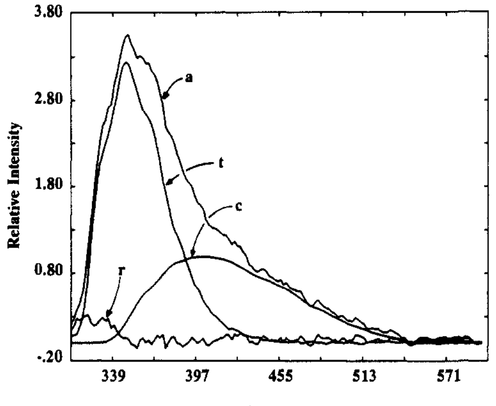

Figure 1. Average of 10 pure base-line-corrected *cis*-stilbene experimental emission spectra, a, together with PCA-SM pure-component stilbene solution spectra, trans, t, and cis, c. The cis spectrum has been smoothed to remove experimental noise. Subtraction of the pure-component spectra from the experimental spectrum gives the residual curve r. All spectra are uncorrected for instrumental nonlinearity.

In this work, highly purified *cis*- and *trans*-stilbene-d_0 and -d_2 were obtained by repeated conversions from trans to cis (fluorenone-sensitized photoisomerization) and cis to trans (iodine catalysis) with careful purification by alumina chromatography (*n*-pentane eluent) at each step, followed by distillation of the cis and sublimation of the trans isomer.[15] Fluorescence measurements were carried out at 30.0 °C in Fisher HPLC grade *n*-hexane. Spectra were measured with a modified Perkin-Elmer MPF-2A fluorometer with operation and data acquisition controlled by a Dell Corporation 80286/87 (12 MHz) microcomputer. To minimize cis → trans photoisomerization in the course of the measurements, 500-mL solutions were circulated from a reservoir through the 4-mL cell compartment. Under these conditions, a gradual increase in trans concentration was reflected in small systematic increases in the trans portion of the fluorescence spectrum (0.87% per spectrum). After correction for this trans buildup, a significant contribution of *trans*-stilbene fluorescence (51-54% of total area) remained, even from the purest *cis*-stilbene solutions (99.98% cis, 0.021% trans, by GLC), Figure 1. The *cis*-stilbene fluorescence spectrum was resolved by use of principal-component-self-modeling analysis (PCA-SM)[16] on a matrix consisting of 76 spectra, $310 \leq \lambda_{em} \leq 596$ nm, from *n*-hexane solutions containing 2.79×10^{-5} M *cis*-stilbene and a series of added *trans*-stilbene concentrations in the range $0 \leq$ [*trans*-stilbene] $\leq 1.16 \times 10^{-7}$ M. Excitation wavelengths were 268.0, 269.6, and 272.0 nm. PCA-SM analysis yielded a structureless spectrum for *cis*-stilbene, $\lambda_{max} \simeq 408$ nm (corrected for nonlinearity of instrumental response), somewhat blue-shifted from spectra obtained in rigid media and low *T*.[1-5] The spectrum contained a small peak at ~320 nm that decreased in size with repeated purification of *cis*-stilbene but could not be entirely eliminated (~3% area in the final spectrum). It was artificially removed by assuming Gaussian shape at the onset of $^1c^*$ emission, Figure 1. Using 9,10-diphenylanthracene as standard, $\phi_f = 0.90 \pm 0.04$,[17,18] at $\lambda_{exc} = 269.6$ nm, the quantum yield of the *cis*-stilbene portion of the spectrum, corrected for instrumental nonlinearity, is $(8.9 \pm 0.7) \times 10^{-5}$. Use of the Strickler-Berg equation[19,20] gives $k_f = (1.4 \pm 0.1) \times 10^8\ s^{-1}$ for $^1c^*$ in *n*-hexane at 30 °C, which is about 40% larger than predicted by the transient lifetimes and our quantum yield. Deuteration at the vinyl positions increases ϕ_f for the trans isomer, $\phi_{fd2}/\phi_{fd0} = 1.54 \pm 0.04$, in agreement with the fluorescence lifetime ratio,[21] but does not affect ϕ_f for the cis isomer $\phi_{fd2}/\phi_{fd0} = 1.01 \pm 0.10$, consistent with the absence of a significant inherent barrier in $^1c^* \rightarrow {}^1p^*$ torsional motion.[22] By analogy with *trans*-1-phenylcyclohexene,[23] we assume that the source of the deuterium isotope effect in the trans isomer is loss of the zero-point energy of the out-of-plane olefinic CH vibration in passing over the inherent torsional barrier.

