

= 0.16, and  $\beta^2 = \gamma^2 = 0.27$ . Varying the difference between  $\beta^2$  and  $\gamma^2$  to fit  $D_{\text{exp}}$  gives  $\beta^2 = 0.30$  and  $\gamma^2 = 0.25$ . Thus,  $d_{xy}$  is more covalent than  $d_{xz,yz}$ , consistent with the flattened  $D_{2d}$  geometry.<sup>24</sup>

Polarized absorption and MCD for the ligand field region of  $\text{Fe}(\text{SR})_4^-$  are presented in Figure 2. By using the  $\text{FeCl}_4^-$  methodology, we make the following band assignments: 7250  $\text{cm}^{-1}$  ( ${}^4T_1^a(x,y)$ ); 7975  $\text{cm}^{-1}$  ( ${}^4T_2^a(x,y)$ ); 10525  $\text{cm}^{-1}$  ( ${}^4T_1^a(z)$ ); and 9540  $\text{cm}^{-1}$  ( ${}^4T_2^a(z)$ ). On the basis of bandshape and temperature dependence of the  $z$  polarized intensity,<sup>31</sup> the 11225  $\text{cm}^{-1}$  transition is assigned as the LF independent  ${}^4E^a$ .

Application of eq 2 with the experimental  ${}^4T_1^a z$  and  $x,y$  energies gives  $D(\text{Fe}(\text{SR})_4^-)_{\text{calcd}} = -1.6 \text{ cm}^{-1}$ , while  $D(\text{Fe}(\text{SR})_4^-)_{\text{exp}} = +2.5 \text{ cm}^{-1}$ . Again,  $D_{\text{exp}}$  requires anisotropic covalency, but now  $\gamma^2 > \beta^2$ . Although the  $\text{FeS}_4$  core has the same geometry<sup>23</sup> as  $\text{FeCl}_4^-$ , it has the opposite anisotropic covalency. This difference results from the C-S-Fe angle<sup>23</sup> of 102.4°, which rotates the S  $p$ - $\sigma$  orbitals off the bond axis and toward the  $xz$  and  $yz$  planes.

A striking feature of  $d \rightarrow d$  transitions in  $\text{Fe}(\text{SR})_4^-$  is their low energy. This is attributed to drastic covalent reduction in electron repulsion,<sup>32,33</sup> which lowers the energy of all states. In the absence of covalency, the  ${}^4E^a$  should occur at the free ion  ${}^4G$  energy (32300  $\text{cm}^{-1}$ );<sup>34</sup> however, our  $\text{FeCl}_4^-$  data indicate a 44% reduction in this energy. For the ferric thiolate an intriguing 65% reduction is observed. This reduction provides strong evidence for a highly delocalized bonding scheme, consistent with calculations on related  $\text{Fe}(\text{SR})_4$  models.<sup>18-20</sup>

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**Registry No.** [ $\text{FeCl}_4^-$ ][ $\text{PPh}_4$ ], 30862-67-0; [ $\text{Fe}(\text{S}-2,3,5,6\text{-Me}_4\text{C}_6\text{H}_4)_4^-$ ][ $\text{NEt}_4$ ], 82741-95-5.

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## Nonequibrated Multiple Luminescence from $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$ in 293 K Solution

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Multiple-state emission is a topic of current investigation and has now been clearly established for a number of transition-metal compounds.<sup>1</sup> A few systems even exhibit multiple emission in fluid solution, but in almost all cases the radiative excited states

have been shown to be thermally equilibrated.<sup>2</sup> Here we report the observation of nonequibrated excited-state luminescence in room temperature solution for the organometallic complex  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ; 4-Phpy = 4-phenylpyridine). The photophysics of this system are especially unusual as distinct orbital emissions are readily observable in solution at 293 K.

Electronic absorption and emission data obtained from  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  and the closely related  $\text{CpRe}(\text{CO})_2(\text{pip})$  ( $\text{pip} = \text{piperidine}$ ) complex in deoxygenated benzene solutions at 293 K are shown in Figure 1. All the experimental results for both compounds, including emission quantum yields, lifetimes, excitation spectra, and low-temperature data, are summarized in Table I. The absorption spectrum of the  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  complex is dominated by two intense  $\text{Re}(d\pi) \rightarrow (\pi^*)\text{L}$  metal-to-ligand charge-transfer (MLCT) transitions, which are referred to as the MLCT( $b_2$ ) and MLCT( $e$ ) bands; these transitions arise from degeneracy removal of the filled " $t_{2g}$ " orbitals to yield levels of  $b_2$  and  $e$  symmetry.<sup>5</sup> Ligand field (LF) states are also present in  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  and appear as a high energy shoulder on the intense MLCT absorption envelope; the positions of these levels are more clearly depicted by the absorption spectrum of the  $\text{CpRe}(\text{CO})_2(\text{pip})$  complex (see Figure 1).<sup>5,6</sup>

