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Photophysics and Photochemistry of Chromophore−Quencher Assemblies on Glass and Powdered Silica

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The photophysical properties of the chromophores $[Ru(bpy)_2(4,4'-(CO_2H)_2bpy)](PF_6)_2$ [$(4,4'-(CO_2H)_2bpy)$ is 4,4′-dicarboxy-2,2′-bipyridine], $[Re(4,4'-(CO_2H)_2bpy)(CO)_3(4-Etpy)](PF_6)$ (4-Etpy is 4-ethylpyridine), and the chromophore-quencher complex $[Re(4,4'-(CO_2H)_2bpy)(CO)_3(py-PTZ)](PF_6)$ have been investigated on high surface area silica particles with 1,2-dichloroethane (DCE) as the external solvent for the index of refraction matching. Surface coverages were estimated by direct absorption measurements with DCE as the external solvent. Decay of the metal-to-ligand charge transfer (MLCT) excited state of $[Ru(bpy)_2(4,4'-(CO_2H)_2bpy)](PF_6)_2$ on silica is exponential and independent of surface coverage from $\Gamma = 1.5 \times 10^{-14}$ to 1.3×10^{-13} mol·cm^{-2}. For $[Re(4,4'-(CO_2H)_2bpy)(CO)_3(4-Etpy)](PF_6)$, MLCT emission shifts from 600 nm in DCE to 605 nm on silica and τ decreases from 487 to 255 ns. On surfaces containing both the Ru complex and the electron transfer quenchers *N*-methyl-*N*-viologenpropanoic acid bis(hexafluorophosphate) $[MV-CO_2H](PF_6)_2$ or 3-(10*H*-phenothiazin-9-yl)propanoic acid, $PTZ-CO_2H$, there is no evidence for cross-surface quenching from lifetime measurements. The transient absorption difference spectrum acquired following laser flash photolysis of $[Re(4,4'-(CO_2H)_2bpy)(CO)_3(py-PTZ)]-(PF_6)$ on silica resembles the spectrum in DCE, with absorptions appearing for $bpy^{\bullet -}$ at ~360 nm (with an additional shoulder at ~390 nm) and $PTZ^{\bullet +}$ at ~520 nm. These features are consistent with formation of the redox-separated state $[Re(4,4'-(CO_2H)_2bpy^{\bullet -})(CO)_3(py-PTZ)^{+}]^{+}$. It returns to the ground state by $bpy^{\bullet -} \rightarrow PTZ^{+}$ electron transfer with $k = 2.9 \times 10^{7}$ s^{-1}.

Introduction

The self-assembly of redox-active carboxylic acid derivatives on glass and metal oxide substrates is a well-established procedure.[1] It complements other procedures for surface or near-surface immobilization of molecules in rigid media,[2] including zeolites,[3] Langmuir−Blodgett films,[4] hydrogels,[5] semiconductor surfaces,[6] porous Vycor glass,[7] and chemically-modified electrodes.[8] We recently investigated the spectroscopic and electrochemical properties of the metal-to-ligand charge transfer (MLCT) absorbers $[M(bpy)_2(4,4'-(CO_2H)_2bpy)](PF_6)_2$ $(4,4'-(CO_2H)_2bpy$ is 4,4′-dicarboxy-2,2′-bipyridine; M = Ru, Os) on glass, In_2O_3, and SnO_2 and on mixed surfaces containing combinations of chromophores and quenchers. Evidence was obtained from resonance Raman measurements for surface interaction via ester formation or H-bonding and from photophysical measurements for surface quenching by electron or energy transfer.[1a] In this manuscript, we extend the attachment chemistry to a silica catalyst support as substrate in order to investigate the influence of surface immobilization on excited state properties and intramolecular electron transfer in a chromophore-quencher assembly.