Use of neutral density filters to attenuate the intensity of the excitation beam by 41%, 53%, and 63% was shown to affect trans/cis contribution ratios in the fluorescence spectra only slightly, eliminating the possibility that a significant portion of $^1t^*$ formation requires absorption of two photons, the first of which produces ground-state trans. This conclusion was confirmed by excitation spectra obtained by monitoring fluorescence from pure cis solutions at 404 nm (~70% cis contribution) and at 350 nm (~90% trans contribution). The resulting spectra are very similar and differ substantially from the excitation spectrum of the pure trans solution, monitored at 350 nm; the latter shows the expected red shift of λ_{max} and the characteristic structure of the absorption spectrum of the trans isomer. After correction for the contribution of the small trans impurity and of the maximum amount of trans isomer that may form from $^1c^*$ in the path of the exciting beam, we conclude that no less than 72% of the trans fluorescence observed from our cis solutions is a direct result of one-photon excitation of $^1c^*$. This remarkable conclusion means that 0.16% of $^1c^*$ molecules avoid or escape nearby excited-state potential energy minima at the perpendicular geometry or at dihydrophenanthrene and undergo adiabatic $^1c^* \rightarrow {}^1t^*$ conversion giving rise to $^1t^*$ fluorescence.[24] Experiments at different temperatures and in different media are in progress.

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Luminescence Line Narrowing: A Highly Specific Probe of Excited States in Rhodium(III) Mixed-Chelate Complexes

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The properties of the lowest excited states of d^6 chelate complexes continue to attract a great deal of interest.[1] Numerous physical and chemical techniques have been used to probe the nature of these excited states. Luminescence line narrowing (LLN) is not among them,[2] and in the present communication we demonstrate the power of this technique when applied to mixed-chelate complexes of Rh^{3+}. It turns out to be highly specific with regard to the ligand involved in the transition. By combining

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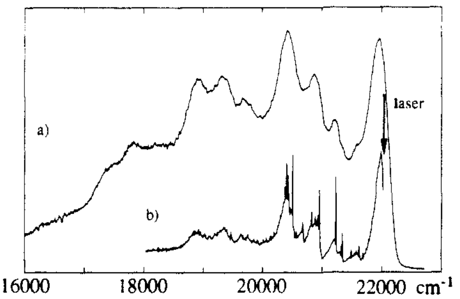

Figure 1. Luminescence spectra of [Rh(phpy)$_2$bpy]PF$_6$ in a nitrile glass at 6 K, using (a) 337-nm and (b) 454.5-nm excitation, respectively.

it with chemical variation we can gain new insight into the nature of the emitting state.

Low-temperature luminescence spectra of Rh^{3+} and Ir^{3+} complexes with π-accepting ligands in glassy matrices are characterized by a structured band in the visible part of the spectrum.[1,3] Figure 1a shows, as an example, the 6 K luminescence spectrum of [Rh(phpy)$_2$bpy]$^+$ in nitrile glass (phpyH = phenylpyridine). The luminescence lines are 100–200 cm^{-1} wide; this width is inhomogeneous, resulting from a very broad distribution of sites in the glass.[2] A small subset of complexes can be excited by choosing a narrow laser line within the inhomogeneously broadened profile of the first excitation origin. In the absence of energy transfer and thermal reorganization of the matrix during the lifetime of the excited state, only the subset of complexes directly excited by the narrow laser will luminesce, resulting in a sharp-line spectrum. The result of such an experiment with [Rh(phpy)$_2$bpy]$^+$ in a nitrile glass is shown in Figure 1b. The narrowing effect, compared to the unselectively excited spectrum (Figure 1a), is dramatic. The sharp lines have widths of 4 cm^{-1} at 6 K, very close to our instrumental resolution. We notice that part of the luminescence intensity is narrowed to a lesser degree, each sharp line being accompanied by a broader sideband at lower energy. This is a direct result of the electronic splitting of the first excited state.[4] For the present discussion we concentrate on the sharp-line spectrum; it represents a distinctive fingerprint of the complexes, even without specific assignments of the vibrations.

