Ruthenium(II) MLCT Excited States. Stabilization toward Ligand Loss in Rigid Media

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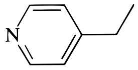
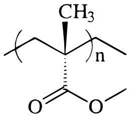
The excited state properties of polypyridyl complexes of Ru(II) and their assemblies are often complicated by the existence of low-lying dd or ligand field states of configuration $d\pi^5 d\sigma^{*1}$. Typically, these states are formed following metal-to-ligand charge transfer (MLCT) excitation followed by a thermally activated surface crossing to the dd state.[1] Once populated, they undergo rapid nonradiative decay or ligand loss photochemistry, and this can greatly limit the use of $\mathrm{Ru^{II}(bpy)}$ constituent units in molecular assemblies for energy conversion and related studies. In rigid media, such as cellulose acetate,[2] poly-ethylene oxide,[2a] SP Sephadex C-25,[2c] solvent glasses,[3] zeolites,[4] porous glass,[5] polysiloxanes,[6] etc.,[7] temperature dependent lifetime data have been acquired which suggest an increase in the activation barrier for MLCT → dd surface crossing.[3,4,8] We report here the additional observation that these rigid media can greatly inhibit ligand loss photochemistry and that they may provide useful matrixes for probing and exploiting energy conversion processes in molecular assemblies.

At room temperature in deaerated acetonitrile solutions that are 10^{-6}−10^{-3} M in $[\mathrm{Ru(bpy)_2(py)_2}]\mathrm{Cl_2}$ with 2−1000 equiv of added $[\mathrm{N(C_4H_9)_4}]\mathrm{Cl}$, MLCT excitation of *cis*-$[\mathrm{Ru(bpy)_2(py)_2}]^{2+}$ from 310 to 550 nm results in photosubstitution to form *cis*-$[\mathrm{Ru(bpy)_2(py)Cl}]^{+}$ ($\lambda_{\max} = 506$ nm) with $\Phi = 0.20$, nearly independent of excitation wavelength.[9] For *trans*-$[\mathrm{Ru(bpy)_2(4\text{-}Etpy)_2}]^{2+}$ ($\lambda_{\max} = 482$ nm), *trans* → cis photoisomerization occurs first, $\Phi = 0.50$, followed by the same ligand loss chemistry.[10] Additional photolysis leads to *cis*-$[\mathrm{Ru(bpy)_2(CH_3CN)Cl}]^{+}$, $\Phi = 0.025$. The quantum yields for loss of py or 4-Etpy are the same within experimental error. In the absence of added chloride, the successive photoproducts are $[\mathrm{Ru(bpy)_2(4\text{-}R\text{-}py)(CH_3CN)}]^{2+}$ and $[\mathrm{Ru(bpy)_2(CH_3CN)_2}]^{2+}$ (R = H, $\mathrm{C_2H_5}$).[11]



4-Etpy



PMMA

In poly(methyl methacrylate) (PMMA), photolysis of *cis*-$[\mathrm{Ru(bpy)_2(py)_2}](\mathrm{PF_6})_2$ under conditions that lead to photochemical ligand loss in $\mathrm{CH_3CN}$ within minutes results in no significant absorption changes ($\lambda_{\max} = 458$) over a period of 120 min. Photolysis of *trans*-$[\mathrm{Ru(bpy)_2(4\text{-}Etpy)_2}](\mathrm{PF_6})_2$ in $\mathrm{CH_3CN}$ ($\lambda_{\max} = 482$) gives *cis*-$[\mathrm{Ru(bpy)_2(4\text{-}Etpy)(CH_3CN)}](\mathrm{PF_6})_2$ ($\lambda_{\max} = 444$), within 1 min, but in PMMA with $\mathrm{CH_3CN}$ in the external solution, only slight *trans* → *cis* isomerization is observed (without significant ligand loss) after 20 min. This shows that photoisomerization continues to occur in PMMA but with decreased efficiency. Photochemical ligand loss also occurs in the presence of a coordinating anion. Photolysis of the salt, *cis*-$[\mathrm{Ru(bpy)_2(py)_2}]\mathrm{Cl_2}$, leads to complete conversion into $\mathrm{Ru(bpy)_2Cl_2}$ ($\lambda_{\max} = 378$ and 558 nm) after a photolysis period of 20 min.