Experimental Section

Materials. The solvents 1,2-dichloroethane (DCE) and CH_3CN (both Burdick & Jackson high purity) were used as received; all other solvents were reagent grade. Hydrazine hydrate, lead dioxide, [Ru-

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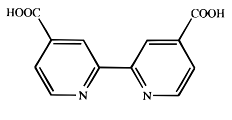
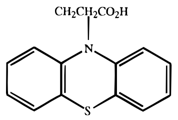
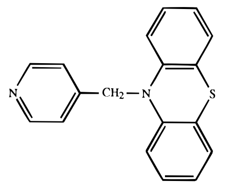
(bpy)$_3$]Cl$_2$, and silica catalyst support (Aldrich; grade 951) were also used as received. [Ru(bpy)$_3$]Cl$_2$ was oxidized to [Ru(bpy)$_3$]$^{3+}$ just prior to use by using PbO$_2$ as oxidant and obtained as the PF$_6^-$ salt by precipitation from water with added NH$_4$PF$_6$. Tin-doped indium oxide (ITO) was purchased as 50 mm × 7 mm slides from Delta Technologies, Ltd., Stillwater, MN, and consisted of a ~2000 Å sputtered metal oxide coating on a float glass substrate. [Ru(bpy)$_2$(4,4′-(CO$_2$H)$_2$bpy)](PF$_6$)$_2$ was synthesized by the literature procedure.[9] [Re(4,4′-(CO$_2$H)$_2$bpy)(CO)$_3$(4-Etpy)](PF$_6$) and [Re(4,4′-(CO$_2$H)$_2$bpy)(CO)$_3$(py-PTZ)](PF$_6$) were synthesized by analogy to previously reported Re(I) polypyridyl complexes as described below.[10] [MV-CO$_2$H](PF$_6$)$_2$[1a] and PTZ-CO$_2$H,[11] were prepared by literature procedures. The various structures are shown below:



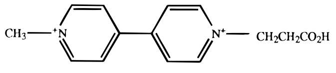
[4,4'-(CO$_2$H)$_2$bpy]



[PTZ-CO$_2$H]



[py-PTZ]



[MV^{2+}-CO$_2$H]

[Re(4,4′-(CO$_2$H)$_2$bpy)(CO)$_3$Cl]. A 244 mg amount of 4,4′-(CO$_2$H)$_2$-bpy and 362 mg of Re(CO)$_5$Cl were added to 50 mL of ethylene glycol dimethyl ester and heated at reflux for 4 h. The solution was cooled to room temperature, and 100 mL of hexane was added with stirring. The resulting precipitate was filtered and dried in air. The reaction was essentially quantitative. IR (cm^{-1}): ν(CO) 1730, 1898, 1922, 2022. NMR (D$_2$O with Na$_2$CO$_3$, ppm): 7.87 (doublet, 2H), 8.68 (singlet, 2H), 9.08 (doublet, 2H).

[Re(4,4′-CO$_2$H)$_2$bpy)(CO)$_3$(4-Etpy)](PF$_6$). A 200 mg amount of [Re(4,4′-(CO$_2$H)$_2$bpy)(CO)$_3$Cl], 140 mg of Ag(CF$_3$SO$_3$), and ~1 mL of 4-ethylpyridine (4-Etpy) were mixed in 75 mL of 3:1 (v:v) CH$_3$OH/H$_2$O and heated at reflux for 4 h. After cooling, AgCl was filtered off. A dilute solution of HPF$_6$ was added to precipitate the product. The solid was collected by vacuum filtration and purified by dissolving it in 50 mL of dilute NH$_4$OH solution followed by precipitation with HPF$_6$; yield, 170 mg. IR (in KBr, cm^{-1}): ν(CO) 1918, 2033. NMR (acetone-d_6, ppm): 1.10 (triplet, 3H), 2.63 (multiplet, 2H), 7.30 (doublet, 2 H), 8.33 (doublet, 2H), 8.42 (doublet, 2H), 9.44 (singlet, 2H), 9.6 (doublet, 2H).

[Re(4,4′-(CO$_2$H)$_2$bpy)(CO)$_3$(py-PTZ)](PF$_6$). This salt was prepared by hydrolyzing the ester analogue. In the procedure, 100 mg of [Re-(4,4′-(CO$_2$Et)$_2$bpy)(CO)$_3$(py-PTZ)](TFMS)[10] (TFMS is the triflate anion and py-PTZ is bound to Re through the pyridine N), dissolved in 30 mL CH$_3$OH, and 5 equiv of LiOH, dissolved in 10 mL H$_2$O, were mixed and stirred at room temperature under Ar for 20 h. The pH of the solution was adjusted to ~3 with HPF$_6$. The yellow precipitate was collected and dried to give 50 mg of the product. IR (in KBr, cm^{-1}): ν(CO) 1919, 1922, 2035. NMR (DMSO-d_6, ppm): 5.15 (singlet, 2H), 6.62 (doublet, 2H), 7.00 (triplet, 2H), 7.11 (doublet, 2H), 7.28 (doublet, 2H), 8.13 (doublet, 2H), 8.31 (doublet, 2H), 8.89 (triplet, 2H), 9.04 (singlet, 2H), 9.36 ppm (doublet, 2H).