In Figure 2 we compare LLN spectra of [Rh(phpy)$_2$bpy]$^+$, [Rh(phpy)$_2$en]$^+$, and [Rh(thpy)$_2$bpy]$^+$, all in a nitrile glass or in Plexiglass at comparable temperature (thpyH = thienylpyridine). Substitution of bpy by en in [Rh(phpy)$_2$bpy]$^+$ has virtually no effect on the sharp-line pattern (Figure 2a,b). It follows immediately that the phpy$^-$ ligand and not the bpy ligand is involved in the lowest energy excited state of [Rh(phpy)$_2$bpy]$^+$. This is fully supported by the result obtained by substituting phpy$^-$ with thpy$^-$ (Figure 1c). This pattern is distinctly different from the pattern in Figure 2a, and it is clear that the active ligand is thpy$^-$ and not bpy. In agreement with this, the spectrum of [Rh(thpy)$_2$en]$^+$ shows the same LLN pattern as [Rh(thpy)$_2$bpy]$^+$ in Figure 2c.

For an understanding of the nature of the first excited state in mixed-chelate d^6 complexes, it is highly relevant to determine which ligand is involved in the excitation process. We have performed Extended-Hückel calculations on model complexes of [Rh(phpy)$_2$bpy]$^+$ and [Rh(thpy)$_2$bpy]$^+$.[5] The lowest energy unoccupied orbital turned out to be essentially a bpy orbital in these calculations. In apparent contrast, the lowest excited state in both complexes has been assigned on the basis of general chemical, spectroscopic, and electrochemical arguments as π–π* on the cyclometalated ligand.[1b,c] Our LLN experiments demonstrate very clearly that the cyclometalated ligand and not bpy is involved in the first excited state. One-electron models are obviously of very limited value in predicting the energy order of excited states in mixed-ligand complexes. It is essential to obtain this information from experiment, and we have shown that LLN can provide it in the most direct and straightforward way. It is a technique that has not been used so far in this area of research but that has a great potential for providing relevant information about the nature of the emitting state. It is easily applied to diluted samples, and the problems connected with crystal quality, energy transfer, and impurities in concentrated crystalline samples can be overcome.

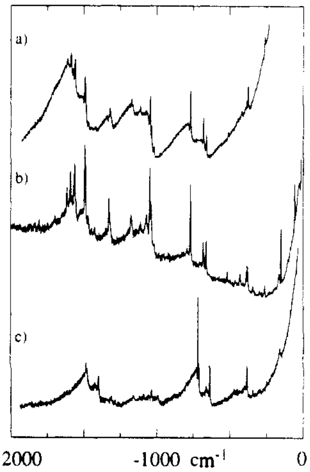

Figure 2. LLN spectra at 6 K relative to the exciting laser line of (a) [Rh(phpy)$_2$en]PF$_6$ in a Plexiglass matrix, excitation at 465.8 nm; (b) [Rh(phpy)$_2$bpy]PF$_6$ in a nitrile glass, excitation at 457.9 nm; and (c) [Rh(thpy)$_2$bpy]PF$_6$ in Plexiglass, excitation at 530.9 nm.

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A Genetically Engineered Monofunctional Chorismate Mutase

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The Claisen rearrangement of chorismic acid **1** to prephenic acid **2** (eq 1) catalyzed by the enzyme chorismate mutase plays a central role in the biosynthesis of phenylalanine and tyrosine. This remarkable transformation is the only documented example of an enzyme-catalyzed pericyclic reaction primary metabolism.[1] To understand the nature of catalysis, we[2] and others[3] have probed the influence of solvent and substituents, as well as conformational and isotope effects on both the enzymic and non-enzymic processes. Several plausible suggestions for catalysis have been put forth; however, the actual role of the enzyme remains obscure.[4] Clearly,

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