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Excited States of N,Si-Chelated Transition Metal Complexes: Characteristics of σ-Bond-to-Ligand Charge-Transfer (SBLCT) Excited States in *fac*-Ir[(6-isopropyl-8-quinolyl)diorganosilyl]$_3$

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Although the photoproperties of a variety of cyclometallated materials have been reported,[1,2] relatively little is known with regard to the photoproperties of metallacyclic compounds in which group IV elements other than C are bonded to a transition metal center. However, the preparation of stable complexes of P,Si-chelating ligands is well-documented,[3–11] and several N,Si-chelated complexes of Re(I),[12] Ir(III),[13] and Rh(III)[13] were recently reported. These types of complexes afford the opportunity to investigate the photochemical characteristics of materials containing metallacycles based upon M–Si rather than M–C bonds. We report here the initial characterizations of the excited states of several Si–Ir(III)-bonded complexes. These complexes are expected to have characteristics intermediate between those of C–M-bonded species and M′–M-bonded materials where M′ is Ge, Sn, or Pb. Spectroscopic characteristics of the excited states of these Si–Ir(III)-bonded complexes bear a close resemblance to those reported for complexes containing Ge–Re(I) or Sn–Re(I) bonds.[14–17] However, the photochemical characteristics of these complexes are distinct: associative quenching of the excited states in coordinating solvents is evident in the Si–Ir(III)-bonded materials, while dissociative rupture of the Ge–Re(I) or Sn–Re(I) bond leads to high quantum yield photochemistry in the latter.[14]

The characteristics of the emitting excited states of a series of N,Si-chelated complexes of the type *fac*-Ir[(6-isopropyl-8-quinolyl)diorganosilyl]$_3$ (diorgano = dimethyl, diphenyl, or phenylmethyl) are very sensitive to the identity of the diorgano groups bonded to silicon. Changes in the emission positions, band shapes and lifetimes indicate that the σ-bond-to-ligand charge-transfer (SBLCT or (Si–Ir)$\sigma_b \rightarrow L\pi^*$) excited state of the dimethyl derivative[18] moves up in energy when the methyl groups are replaced by electron-withdrawing phenyl groups; this results in increased ligand-centered (LC or (L)$\pi\pi^*$) character in the low-energy excited state of the diphenyl derivative in particular.