The carboxylic acid derivatives were attached to either ITO electrodes or powdered silica catalyst support according to previously published methods[1a] by soaking the substrate in a fresh acetonitrile solution containing the complex for at least 2 h (typically overnight). Qualitatively, the degree of surface loading was found to be a function of the concentration of the derivatizing complex, derivatization time, and dryness of the solvent. After attachment, the substrates were soaked for 15 min and rinsed repeatedly with CH$_3$CN or CH$_2$Cl$_2$ until the rinsings were spectroscopically free of complex. In the last step, the derivatized ITO electrodes or silica powders were dried in air or at 25 °C under vacuum. Surface attachment of [Ru(bpy)$_2$ (4,4′-(CO$_2$H)$_2$bpy)](PF$_6$)$_2$ to the semiconductor side of the ITO electrodes was confirmed by the appearance of the Ru$^{III/II}$ wave in cyclic voltammograms. Spectroscopic measurements on the derivatized powdered silica samples were performed in 1 cm cuvettes which were mixed with enough DCE to form a transparent mixture.

Mixed surfaces were prepared by competitive binding; both carboxylic acid-containing molecules were present in the derivatizing solution in varying proportions. Mixed, powdered silica containing [Re(4,4′-(CO$_2$H)$_2$bpy)(CO)$_3$(4-Etpy)](PF$_6$) and either PTZ-CO$_2$H or [MV-CO$_2$H](PF$_6$)$_2$ in differing Re/quencher ratios were prepared by stirring the following acetonitrile solutions with the silica catalyst in the dark for >16 h: (a) 1.33 mM quencher and 2.67 mM Re(I) complex, (b) 0.667 mM quencher and 0.667 mM Re(I) complex, and (c) 0.267 mM quencher and 1.33 mM Re(I) complex. The resulting samples were washed and dried as before.

Estimates of the degree of surface loading on silica were made on the basis of electronic absorption measurements by using solution molar absorptivities (ϵ) for structurally related models in solution. These values are only approximate. If absorptions were too high, samples were diluted by the addition of underivatized silica gel. The absorbances were corrected by the mass fraction of added silica. The values for ϵ used in the calculations were as follows: (a) [Re(4,4′-(CO$_2$H)$_2$-bpy)(CO)$_3$(4-Et-py)](PF$_6$) at 398 nm, 4900 M^{-1} cm^{-1};[10] (b) [Re(4,4′-(CO$_2$H)$_2$bpy)(CO)$_3$(py-PTZ)](PF$_6$) at 394 nm, 6000 M^{-1} cm^{-1};[10] and (c) [Ru(bpy)$_2$(4,4′-(CO$_2$H)$_2$bpy)](PF$_6$)$_2$ at 460 nm, 12 700 M^{-1} cm^{-1}.[12] Estimates for bound [MV-CO$_2$H](PF$_6$)$_2$ were obtained by reducing the derivatized silica samples to [MV$^{\bullet+}$-CO$_2$H] with excess hydrazine hydrate and using $\epsilon = 13\,900$ M^{-1} cm^{-1} at 610 nm for MV$^{\bullet+}$-CO$_2$H.[13] The amount of bound PTZ-CO$_2$H was determined by oxidation with excess Ru(bpy)$_3^{3+}$ and measurement of the Ru(bpy)$_3^{2+}$ produced by using $\epsilon = 14\,300$ M^{-1} cm^{-1} at 452 nm.[14] Surface coverages in mol L^{-1} were converted to mol cm^{-2} by using 2.2 g/mL as the density of amorphous silica gel[15] and 600 m^2/g as the BET surface area of the silica catalyst.[16]

