarrow bpy(\pi^*)$ MLCT previously at 414 nm is shifted to 448 nm upon the reduction of the dpb ligands. This effect has been observed by Wertz et al. upon the reduction of $\{[(bpy)_2Ru]_2(dpq)\}^{4+}$.[8] This red shift is a result of the decreased π acidity of the dpb ligand upon reduction, giving rise to more π back-bonding with the bpy ligand, resulting in a stabilization of the bpy-based π^* orbitals. This shifts the MLCT terminating on this orbital to lower energy.

Figure 1 also shows the results of the photolysis of $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ at 650 nm in the presence of 0.035 M dimethylaniline. The photolysis was performed in a 1-cm cylindrical cell that was deoxygenated and thermostated during the experiment. The reaction was monitored spectroscopically and reached completion at 30 min of photolysis. The spectrum generated upon exhaustive photolysis is very similar to that of the electrochemically generated two-electron-reduced species, $\{[(bpy)_2Ru(dpb^-)]_2IrCl_2\}^{3+}$.

Hand and Nelson reported on the oxidation of dimethylaniline in acetonitrile.[9] They observed that the product of this oxidation varied as a function of dimethylaniline concentration. Specifically, at low dimethylaniline concentrations *N,N,N′,N′*-tetramethylbenzidine (TMB) is formed. As dimethylaniline concentration increased and electrolysis time increased two other products appeared, 4,4′-methylenebis(*N,N*-dimethylaniline) and crystal violet. In our photochemical experiment, the concentration of dimethylaniline is high (0.035 M), although the concentration of oxidized dimethylaniline remains low (2.6×10^{-5} M). In the electrochemical experiment it is necessary to keep the concentration of dimethylaniline low, in order to have the oxidation product of dimethylaniline at twice the concentration of the trimetallic and still be able to observe the electronic absorption spectroscopy of the solution. This gives rise to different concentrations of dimethylaniline and thus could lead to differences in the product distributions. This assertion is strengthened by the observation of a small peak at ca. 590 nm in the photochemical experiment. This peak is located at the position reported by Hand and Nelson for the product crystal violet. This product also has a broad, less intense peak at 700 nm. This would give rise to the slight discrepancy between the electrochemical and photochemical result in this region, i.e. 550–800 nm. The slight decrease in absorbance of the photolysis sample in the 400–500-nm region could result from varying concentrations of TMB, which displays a broad absorbance centered around 450 nm.

Photolysis of the trimetallic in the presence of triphenylamine leads to much cleaner spectroscopy since no contribution is

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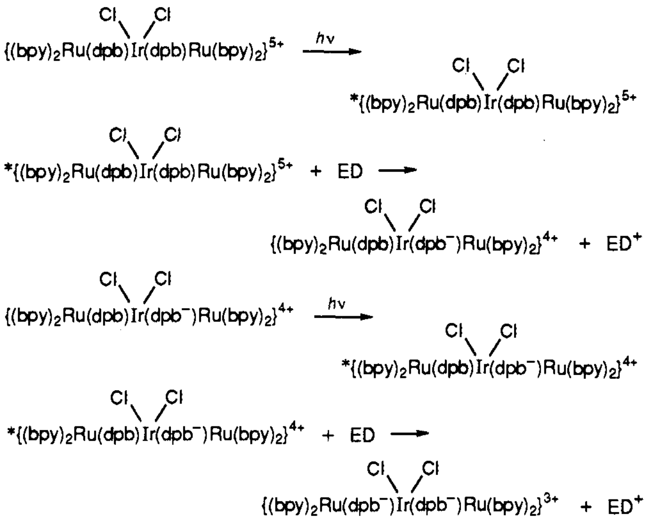
observed in the region of interest from the oxidation of the triphenylamine. Much higher light intensities are needed due in part to the limited solubility of NPh_3 in CH_3CN. Figure 2 illustrates a comparison of the photochemical and electrochemical generation of the two-electron-reduced trimetallic, $\{[(bpy)_2Ru(dpb^-)]_2IrCl_2\}^{3+}$, using the same solution. The spectrum generated upon exhaustive photolysis is virtually superimposable with that of the electrochemically generated two-electron-reduced species. Spectra taken along the course of the photolysis reaction are also indistinguishable from spectra taken as the complex is electrochemically reduced by one and then a second electron.