Stabilization in PMMA is also apparent in excited state lifetimes. Room temperature emission decays of $[\mathrm{Ru(bpy)_3}](\mathrm{PF_6})_2$, *cis*-$[\mathrm{Ru(bpy)_2(py)_2}](\mathrm{PF_6})_2$, and *trans*-$[\mathrm{Ru(bpy)_2(4\text{-}Etpy)_2}](\mathrm{PF_6})_2$ are the same in the presence or absence of $\mathrm{O_2}$ and are nonexponential. The decay data can be fitted to the Williams−Watts distribution function, in eq 1.[12] β is the distribution width, and the average lifetime $\langle\tau\rangle$ is defined in eqs 2.[13] For $[\mathrm{Ru(bpy)_3}]^{2+}$, $\beta = 0.89$ and $k = 7.0 \times 10^5\ \mathrm{s^{-1}}$ with $\langle\tau\rangle = 1500$ ns. For *cis*-$[\mathrm{Ru(bpy)_2(py)_2}]^{2+}$, $\beta = 0.30$ and $k = 7.9 \times 10^7\ \mathrm{s^{-1}}$ with $\langle\tau\rangle = 80$ ns, and for *trans*-$[\mathrm{Ru(bpy)_2(4\text{-}Etpy)_2}]^{2+}$, $\beta = 0.77$ and $k = 1.2 \times 10^7\ \mathrm{s^{-1}}$ with $\langle\tau\rangle = 100$ ns. Emission $\lambda_{\max}$ values in PMMA are 590, 630, and 620 nm for $[\mathrm{Ru(bpy)_3}]^{2+}$, *cis*-$[\mathrm{Ru(bpy)_2(py)_2}]^{2+}$, and *trans*-$[\mathrm{Ru(bpy)_2(4\text{-}Etpy)_2}]^{2+}$. By comparison, $k = 1.0 \times 10^6\ \mathrm{s^{-1}}$ ($\tau = 1000$ ns) and $\lambda_{\max}$ for emission = 612 nm for $[\mathrm{Ru(bpy)_3}]^{2+*}$ in deaerated $\mathrm{CH_3CN}$, and $k > 2.0 \times 10^8\ \mathrm{s^{-1}}$ ($\tau < 5$ ns) for *cis*-$[\mathrm{Ru(bpy)_2(py)_2}]^{2+}$ and *trans*-$[\mathrm{Ru(bpy)_2(4\text{-}Etpy)_2}]^{2+}$. In fluid solution the latter lifetimes are greatly decreased because of rapid MLCT → dd barrier crossing followed by decay and decomposition.

Stabilization also occurs in silica sol−gel monoliths prepared

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(10) Solution quantum yields were determined by irradiating the sample in a stirred solution contained in a jacketed cell in which at least 98% of the incident radiation was absorbed. The yields were calculated relative to a Reineckate actinometer by following the change in absorbance with time for the first 5% of the reaction. The optical train for all the photolyses described consisted of a 75 W Xe lamp powered by a high-precision constant current source and an *f4* matched monochromator with 1200 line/mm gratings using glass optics to focus the beam inside the sample.

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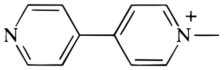
$$I_i = I_0 \exp[-(kt)^{\beta}] \tag{1}$$

$$\langle \tau \rangle = \Gamma(1/\beta)/(k/\beta) \tag{2a}$$

$$\Gamma(n) = \int_0^{\infty} x^{n-1} \mathrm{e}^{-x}\, \mathrm{d}x = \frac{1}{n}\prod_{m=1}^{\infty}\left[\left(1+\frac{1}{m}\right)^{n} \Big/ \left(1+\frac{n}{m}\right)\right] \tag{2b}$$