Measurements. Electronic spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer in 1 cm cuvettes. Infrared spectra were recorded in 1,2-dimethoxyethane between NaCl plates by using a Mattson Galaxy Series FTIR 5000 spectrometer. ^{1}H NMR spectra were recorded at 200 MHz on a Bruker AC 200 spectrometer. Room temperature, continuous wave (cw) emission spectra were recorded on a Spex Fluorolog-F212 emission spectrometer equipped with a 450 W Xenon lamp and cooled Hamamatsu 1477 or 666-1 or R928 photomultipliers. Electrodes were placed against the internal front face of a standard cuvette with degassed CH$_2$Cl$_2$ in the external solution. Emission from ITO surfaces was collected with a front face (45°) geometry and from solution and powdered silica samples at 90°. The spectra were corrected for the spectral sensitivity of the detector. Solutions employed for luminescence lifetime or transient absorption experiments were freeze−pump−thawed three or more times to ~10^{-5} Torr by using a diffusion pump of standard design. Equivalent results were obtained by preparing the samples in a nitrogen-purged glovebox and sealing in airtight cuvettes.

Emission lifetimes were measured following laser flash excitation by using a PRA nitrogen laser Model LN1000 and a PRA dye laser Model LN102. Emission decays were monitored at the emission maximum by using a PRA monochromator Model B204-3 and a Hamamatsu R-928 phototube and recorded on LeCroy 9400 or 72000A digital oscilloscopes interfaced to an IBM PC. The digitized traces were fit to the appropriate model with a Levenberg−Marquardt routine.

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Table 1. Comparison of Photophysical and Photochemical Properties of $[Ru(bpy)_2(4,4'\text{-}(CO_2H)_2bpy)](PF_6)_2$

medium/ external solvent	λ_{abs}, nm (lowest MLCT)	λ_{em}, nm (emission max)	τ, μs	
			emission	absorption
solution/CH_3CN	474	680	1.42	1.38
glass[a]/CH_2Cl_2	*b*	644–674[c]	<0.010[d]	*b*
silica/DCE	464	658	1.45	1.42

[a] On the glass side of glass plates coated with ITO. [b] Absorption and transient absorption features were too weak on this surface to provide meaningful data. [c] Varies with surface coverage.[1a] [d] The decay kinetics were nonexponential. The average lifetime $\langle\tau\rangle$ varied with surface coverage[1a]

Derivatized ITO samples were mounted with the glass side of the electrode flush against the front face of a standard 1 cm cuvette with DCE in the external solution. Emission decay traces were collected at 45° to the excitation beam. Solution and powdered silica samples were measured at 90° to the excitation beam. A solution potassium dichromate filter was employed between the sample and monochromator to eliminate scattered light. Traces from 100 laser shots were averaged and collected.

Transient absorption difference spectra were measured by using an apparatus described previously.[17] Laser excitation at 420 nm was achieved by using the third harmonic (354.7 nm) of a Quanta Ray DCR-2A Nd:YAG laser to pump a Quanta Ray PDL-2 dye laser containing stilbene dissolved in dioxane. An Applied Photophysics laser kinetic spectrometer (consisting of a 300 W pulsed Xe lamp source, an f/3.4 grating monochromator, and a five-stage photomultiplier tube) and a LeCroy 9400 oscilloscope interfaced to an IBM PC were employed as the detection system. Optical densities of <0.3 were typically employed and collinear excitation was used along with appropriate Oriel or Corning cutoff filters to exclude high-energy scattered light. Electronic control and synchronization of the laser, probe, and digitizer were provided by electronics of our own design.[17c] The results of 10 laser shots were collected and averaged. The resulting decay traces were corrected for emission and scattering from the solid substrate.

Intensity–time decay profiles were fit to either a single exponential decay function or to the Williams–Watts (Kolrausch) function[18] in eq 1 by using a Levenberg–Marquardt[19] fitting routine. The physical basis

$$I(t) = I_0 \exp\{(-kt)^{\beta}\} \tag{1a}$$

$$\langle\tau\rangle = \frac{1}{k\beta}\Gamma(1/\beta) \tag{1b}$$

for application of this function is to an asymmetrical distribution of exponential decays. In eq 1, $I(t)$ is the emission intensity at time t, I_0 is the emission intensity at $t = 0$, k is the decay rate constant, β is a constant which represents the degree of deviation from exponentiality, $\langle\tau\rangle$ is the average lifetime, and Γ is the gamma function.[19c]

