

Near-IR Phosphorescence of Iridium(III) Corroles at Ambient Temperature

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Abstract: The photophysical properties of Ir(III) corroles differ from those of phosphorescent porphyrin complexes, cyclometalated and polyimine Ir(III) compounds, and other luminescent metallocorroles. Ir(III) corrole phosphorescence is observed at ambient temperature at wavelengths much longer (>800 nm) than those of most Ir(III) phosphors. The solvatochromic behavior of Ir(III)-corrole Soret and Q absorption bands suggests that the lowest singlet excited states (S_2 and S_1) are substantially more polar than the ground state.

Porphyrin complexes displaying phosphorescence at ambient temperatures have been employed for photodynamic therapy,¹ oxygen detection,² and organic light-emitting diodes.³ A great deal of research has been done on d^8 (mainly Pt^{II} , Pd^{II} , and Au^{III}) complexes,⁴ which emit at relatively long wavelengths (>600 nm) with lifetimes in the microsecond range. In sharp contrast, d^6 metalloporphyrins have scarcely been investigated, although room temperature phosphorescence of ruthenium(II) porphyrins has been reported.⁵

Metallocorroles have shown promise as therapeutic agents,⁶ with biodistribution and bioavailability profiles as well as cellular uptake and intracellular locations⁷ determined for fluorescent gallium(III) derivatives.⁸ Although progress has been made, much work remains before we can claim to have developed optimized compounds for optical examination of biological systems.⁹ It would be beneficial to have agents that emit with microsecond lifetimes beyond 700 nm, as the most common obstacles to efficient biological imaging—tissue absorbance and intrinsic fluorescence—could thus be circumvented.

Here we report the photophysical properties of iridium(III) corroles,¹⁰ which differ significantly from those of cyclometalated and polyimine Ir(III) compounds,¹¹ other luminescent metallocorroles,¹² and free-base corroles.¹³ Iridium(III) corrole phosphorescence is observed at ambient temperature at wavelengths much longer (>800 nm) than those of most other luminescent Ir(III) complexes.¹¹ Our investigations focused on the three corroles shown in Figure 1.

Emission spectra were recorded in toluene at 298 and 77 K (Figure 2). The spectra display two intense features separated by approximately 1400 cm^{-1} . It is likely that a ring-based vibration is excited in the transition to the lower energy component.¹⁴

At low temperature, the higher energy emission maximum of each Ir(III) corrole blue shifts by 10 nm (a rigidochromic effect indicating that the transition involves charge transfer)¹⁵ (Figure 2b). We conclude from emission band shapes and vibronic splittings taken together with results from electronic structure calculations¹⁶

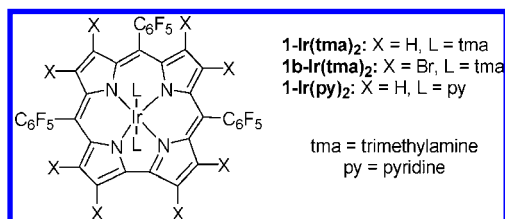


Figure 1. Details of synthesis and characterization (NMR, MS, XRD) of the three corroles are reported in the Supporting Information.

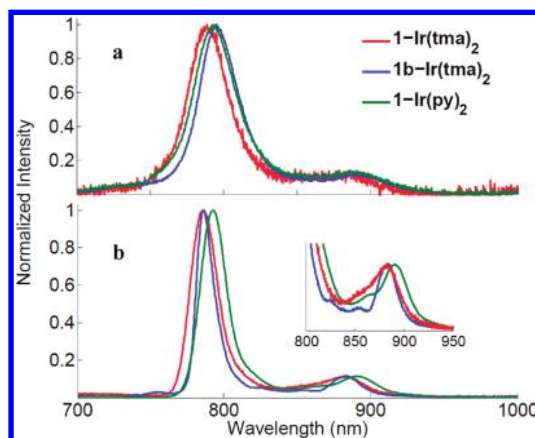


Figure 2. Emission spectra of Ir(III) corroles in degassed toluene solution ($\lambda_{\text{ex}} = 496.5\text{ nm}$): (a) 298 K; (b) 77 K.

that the phosphorescence in each case is attributable to a transition from a corrole $\pi \rightarrow \pi^*$ triplet state that likely has partial $^3\text{MLCT}$ character.

Luminescence quantum yields and lifetimes in degassed and aerated toluene solutions at room temperature (and lifetimes at 77 K) are set out in Table 1. **1-Ir(tma)₂** and **1b-Ir(tma)₂** have relatively short lifetimes and low quantum yields, but **1-Ir(py)₂** exhibits a much higher luminescence quantum yield (1.2%) and a longer lifetime. We also measured luminescence lifetimes in methanol solutions (Table S1, Supporting Information). These lifetimes are similar to those in toluene at 77 K, but they are substantially shorter in the more polar solvent at room temperature.

