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Widely Varying Photophysical Properties of Ligand-Nitrated Bis(μ-chloro)tetrakis(2-phenylpyridinato)diiridium(III)

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We report here the effects of the strongly electron-withdrawing NO_2 group on the photophysical properties of cyclometalated complexes[1] of the type: *bis(μ-chloro)tetrakis(2-(4′-R′-phenyl)-5-R-pyridinato)diiridium(III)* (R = R′ = H (**1**); R = H, R′ = NO_2 (**2**); and R = NO_2, R′ = H (**3**)). While the unsubstituted dimer (**1**)is known to be a powerful photoreducing agent,[2] replacing one of the H atoms on the pyridyl ring with NO_2 gives a strong photooxidizing agent (**3**). Alternatively, substitution of NO_2 on the phenyl ring gives a complex (**2**) with photoredox properties intermediate between those of **1** and **3**. To the best of our knowledge, no other series employing ligand modifications exhibits as large a range of photoredox potentials as these.[3]

The NO_2-substituted ligands were synthesized in a manner described previously.[4] The dimer synthesis was analogous to the reported synthesis of **1**.[2b] Complexes **2** and **3** were characterized by ^1H NMR and mass spectrometry. These methods indicate they are isostructural with **1**.

Table I. Ground-State[a] and Excited-State Redox Properties

complex	$M^{+/0}$	$M^{2+/+}$	$M^{+/*}$	$M^{0/-}$	$M^{-/2-}$	$M^{*/-}$
1	1.01	1.27	−1.40	<−1.8		>0.7
2	1.44	1.70	−0.71	−1.17	−1.24	0.98
3	>1.5		>−0.4	−0.86		1.06
$Ru(bpy)_3^{2+}$ [b]	1.29		−0.85	−1.33	−1.52	0.81
$Ir(ppy)_3$ [c]	0.77		−1.74			

[a] 0.1 M TBAH, CH_2Cl_2, SCE. [b] References 3c,d; ACN vs SSCE. [c] Reference 4a; ACN vs SCE.

The cyclic voltammogram of **1** exhibits two reversible oxidations, with $E_{1/2}$ separation of 260 mV (Table I), but no reductions are seen within the solvent window. The two oxidation waves are assigned to sequential oxidations of the Ir centers.[2a] A single reversible oxidation of **2** occurs at +1.44 V vs SCE; although a second oxidation wave is not observed, an $E_{1/2}$ separation comparable to that seen above for **1** (260 mV) would place a second wave at the edge of our solvent window (+1.7 V). Two closely spaced reductions of **2** at −1.17 and −1.24 V vs SCE are believed to arise from reduction of a single ligand on one metal center followed by reduction of one ligand on the opposite metal center. For **3**, no oxidation waves are seen within the solvent window, but two overlapping one-electron reductions, separated by only 70 mV, are observed. **3** exhibits an additional reduction feature, irreversible and approximately 400 mV anodic, probably due to reduction of the second ligand on one or both of the metal centers.

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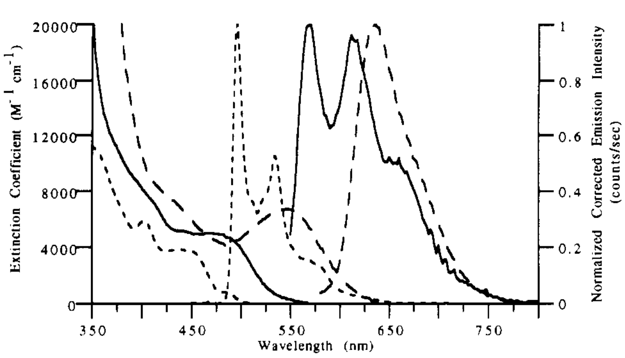

Figure 1. Absorption spectra (left) in CH_2Cl_2 at ambient temperature and emission spectra (right) in toluene at 77 K: bis(μ-chloro)tetrakis(2-phenylpyridinato)diiridium(III) (···); bis(μ-chloro)tetrakis(2-(4-nitrophenyl)pyridinato)diiridium(III) (—); bis(μ-chloro)tetrakis(2-phenyl-5-nitropyridinato)diiridium(III) (- - -).

Table II. Emission Positions, Lifetimes, and Quantum Yields[a]

	λ_{max} (nm)		τ_m (μs)			
complex	77 K	RT	77 K	RT	ϕ_{em}	τ_r (μs)
1	496	517	6.86	0.045	0.005	9.0
2	569	574	2.20	1.34	0.057	24
3	636	651	3.23	0.42	0.047	8.9

[a] In toluene.