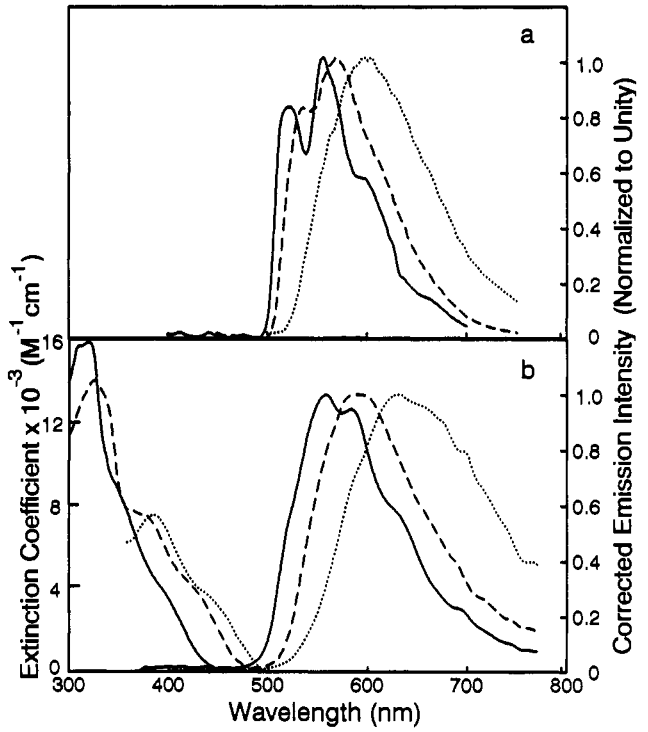

Figure 1. Absorption and emission spectra of *fac*-Ir(dmiprsiqn)$_3$ (···), *fac*-Ir(pmiprsiqn)$_3$ (---), and *fac*-Ir(dpiprsiqn)$_3$ (—): (a) emission spectra in 2-methyltetrahydrofuran glass at 77 K (measured with a Spex DM3000 spectrophotofluorimeter with excitation at 380 nm); (b) emission (right side) and absorption (left side) spectra in nitrogen-saturated toluene at 298 K (measured with an Oriel 512 element Instaspec diode array and Oriel Multispec monochromator; samples excited at 336 nm by pulsed excitation from a Laser Photonics UV-24 nitrogen laser for emission measurements; white light for absorption analysis was provided by a Xenon Corp. 437B nanopulse lamp discharged in nitrogen gas). See text for abbreviations of ligands; all emission data have been corrected for instrumental response functions to give spectral distributions proportional to number of photons emitted.

The broad, structureless emission of *fac*-tris[(6-isopropyl-8-quinolyl)dimethylsilyl]iridium(III) (Ir(dmiprsiqn)$_3$) in 2-methyltetrahydrofuran (MeTHF) at 77 K blue-shifts and becomes progressively more structured upon replacement of one and then two methyl groups by phenyl groups in *fac*-tris[(6-isopropyl-8-quinolyl)phenylmethylsilyl]iridium(III)[19] (Ir(pmiprsiqn)$_3$) and *fac*-tris[(6-isopropyl-8-quinolyl)diphenylsilyl]iridium(III) (Ir(dpiprsiqn)$_3$ (Figure 1 a)). The measured emission lifetimes (τ_{em}) increase regularly from 39 μs for *fac*-Ir(dmiprsiqn)$_3$ to 200 μs for

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(19) Several diastereomers of Ir(pmiprsiqn)$_3$ are possible, and three of these have been isolated in this laboratory. The one used in this study was a racemic mixture of the ΔRRR,ΛSSS diastereomer, which is the predominant one formed in our synthetic procedure.

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Table I. Luminescence Lifetimes[a] (τ_{em}) and Quantum Yields[b] (Φ_{em}) of N,Si-Chelated Iridium(III) Complexes[c]

	luminescence lifetimes[e]					
	μs (77 K)		ns (298 K)		luminescence quantum yield (298 K, Tol)	τ_{em}/Φ_{em}, μs (298 K, Tol)
complex[d]	MeTHF[f]	MP[f]	MeTHF	Tol[f]		
$Ir(dmiprsiqn)_3$	39	28	310	980	0.010	98
$Ir(pmiprsiqn)_3$[g]	71	52	1000	4000	0.027	148
$Ir(dpiprsiqn)_3$	200	172	<10[h]	201	0.001	201

[a] Measured following excitation at 336 nm with a pulsed nitrogen laser (Laser Photonics UV-24) using detection and analysis methods described in prior publications.[20] [b] Quantum yields measured by a modified Parker–Rees method[21–23] using quinine bisulfate in 0.5 N H_2SO_4 at 298 K as a reference standard with $\Phi_{em} = 0.546$. [c] Samples of complexes used in this study were prepared and purified by methods described in a prior publication.[13] [d] Abbreviations for complexes: $Ir(dmiprsiqn)_3$ = *fac*-tris[(6-isopropyl-8-quinolyl)dimethylsilyl]iridium(III); $Ir(pmiprsiqn)_3$ = *fac*-tris[(6-isopropyl-8-quinolyl)phenylmethylsilyl]iridium(III); $Ir(dpiprsiqn)_3$ = *fac*-tris[(6-isopropyl-8-quinolyl)diphenylsilyl]iridium(III). [e] Lifetimes in fluid solutions at 298 K are extremely sensitive to traces of oxygen. Solvents were vigorously bubbled with nitrogen for 15 min prior to measurements and purged slowly with nitrogen during the measurement. [f] Abbreviations for solvents: MeTHF = 2-methyltetrahydrofuran (Aldrich, distilled); MP = 3-methylpentane (Aldrich, distilled); Tol = toluene (Fischer). [g] Racemic mixture of the Δ*RRR*,Δ*SSS* diastereomer. [h] Very weak emission with lifetime too short to measure.

fac-$Ir(dpiprsiqn)_3$; a similar lifetime trend is seen when 3-methylpentane is used as a glassy solvent for measurements at 77 K (Table I).