The photochemical data can be described in terms of a series of elementary steps:



$$\{(bpy)_2Ru(dpb)Ir(dpb)Ru(bpy)_2\}^{5+} \xrightarrow{h\nu} {}^*\{(bpy)_2Ru(dpb)Ir(dpb)Ru(bpy)_2\}^{5+}$$

$${}^*\{(bpy)_2Ru(dpb)Ir(dpb)Ru(bpy)_2\}^{5+} + ED \longrightarrow \{(bpy)_2Ru(dpb)Ir(dpb^-)Ru(bpy)_2\}^{4+} + ED^+$$

$$\{(bpy)_2Ru(dpb)Ir(dpb^-)Ru(bpy)_2\}^{4+} \xrightarrow{h\nu} {}^*\{(bpy)_2Ru(dpb)Ir(dpb^-)Ru(bpy)_2\}^{4+}$$

$${}^*\{(bpy)_2Ru(dpb)Ir(dpb^-)Ru(bpy)_2\}^{4+} + ED \longrightarrow \{(bpy)_2Ru(dpb^-)Ir(dpb^-)Ru(bpy)_2\}^{3+} + ED^+$$

The first step involves the excitation of one of the ruthenium to dpb MLCT excited states. This state undergoes excited-state electron transfer in a bimolecular process, leading to reduction of the trimetallic species and oxidation of the electron donor in the second step. Due to the presence of two ruthenium centers, this series of events can be repeated to give the doubly reduced complex, $\{[(bpy)_2Ru(dpb^-)]_2IrCl_2\}^{3+}$. Due to the comproportionation of any doubly reduced complex with the unreduced species to yield the singly reduced complex, a buildup of the singly reduced trimetallic should occur during the first half of the photolysis. In the last half of the photochemical reaction, steps 3 and 4 dominate as the singly reduced complex is converted to the desired doubly reduced species. Reoxidation of this photochemically two electron reduced complex can be achieved electrochemically.

Figure 3 illustrates the changes in the visible spectroscopy as a function of time for the photolysis of a 3.0×10^{-5} M solution of $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ in the presence of 0.035 M dimethylaniline. Similar results are obtained for the photolysis in the presence of triphenylamine. This data is quite similar to that obtained as one monitors the progress of the electrochemical generation of the two-electron-reduced complex, $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{3+}$. This is consistent with the photochemical scheme proposed in which the complex is first reduced by one and then by a second electron.

An analysis of the effect of dimethylaniline concentration on the quenching of the trimetallic complex was carried out. Dimethylaniline was chosen for this study instead of triphenylamine due to the limited solubility of the later. The $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ concentration was held constant at 2.8×10^{-5} M, while the concentration of dimethylaniline was varied from 35.2 to 9.85 mM. The results of this quenching study are presented in Figure 4. $\Phi_{apparent}$ values are obtained utilizing ΔA at 660 nm, as described in the Experimental Section. The quantum yields in Figure 4 were obtained by plotting $\Phi_{apparent}$ versus photolysis

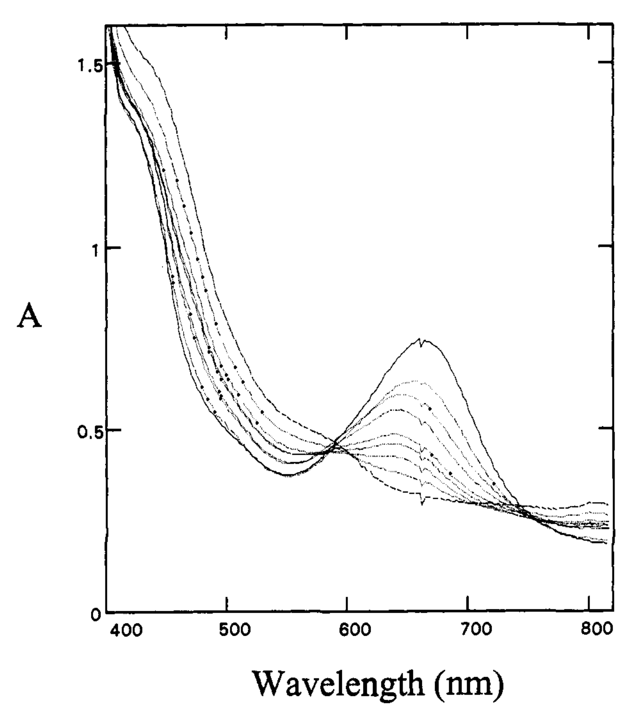


Figure 3. Electronic spectroscopy in acetonitrile of 3.0×10^{-5} M $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ and 0.035 M dimethylaniline as a function of photolysis time. (—) initial; (···) intermediate times; and (- - -) 30 min of photolysis.

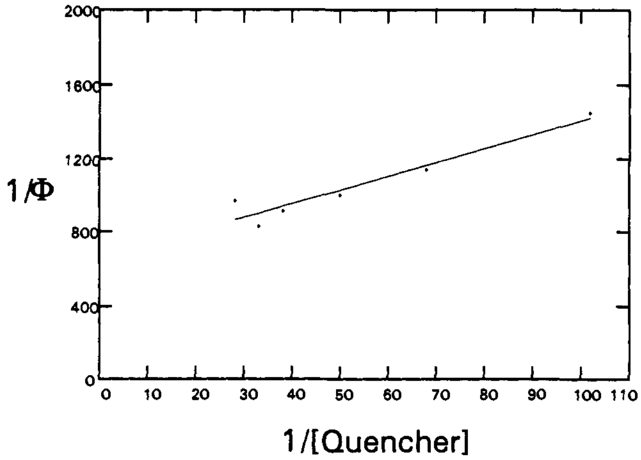


Figure 4. Quenching plot for the photolysis of 2.8×10^{-5} M $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ in the presence of dimethylaniline.

time for each dimethylaniline concentration and extrapolating using data collected at short times to get the quantum yield at zero time, $\Phi_{limiting}$. It is these limiting quantum yields that are utilized in Figure 4. Since short photolysis times are used for the quenching study, contributions to the spectroscopy from oxidized dimethylaniline are minimal. Our spectroscopic quenching analysis only considers the first excited state electron transfer quenching step since it requires that we analyze the data at early photolysis times.