The absorption spectrum of **2**, which is similar to that of **1**,[2b] includes three intense overlapping bands at 266, 292, and 315 (sh) nm ($\epsilon \sim 50\,000$ M^{-1} cm^{-1}). These are assigned to metal-perturbed ligand-centered (LC) bands, originating from the unmetalated ligand transition at 306 nm. Broad poorly resolved visible features, with the lowest energy band centered at 490 nm ($\epsilon \sim 5000$ M^{-1} cm^{-1}; Figure 1), are assigned as metal-to-ligand charge-transfer (MLCT) transitions by analogy to the visible bands of **1**. Two poorly resolved UV absorption features are seen for **3** at 318 (sh) and 338 nm ($\epsilon \sim 40\,000$ M^{-1} cm^{-1}); these originate from an LC band at 318 nm for the unmetalated ligand. In addition, several unresolved features and a well-resolved lowest energy peak at 546 nm ($\epsilon \sim 7000$ M^{-1} cm^{-1}) are seen in the visible absorption. Their extinction coefficients and solvatochromic behaviors support the assignment of these bands as MLCT transitions.

The 77 K emission spectrum of **1** in toluene is characterized by a vibrational progression with $\Delta\nu \sim 1400$ cm^{-1} (Figure 1). The relatively long emission lifetime (6.86 μs) is substantially shorter in ambient fluid solutions (45 ns), and the emission profile is substantially broadened and red-shifted (Table II). The emission quantum yield[5,6] (ϕ) of 0.005 in fluid solutions indicates a radiative lifetime ($\tau_r = \tau_m/\phi$) of $\sim$9 μs. Prior studies of this complex indicate it undergoes slow thermal cleavage in coordinating solvents (DMF) to yield a solvated monomer. This could be an explanation for the decreased emission under ambient conditions, in coordinating solvents.[2b] However, this thermal cleavage does not occur in less coordinating solvents. The presence of two oxidations for **1** in cyclic voltammetry, measured in CH_2Cl_2, suggests that **1**, and not a monometalic complex, is the major species in solution. Furthermore, ^{1}H NMR studies of **1** in $CDCl_3$, indicate that all ligands are equivalent, giving no evidence for a solvated monomer. These factors suggest that thermal cleavage, yielding a high concentration of solvated monomer, is not the cause for the short lifetime and broadening of the emission spectrum of **1** in a noncoordinating solvent such as toluene. However, rapid nonradiative decay, involving dissociative cleavage of **1** in the excited state and re-formation of the dimer in the ground state, could contribute to the shortening witnessed in the emission lifetime at 298 K.

Although the τ_m values of **2** and **3** at 77 K (2.2 and 3.23 μs) are shorter than that of **1**, they are substantially longer than that of **1** at 298 K (1.34 μs and 420 ns). The larger quantum yields indicate that the τ_r values of **2** and **3** ($\sim$24.1 and $\sim$8.9 μs, respectively) are, however, similar to that of **1**. The longer ambient τ_m's of **2** and **3** may be due to stabilization of the Ir–Cl bridge toward photochemical cleavage, caused by the electron-withdrawing ability of the NO_2 group. The emission energies and lifetimes for **2** and **3** indicate that these emissions, like those of **1** and other cyclometalated Ir(III) complexes,[4] originate from MLCT excited states.

Estimates of excited-state reduction potentials from ground-state reduction potentials and excited-state energies are summarized in Table I. The truly notable feature of this system is the extreme variability manifest in the photophysical properties with relatively simple ligand modifications. Calculations have shown the unsubstituted 2-phenylpyridine ligand is a stronger σ-donor and weaker π-acceptor than the structurally similar 2,2′-bipyridine.[7] Replacement of an H atom of 2-phenylpyridine with the strongly electron-withdrawing NO_2 group significantly decreases the ligand σ-donor ability while concomitantly increasing the π-accepting ability. This substantially influences the redox potentials of the resulting complexes while having smaller effects on their MLCT energies, these being related to *differences* in metal oxidation and ligand reduction potentials.[8] In addition, the present results indicate that the excited-state redox potentials are strongly dependent upon whether a hydrogen on the pyridyl or the phenyl ring is replaced by NO_2. An NO_2 group on the strongly σ-donating phenyl ring in **2** yields an MLCT excited state which is both moderately reducing and oxidizing. However, NO_2 on the π-accepting pyridine ring in **3** yields a strongly oxidizing MLCT excited state with little reducing power.

Bis-bidentate chelates have been readily incorporated into DNA structure probes, supramolecular systems, environmental probes, and photoconversion sensitizers.[9] Due to their photophysical properties, these complexes may have similar utility. Facile bridge cleavage, chloride removal, and ligation of bis(chloro)-bridged dimers of the type studied here indicate that incorporation of the bis-bidentate fragments into structures with one or two adjacent ligating sites should be straightforward. This suggests these fragments may be useful in the aforementioned areas of intense contemporary interest, particularly in cases where a wide range of excited-state redox potentials is advantageous.

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