The emission spectra broaden somewhat but shift little when recorded in fluid toluene solvent at 298 K (Figure 1b). However, the trend in τ_{em} values at 298 K is reversed from the trend noted at 77 K. Correction of the lifetime data for luminescence quantum yield effects (Φ_{em}) reverses this trend to reveal a trend in radiative lifetimes ($\tau_r = \tau_{em}/\Phi_{em}$; Table I) which parallels the trend seen in τ_{em} at 77 K. The similarity in τ_r's estimated from the room-temperature data and the τ_{em}'s at 77 K suggests that luminescence quantum yields at 77 K are very high, and near unity in the case of the diphenyl derivative. The τ_{em}'s for these complexes at 77 K are similar to those reported for complexes of the type $(Ph)_3ERe(CO)_3L$ (E = Sn or Ge; L = 1,10-phenanthroline or 2,2′-bipyridine) but substantially longer than radiative lifetimes for MLCT excited states of a variety of Ir(III) complexes.[1,2] Although the initial assignment of the emissions of the $(Ph)_3ERe(CO)_3L$ to $(E\text{–}Re)\sigma_b \rightarrow L\pi^*$ (SBLCT) excited states was later questioned[16,17] on the basis of resonance Raman data for excitation in the low energy absorption band in $(Ph)_3SnM(CO)_3(\alpha\text{-diimine})$ (M = Mn, Re), this may be primarily due to the difference in the nature of the excited state monitored in absorption versus emission spectroscopy in these complexes. These considerations suggest that the emissions of all three of the Si–Ir bonded complexes arise from excited states with substantial SBLCT character, although it is evident that mixing of the SBLCT configuration with an LC configuration of the quinoline moiety is influential, particularly in the diphenyl derivative.

The absorption spectra of all three of these complexes are characterized by two shoulders in the range 350–500 nm, and in each case the long-wavelength shoulder has an extinction coefficient of about 4×10^3 M^{-1} cm^{-1}. The shorter-wavelength shoulder has an extinction coefficient about twice that of the longer-wavelength feature, and the trend in the positions of these shoulders parallels the trends noted above in the positions of the emission spectra. These trends and the values of the extinction coefficients are consistent with absorption transitions due to charge transfer, which may be either SBLCT or MLCT in nature.

Lifetimes monitored in MeTHF at 298 K are substantially shorter than those monitored in toluene solvent. This effect is even more extreme in acetonitrile, where luminescence intensities are extremely weak and lifetimes have not yet been measured. The absence of absorption changes for solutions used in these studies during the photolysis periods needed for the spectroscopic measurements indicates that the quantum yield for any net photochemical process must be quite low, but the strong solvent quenching effects noted above suggest that coordination of the solvent following formation of the excited state contributes to the quenching process. This behavior is in contrast to the reported absence of bimolecular quenching of SBLCT excited states of $Ph_3ERe(CO)_3L$ by chlorocarbons, even though these undergo photochemical reactions to yield $ClRe(CO)_3L$.[14] While the latter result was taken as evidence for a dissociative mechanism due to cleavage of the E–Re bond in the excited state (which occurs in competition with SBLCT emission), the present result is indicative of an associative process for the Si–Ir bonded complexes.[24] This strong interaction of the excited state with coordinating solvents is not at all characteristic of MLCT excited states and provides further strong evidence for a charge-transfer excited state primarily due to SBLCT rather than MLCT. Solvent association might lead to transient photochemical cleavage of an Ir–Si bond, for example, which could re-form again at a later time due to the chelate effect of the bidentate ligand. Alternatively, attack of the coordinating solvent at the Ir–Si bond might lead only to quenching of the excited state without bond cleavage. The transient absorption spectroscopy of these species is presently being studied in order to further characterize the nature of the process which leads to quenching of the emissions in coordinating solvents.[25]

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