The luminescence spectrum of  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  is striking as it exhibits three distinct maxima.<sup>7</sup> The two lowest lying emission features are both solvent and temperature dependent and, therefore, are associated with the  ${}^3\text{MLCT}(b_2)$  and  ${}^3\text{MLCT}(e)$  excited states.<sup>8,9</sup> A third weak emission band is observable at higher energy, but this exhibits relatively little solvent and temperature sensitivity and, consequently, is assigned to a  ${}^3\text{LF}$  emission. Strong support for the  ${}^3\text{LF}$  assignment is obtained from the room temperature emission data of the closely related  $\text{CpRe}(\text{CO})_2(\text{pip})$  complex.<sup>6,9</sup> Excitation spectra monitored at each of the luminescence maxima of both complexes are also concordant with these LF and MLCT assignments. Spectra obtained while monitoring emission of  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  at either MLCT maxima (542 or 710 nm) depict bands centered at 346, 402, and 450 nm, consistent with the LF and MLCT absorption positions (see Table I). On the other hand, monitoring at the high energy LF emission (440 nm) of  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  results in a single excitation maximum centered at 346 nm, indicating the LF absorption energy. The  $\text{CpRe}(\text{CO})_2(\text{pip})$  complex exhibits a single excitation maximum at 344 nm, in accordance with the LF assignment.

The two lowest lying MLCT emitting states of  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  are apparently in thermal equilibrium under room temperature solution conditions because the observed decay lifetimes are identical for both emission bands.<sup>10</sup> Additionally, the relative ratio of the emission band intensities remains constant

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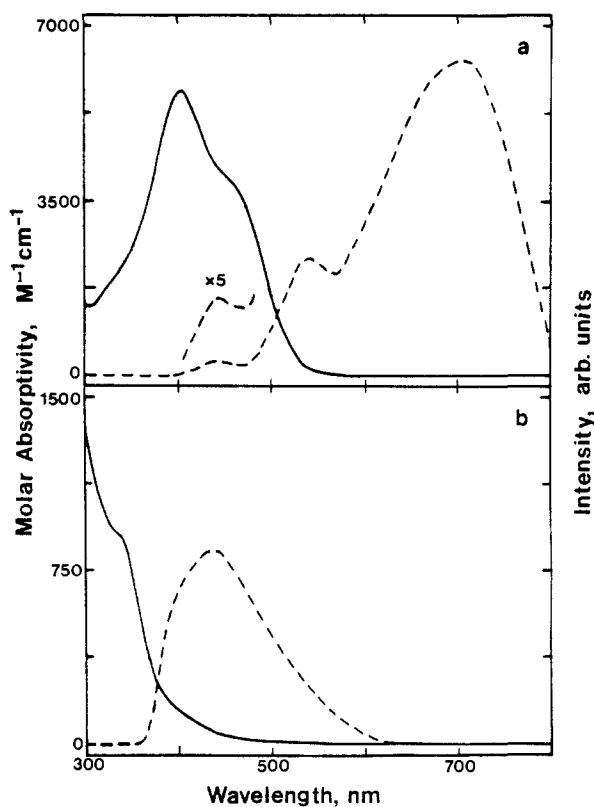
(10) Studies of the emission temperature dependence over the 213-293 K range are consistent with two close lying MLCT states in thermal equilibrium and not a thermal activation model; details of this work will be reported in a subsequent full paper.

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**Table I.** Electronic Absorption, Excitation, and Emission Spectral Data for  $\text{CpRe}(\text{CO})_2\text{L}$  Complexes in Deoxygenated Benzene at 293 K and EPA Glasses at 80 K<sup>a</sup>