Results

The photophysical and photochemical properties of $[Ru(bpy)_2(4,4'\text{-}(CO_2H)_2bpy)](PF_6)_2$ attached to the glass side of an ITO electrode, to the high surface area silica catalyst support, and in CH_3CN are summarized in Table 1. Emission is nearly completely quenched from the semiconductor side of the electrode.[1a] As previously reported, ground state–excited state interactions occur between complexes on highly-loaded glass slides.[1a] These interactions manifest themselves in decreased emission intensities, decreased emission lifetimes, and a red shift in the emission maximum as the surface coverage is increased. The emission decays are nonexponential, but the data could be fit satisfactorily to eq 1a with $\langle\tau\rangle$ in the range <10 to ~550 ns. On mixed surfaces containing both $[Ru(bpy)_2(4,4'\text{-}(CO_2H)_2bpy)](PF_6)_2$ and an electron transfer quencher such as $[MV\text{-}CO_2H](PF_6)_2$, quenching of the emission was observed.[1a]

For $[Ru(bpy)_2(4,4'\text{-}(CO_2H)_2bpy)](PF_6)_2$ on high surface area silica, there were no signs of ground state–excited state interactions on silica particles with coverages of 1.5×10^{-14} to 1.3×10^{-13} mol/cm^2. The emission maximum was ~658 nm regardless of the degree of loading. Emission decay was exponential with $\tau = 1.45$ μs with DCE in the external solution. In the transient absorption difference spectrum, a maximum appears for $bpy^{\bullet-}$ at ~370 nm and a bleach at ~460 nm for loss of the $Ru^{II} \rightarrow (bpy; 4,4'\text{-}(CO_2H)_2bpy)$ chromophores. These two features are reversible and are temporally correlated.

Data for $[Re(4,4'\text{-}(CO_2H)_2bpy)(CO)_3(py\text{-}PTZ)](PF_6)$ and the model, $[Re(4,4'\text{-}(CO_2H)_2bpy)(CO)_3(4\text{-}Et\text{-}py)](PF_6)$, are listed in Table 2. For the latter, the emission maximum is slightly red-shifted on silica (from 600 to 605 nm), and τ for emission decay decreases to 255 ns compared to 487 ns. The trend is consistent with the slightly decreased energy gap, but other factors probably play a role as well.[20] Within experimental error, τ was independent of surface coverage from 9.9×10^{-15} to 2.6×10^{-13} mol/cm^2. The $\pi \rightarrow \pi^*$ band for $bpy^{\bullet-}$ at 380 nm appeared in the transient absorption difference spectrum on silica. On surfaces containing $[Re(4,4'\text{-}(CO_2H)_2bpy)(CO)_3(4\text{-}Et\text{-}py)](PF_6)$ and $[MV\text{-}CO_2H](PF_6)_2$ or $[PTZ\text{-}CO_2H]$,[21] there was no sign of electron transfer quenching at the chromophore: quencher ratios from 1:1 to 1:3, Re/quencher. The excited state lifetime of the Re(I) complex was unaffected, and there was no evidence for either $[MV^{\bullet}\text{-}CO_2H\ ]^+$ (605 nm)[13] or $PTZ^{\bullet+}\text{-}CO_2H$ (520 nm)[22] following laser flash excitation. Intramolecular electron transfer quenching does occur in the chromophore–quencher complex $[Re(4,4'\text{-}(CO_2H)_2bpy)(CO)_3(py\text{-}PTZ)](PF_6)$. No emission was observed following 420 nm excitation in solution or when attached to the silica substrate. The transient absorption difference spectra for the complex in both media are shown in Figure 1. The spectra are similar with prominent absorptions for $bpy^{\bullet-}$ at ~360 nm for PTZ^+ and at ~520 nm but with a new shoulder at ~390 nm on silica. Decay lifetimes were comparable at 360 and 520 nm (37 and 33 ns), and slightly decreased from DCE (49 and 43 ns). No evidence of a rise time was observed in the formation of $[(4,4'\text{-}(CO_2H)_2bpy^{\bullet-})Re^{I}(CO)_3(py\text{-}PTZ^{\bullet+})]^+$, either in solution or on silica on the time scale of the experiment (5–10 ns) over a monitoring range of 325–600 nm.