UV–vis absorption spectra (Figure 3) of the Ir(III) corroles exhibit split Soret ($S_0 \rightarrow S_2$) and Q ($S_0 \rightarrow S_1$) bands. The splitting of the Soret bands is $1400\text{--}1700\text{ cm}^{-1}$ in all cases; the Q bands are split by roughly 1800 cm^{-1} in the spectra of **1-Ir(tma)₂** and **1b-Ir(tma)₂** but only by 1000 cm^{-1} in the spectrum of **1-Ir(py)₂**.

The effect of solvent polarizability on Ir(III)-corrole spectra was investigated to probe the extent of charge transfer in initially formed electronic excited states. UV–vis spectra were obtained in a variety of solvents: Soret band maxima were plotted against polarizability f (Figure 4), defined as $f(n) = (n^2 - 1)/(2n^2 + 1)$,¹⁷ where n is the refractive index of the solvent (the ground states are relatively

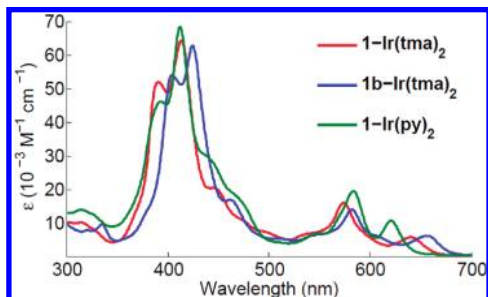
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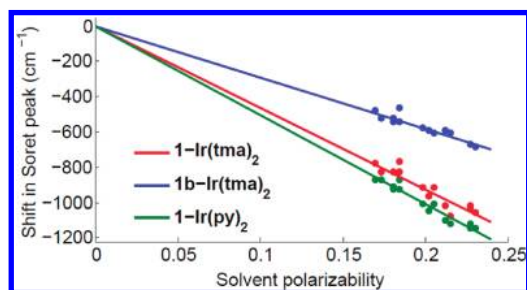
Table 1. Photophysical Data for Ir(III) Corroles in Toluene Solutions^a

	1-Ir(tma) ₂	1b-Ir(tma) ₂	1-Ir(py) ₂
Φ_{ph}^b	3.3×10^{-4}	3.9×10^{-3}	1.2×10^{-2}
$\lambda_{\text{Ar}}(\text{nm})/\tau_{\text{Ar}}(\mu\text{s})$	788/0.220	795/1.19	792/4.91
$\tau_{\text{air}}^c(\mu\text{s})$	0.170	0.760	0.380
$\lambda_{77\text{K}}(\text{nm})/\tau_{77\text{K}}(\mu\text{s})$	786/2.77	786/4.72	793/7.69
$k_{\text{r}}(\text{s}^{-1})$	1.5×10^3	3.28×10^3	2.44×10^3
$k_{\text{nr}}(\text{s}^{-1})$	4.54×10^6	8.4×10^5	2.0×10^5

^a At 298 K unless noted otherwise. ^b Luminescence quantum yields were standardized against free-base tetraphenylporphyrin ($\Phi_{\text{f}} = 0.13$ in toluene solution at 298 K). ^c Measured under atmospheric conditions.

**Figure 3.** UV-vis spectra of Ir(III) corroles in toluene solution at 298 K.

nonpolar, so inclusion of a solvent dielectric term is not appropriate). The strong negative correlation ($R^2 > 0.9$) between the polarizability of the solvent and the energy of the Soret transition indicates that in each case the excited state is substantially more polar than the ground state.¹⁸ The Q-band maxima display a similar trend. The striking solvatochromic behavior of Ir(III) corroles potentially could be exploited in optical sensors as well as other applications requiring solvent-based tuning of absorption and emission properties.

**Figure 4.** Shift in the lower energy Soret component as a function of solvent polarizability (n used is that of the sodium D line at 20 °C).

Although the Soret solvatochromic shifts of **1-Ir(tma)₂** and **1-Ir(py)₂** are similar, **1b-Ir(tma)₂** exhibits a somewhat weaker trend, which we suggest is attributable to bromine atom “pre-polarization” of the electron density on the corrole, thereby decreasing the change in dipole moment upon excitation. But we cannot rule out a simpler explanation, namely, that the initially formed **1b-Ir(tma)₂** excited state is not as polar as those of the other corroles.

Our work has established that Ir(III) corroles phosphoresce in the near-infrared region at ambient temperature with lifetimes and quantum yields that depend strongly on the nature of the axial

ligand. We also have shown that substitutions on the corrole framework can tune the redox and photophysical properties as well as the solubility behavior of these molecules over a very wide range. We intend to employ these and related Ir(III) corroles in experiments that require tunable near-IR phosphors.

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Supporting Information Available: Additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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