by a slight modification of a literature procedure[14] in which metal complex salts are added to a mixture of tetramethylorthosilicate, formamide, and methanol with a catalytic amount of nitric acid in water. Slow drying of the resulting gels in a polystyrene cuvette at 60 °C produced rectangular solids free of cracks and macroscopic defects. For *cis*-$[Ru(bpy)_2(py)_2](PF_6)_2$ in CH_2Cl_2 at room temperature, the emission quantum yield and excited state lifetimes are $\Phi_{em} < 0.0001$ and $\tau < 5$ ns. In the silica gel matrix, $\Phi_{em} > 0.01$ (Figure 1) and the lifetime increases dramatically to 620 ns under N_2. Φ_{em} decreases by ~10% in the presence of air.

The chromophore−quencher assembly salts *cis*- and *trans*-$[Ru(bpy)_2(MQ^+)_2](PF_6)_4$ (MQ^+ is *N*-methyl-4,4′-bipyridinium cation) are also stabilized in silica monoliths. Under photolysis



MQ⁺

conditions in water where the *cis* assembly (λ_{max} = 452 nm) decomposes completely to give $[Ru(bpy)_2(H_2O)_2]^{2+}$ (λ_{max} = 480 nm) on a timescale of a few minutes, only a 5−10% decrease in absorbance at 452 nm was observed after 8 h of photolysis with the monoliths immersed in water. In a gel matrix in dichloromethane, isomerization of *trans*- (λ_{max} = 466 nm) to *cis*-$[Ru(bpy)_2(MQ^+)_2](PF_6)^{4+}$ (λ_{max} = 452 nm) occurred within 2−4 min followed by much slower decomposition of the *cis* product. Approximately 80% of the *cis* assembly remained after 120 min of continuous photolysis. Local medium effects play a role in the sol−gels. The gels used in this study have large open pores available for solvent inclusion. Relative rates of ligand loss from *cis*-$[Ru(bpy)_2(MQ^+)_2](PF_6)_4$ vary with immersing solvent in the order $H_2O < CH_3CN < CH_2Cl_2$.

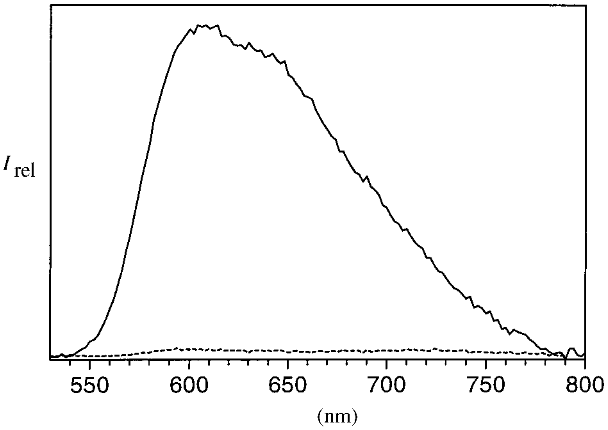


Figure 1. Room temperature emission spectra (relative emission intensity, I_{rel}, normalized to the same optical density) for *cis*-$[Ru(bpy)_2(py)_2](PF_6)_2$ in a sol−gel matrix immersed in CH_2Cl_2 (—) and in CH_2Cl_2 solution (---).

The microscopic origins of the rigid medium stabilization effect are currently under investigation. They appear to include a combination of inhibited MLCT → dd surface crossing, decreased reactivity of the dd states, and a cage effect in rigid media which promotes ligand rebinding. For example, the lifetime of *cis*-$[Ru(bpy)_2(py)_2]^{2+*}$ in PMMA is short compared to that of $[Ru(bpy)_3]^{2+*}$ even though their emission energies are comparable. This points to MLCT → dd surface crossing in PMMA but with decreased reactivity or ligand rebinding. The long lifetime in the sol−gel is consistent with inhibited MLCT → dd surface crossing. In any case, our results demonstrate that dramatic enhancements in both lifetime and photochemical stability can be achieved in rigid media. This points to the possible use of PMMA or silica sol−gels to stabilize otherwise unstable molecular assemblies in translationally fixed, optically transparent environments ideally suited for possible device applications.

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