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$$\Gamma(n) = \int_0^{\infty} x^{n-1} e^{-x}\,dx = (1/n)\prod_{m=1}^{\infty}[(1 + (1/m))^n/(1 + (n/m))],\ n = 1, 2, ...$$

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(21) The compositions of the mixed surfaces were as follows: (1) 1.3×10^{-13} mol·cm^{-2} $[Re(4,4'\text{-}(CO_2H)_2bpy)(CO)_3(4\text{-}Etpy)]^+$ and 4.3×10^{-14} mol·cm^{-2} $[MV\text{-}CO_2H](PF_6)_2$, (2) 5.4×10^{-14} mol·cm^{-2} Re and 5.3×10^{-14} mol·cm^{-2} $[MV\text{-}CO_2H](PF_6)_2$, (3) 7.4×10^{-14} mol·cm^{-2} Re and 6.6×10^{-14} mol·cm^{-2} $PTZ\text{-}CO_2H$, and (4) 9.1×10^{-14} mol·cm^{-2} Re and 4.4×10^{-14} mol·cm^{-2} $PTZ\text{-}CO_2H$.

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(23) Baxter, S. M.; Jones, W. E., Jr.; Danielson, E.; Worl, L.; Strouse, G.; Younathan, J.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47.

(24) Surridge, N. A.; McClanahan, S. F.; Hupp, J. T.; Danielson, E.; Gould, S.; Meyer, T. J. *J. Phys. Chem.*. **1989**, *93*, 294.

Table 2. Transient Absorption and Emission Data for [Re(4,4′-$(CO_2H)_2$bpy)$(CO)_3$(py-X)](PF_6) in Different Media

		medium[a]	
salt		DCE	silica/DCE
[Re(4,4′-$(CO_2H)_2$bpy)$(CO)_3$(4-Etpy)](PF_6)	λ_{max}(em), nm (τ, ns)	600 (487)	605 (255)
	λ_{max}(bpy)$^{\bullet-}$), nm (τ, ns)	380 (542)	390 (246)
[Re(4,4′-$(CO_2H)_2$bpy)$(CO)_3$(py-PTZ)](PF_6)	λ_{max}(bpy$^{\bullet-}$), nm (τ, ns)	380 (49)	380 (37)
	λ_{max}(PTZ$^{\bullet+}$), nm (τ, ns)	520 (43)	520 (33)

[a] For the transient absorption data, the chromophore that dominates absorptivity changes at the monitoring wavelength is indicated.

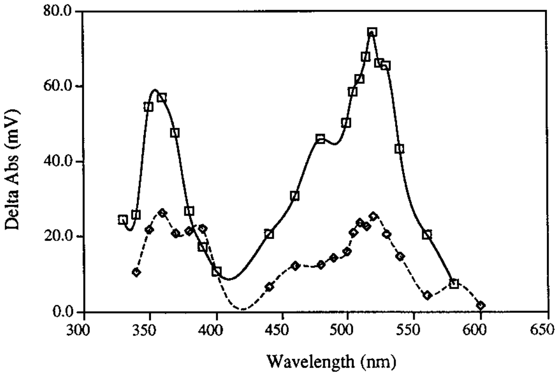


Figure 1. Transient absorption difference spectra for [Re(4,4′-$(CO_2H)_2$-bpy)$(CO)_3$(py-PTZ)] (PF_6) in DCE (solid line) and attached to powdered silica, grade 951 (dotted line) with external DCE. The spectra were obtained 40 ns after the laser pulse by using 420 nm collinear excitation with a laser power of ~1.3 mJ/pulse.