The kinetic scheme that is applicable to this problem is outlined below with A = $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ and Q = NMe_2Ph.

$$A + h\nu \xrightarrow{I_a} {}^*A \qquad \text{excitation}$$

$${}^*A \xrightarrow{k_1} A + h\nu' \qquad \text{radiative decay}$$

$${}^*A \xrightarrow{k_2} A + \text{heat} \qquad \text{nonradiative decay}$$

$${}^*A + Q \xrightarrow{k_q} A^- + Q^+ \qquad \text{electron-transfer quenching}$$

$$^*A + Q \xrightarrow{k_3} A + Q \quad \text{all other bimolecular quenching}$$

and $k_q' = k_q + k_3$ and $k_t = k_1 + k_2$.

Applying a steady-state approximation to [$^*A$], one concludes that $1/\phi_{(A^-)} = k_t/k_q[Q] + k_q'/k_q$. From the ratio of the intercept to the slope of the plot in Figure 3, one obtains a bimolecular quenching constant of 85 M^{-1}. Using limiting values of the slope and intercept, one can determine the error of this measurement. Applying this method, one obtains a range of 60–150 M^{-1} for this bimolecular quenching constant. This constant represents the product of the bimolecular rate constant for the sensitization, k_q', and the excited-state lifetime of $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$, τ.

One can calculate an upper limit for the bimolecular rate constant assuming diffusion control.[10] $K_{diff} = 8RT/3000n$, where n is the viscosity of the solvent and $T = 298$ K. Using this method, one estimates $K_{diff} = 1.9 \times 10^{10}$ M^{-1} s^{-1}. Given that $k_q' \tau = 85$ M^{-1}, one calculates a lower limit for the lifetime of $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ of 4.5 ns. Given that $\{[(bpy)_2Ru(dpp)]_2IrCl_2\}^{5+}$ and $\{[(bpy)_2Ru(dpq)]_2IrCl_2\}^{5+}$ have lifetimes of 32 and 5 ns, respectively, the lifetime of the dpb trimetallic should be on the order of a few nanoseconds (dpp = 2,3-bis(2-pyridyl)pyrazine and dpq = 2,3-bis(2-pyridyl)quinoxaline).[3] This complex does not display an emission that is detectable with our system.[11] Attempts to measure its lifetime by transient absorbance spectroscopy indicate that $\tau < 10$ ns. The lower limit of the lifetime obtained by quenching analysis, 4.5 ns, applies if all excited states are quenched at a diffusionally controlled rate. Any deviation from this would dictate a longer lifetime of the trimetallic complex, presuming the applied dynamic quenching mechanism. Given this, the expected lifetime of the trimetallic complex may be insufficient to fully explain these results using only a dynamic quenching model. This may indicate that a preassociation of the dimethylaniline with the trimetallic complex leading to static quenching may also be important. This is not surprising since the extended π system of the dpb bridging ligands could have a π-stacking interaction with the dimethylaniline.

The intercept of the plot obtained for the quenching study, Figure 4, yields a value of Φ at infinite quencher concentration of 0.0015. This indicates that other bimolecular quenching processes such as energy transfer or bimolecular deactivation may be important and that these processes do not lead to the ultimate observation of product. In addition, this low quantum efficiency could result from slow cage escape and/or rapid back electron transfer.

Conclusions

This study clearly illustrates that complexes can be designed and constructed which incorporate multiple light absorbers and that these covalently linked light absorbers can both function within a single molecule. The complex $\{[(bpy)_2Ru(dpb)]_2IrCl_2\}^{5+}$ has been shown to function as a molecular device for photoinitiated electron collection. A series of these types of mixed-metal trimetallics have been prepared in our laboratory, and many other members of this series may also serve this function. Modification of this system to tune the redox potential of the photochemically generated two-electron-reduced complex should be possible within this framework due to the multicomponent nature of these supramolecular complexes. In this study, dimethylaniline is used as the electron donor. The results of a quenching analysis indicate a preassociation of the dimethylaniline may play a role in the quenching observed, i.e. static quenching. The low value of the quantum yield at infinite quencher concentration indicates the presence of other bimolecular quenching processes that do not lead to the formation of product. These may include fast, efficient back electron transfer. In addition, bimolecular deactivation of the excited state could occur. The low quantum efficiency for this process dictates the modification of this structural design. The incorporation of covalently attached electron donors to ruthenium chromophores possessing these polyazine bridging ligands has been accomplished in our laboratory.[12] Application of other polypyridine based light absorbers is also in progress.[13] The ultimate goal of these studies is to use these molecular devices to deliver two electrons to a substrate.

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