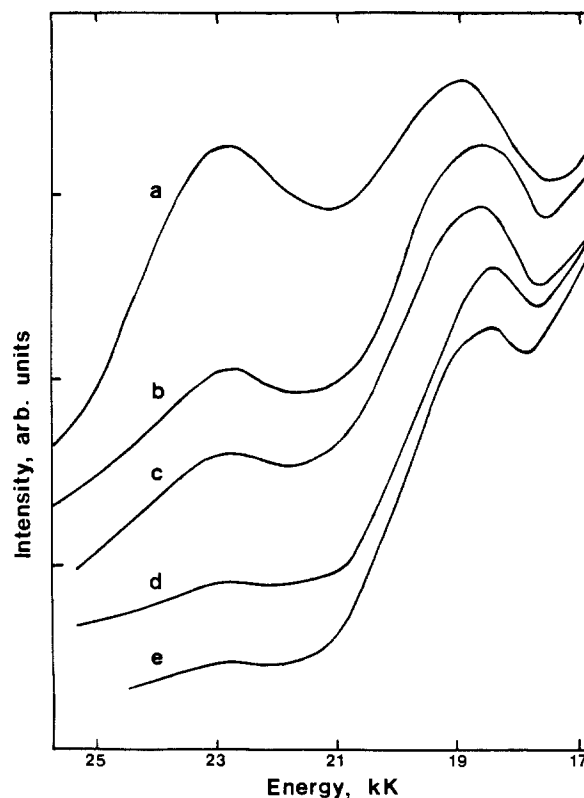
complex	solvent	temp, K	absorption $\lambda_{\text{max}}$ , nm	excitation $\lambda_{\text{max}}$ , nm	emission		
					$\lambda_{\text{max}}$ , nm	$\phi_e \times 10^4$	$\tau_e$
$\text{CpRe}(\text{CO})_2(4\text{-Phpy})$	$\text{C}_6\text{H}_6$	293	338, 404, 448	346, 402, 450	440 <sup>b</sup>	0.02 ( $\pm 0.005$ ) <sup>c</sup>	<0.5 ns
					542	0.47 ( $\pm 0.07$ ) <sup>d</sup>	4.5 ( $\pm 0.9$ ) $\mu\text{s}$
					346, 402, 450	710	1.7 ( $\pm 0.3$ ) <sup>d</sup>
	EPA	80	386, 435	430 (sh) <sup>b</sup>	512		8.3 ( $\pm 0.4$ ) $\mu\text{s}$
					656		71 ( $\pm 10$ ) $\mu\text{s}$
$\text{CpRe}(\text{CO})_2(\text{pip})$	$\text{C}_6\text{H}_6$	293	338	344	440 <sup>b</sup>	13 ( $\pm 2$ ) <sup>d</sup>	0.5 ( $\pm 0.1$ ) ns
	EPA	80	336		432		11.5 ( $\pm 0.3$ ) $\mu\text{s}$

<sup>a</sup> Excitation and emission spectra are fully corrected for wavelengths variations in instrumental response; emission data recorded following excitation at 380 nm unless otherwise noted; lifetimes and excitation data obtained at the corresponding emission maxima. <sup>b</sup> Excitation at 330 nm. <sup>c</sup> Absolute yield measured relative to 0.55 value for quinine sulfate in 0.2 M  $\text{H}_2\text{SO}_4$  (see ref 3). <sup>d</sup> Absolute yield measured relative to 0.042 value for  $\text{Ru}(\text{bpy})_3^{2+}$  in aqueous solution (see ref 4).



**Figure 1.** Electronic absorption (—) and emission spectra (---) of (a)  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  and (b)  $\text{CpRe}(\text{CO})_2(\text{pip})$  in deoxygenated benzene at 293 K. Emission spectra were recorded following excitation at 330 nm and are fully corrected for wavelength variations in detector response.

on excitation at any wavelength throughout the MLCT absorption band envelope. In contrast, the upper  $^3\text{LF}$  emission is clearly not in thermal equilibrium with the  $^3\text{MLCT}$  manifold as its room temperature lifetime is much shorter, and the band exhibits a substantial excitation wavelength dependence (see Figure 2). The radiative decay constant ( $k_r$ ) derived from the quantum efficiency ( $\phi_e$ ) and lifetime ( $\tau_e$ ) data ( $k_r = \phi_e \tau_e$ ) of the  $^3\text{LF}$  state of  $\text{CpRe}(\text{CO})_2(\text{pip})$  at 293 K is  $2.6 \times 10^6 \text{ s}^{-1}$ , much greater than the previously reported  $^3\text{MLCT}$  emissions of other metal carbonyl complexes.<sup>8,11</sup> This rate represents deactivation from an excited state characterized by efficient photodissociation pathways,<sup>5,12</sup> and it closely matches the recent report of  $^3\text{LF}$  emission from  $\text{XRe}(\text{CO})_4\text{L}$  ( $\text{X} = \text{Cl, I}$ ;  $\text{L} = \text{pip, PPh}_3$ ) complexes.<sup>13</sup> At low-temperature the entire photophysical system becomes nonequilibrated; the relative emission band intensities are all substantially dependent



**Figure 2.** Excitation wavelength dependence of emission spectra from  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  in deoxygenated benzene at 293 K; excitation wavelengths are (a) 305, (b) 310, (c) 320, (d) 330, and (e) 340 nm. Individual spectra are normalized following correction for detector response.

on the exciting wavelength, and the lifetimes of each excited state are different (see Table I).

Nonequilibrated emissions from metal complexes in fluid solution are exceedingly rare and have been limited to molecules with fluorescence and phosphorescence features.<sup>14</sup> The  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$  complex here illustrates that distinct orbital emissions involving triplet-centered levels may also be nonequilibrated. The key characteristic of this photophysical system is the presence of a rapid deactivating  $^3\text{LF}$  state ( $k_r > 10^6 \text{ s}^{-1}$ ) that effectively competes with rates of bond dissociation and internal conversion to the  $^3\text{MLCT}$  excited-state manifold.

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**Registry No.**  $\text{CpRe}(\text{CO})_2(4\text{-Phpy})$ , 60718-64-1;  $\text{CpRe}(\text{CO})_2(\text{pip})$ , 60718-65-2.

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