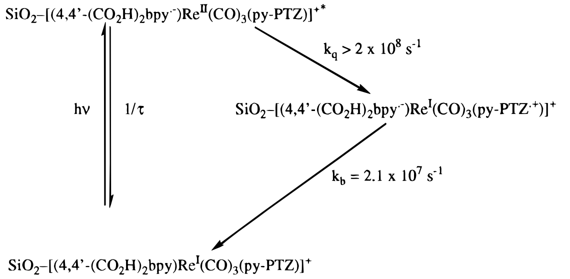
Discussion

The ITO electrodes used in the earlier study were glass plates coated more on the side with ITO. On the glass side, approximate monolayer coverages (~l × 10^{-10} mol cm^{-2}, based on a radius of 7.4 Å for the complex) of [Ru$(bpy)_2$(4,4′-$(CO_2H)_2$-bpy)]$(PF_6)_2$ were obtained, but, at these loadings, there is evidence for excited state−ground state interactions. Even at surface coverages (5 × 10^{-12} mol cm^{-2}) far less than monolayer, emission decay was nonexponential, and there are apparently multiple sites on these surfaces as well. Similar observations have been made by Wrighton *et al.*[8a] in their investigation of the photophysics of [(4,4′-$(CO_2R)_2$bpy)Re$(CO)_3$(py-PTZ)]$^+$ with R = (n-pr)$SiCl_3$ attached to metal oxide and powdered silica surfaces through silanyl links. In these structures, there are up to five monomolecular layers on the silica substrate.

Surface coverages on the high surface area silica substrate are far less than on glass or ITO electrodes. The highest loadings obtained were ~2.6 × 10^{-13} mol cm^{-2} based on a surface area of 600 m^2/g by BET measurements.[16] Thus, only a small fraction (~$^1/_{400}$) of the surface area is available for binding. Presumably, the bulk of the surface area is in microcavities and channels which are inaccessible to the complex and quenchers. The molecules that are on the surface are well-separated. Emission decays are single exponential and independent of surface coverage from 9.9 × 10^{-15} to 2.6 × 10^{-13} mol cm^{-2}. There is no sign of electron transfer quenching by [MV-CO_2H]$(PF_6)_2$ or PTZ-CO_2H on mixed surfaces. Surface binding of [Ru$(bpy)_2$(4,4′-$(CO_2H)_2$bpy)]$(PF_6)_2$ to metal oxides may occur by ester bond formation or hydrogen bonding to the surface, or even by a combination of the two.[1a] The similarities between MLCT absorption and emission energies on silica and in solution are also consistent with surface binding by ester formation or hydrogen bonding with the proton retained in the carboxylic acid group. These energies are known to be sensitive to changes between the acid (or ester) forms of the complexes and the deprotonated anions.[1a,12]

In solution, MLCT excitation of [(4,4′-$(X)_2$bpy)Re$(CO)_3$(py-PTZ)]$^+$ (X = OCH_3, CH_3, H, $CO_2C_2H_5$) is followed by rapid, intramolecular electron transfer to give the redox-separated states [(4,4′-$(X)_2$bpy$^{\bullet-}$)Re$(CO)_3$(py-PTZ$^{\bullet+}$)$^+$].[10] The same photochemistry exists on silica, Scheme 1, as shown by the transient absorption measurements and emission quenching. Unlike the example cited from the work of Wrighton et al., where there are up to five monolayers, there is no evidence for a rise time for electron transfer quenching on the time scale of our experiments (5−10 ns) and k_q > 2 × 10^8 s^{-1}. Back-electron transfer, k_b in Scheme 1, occurs with k_b = 2.9 × 10^7 s^{-1} compared to k_b = 2.1 × 10^7 s^{-1} for [4,4′-$(CO_2H)_2$bpy)Re$(CO)_3$-(py-PTZ)]$^+$ in DCE.

Scheme 1



The photophysical properties of the MLCT emitter and chromophore−quencher complex are relatively unperturbed on silica with external DCE compared to DCE solution. One exception is the apparent splitting that appears in the $\pi \rightarrow \pi^*$ (bpy$^{\bullet-}$) band in the transient absorption difference spectrum in Figure 1. This could be a consequence of reduced symmetry at the surface due to surface binding by only one of the acid groups. It is also consistent with more than one photochemical intermediate; for example, the simultaneous appearance of a Re^{II}(4,4′-$(CO_2H)_2$bpy$^{\bullet-}$) MLCT excited state. The nearly complete quenching of excited state emission would appear to rule out the latter possibility.

The observation of comparable photophysical behaviors (exponential decays, comparable spectra, and lifetimes) for these polypyridyl compounds of ruthenium(II) and rhenium(I) on powdered silica and in solution is important. It suggests a relatively homogeneous distribution of surface sites and interactions with the surface that leave the complexes relatively unperturbed. Consequently, high surface area silica may prove to be a useful substrate for the study of surface-bound photochemical reactions and for the investigation of isolated molecular assemblies. Due to surface immobilization, back-electron transfer by diffusion should not play a role and it may be possible to achieve long lifetimes for electron transfer intermediates.

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