

Chapter 3

NEAR-IR PHOSPHORESCENCE OF IRIDIUM(III) CORROLES AT AMBIENT TEMPERATURE

In my initial communication to JACS, I noted that the progress of iridium insertion into the corrole framework could be monitored by observing the disappearance of the strong red luminescence of free-base H₃tpfc. The lack of any visible fluorescence from the iridium products hardly comes as a surprise, given that heavy metal atoms often promote ultra-fast ISC from a luminescent singlet state to a non-radiating triplet. However, cyclometalated and polyimine Ir(III) complexes often display bright phosphorescence from the triplet state, and heavy-metal porphyrins (particularly platinum complexes) are well-known for their triplet luminescence. With this in mind, I decided to measure the luminescence of a few of my compounds despite the fact that they are not visibly fluorescent, and the results turned out to be quite intriguing.

At first, I thought the large emission peaks I was seeing around 800 nm from degassed Ir corrole solutions might be artifacts of the correction file on my group's fluorimeter. R928P Hamamatsu PMTs are not particularly sensitive past 750 nm, and the multiplication of photon intensity that the software performs to make up for this lack of sensitivity can sometimes cause strange effects. However, the experiments were reproducible, and the intensity of the emission scaled well with the concentration of the luminophore, so Jay Winkler, director of BILRC at Caltech, purchased an instrument designed for detection of more red-shifted luminescence than the fluorimeter could comfortably handle, and I

quickly confirmed that the near-IR phosphorescence being observed was true emission and not an instrumental artifact.

Along with another Gray group student, Alec Durrell, I set about examining the luminescence lifetimes and quantum yields of the Ir(III) corroles. Our main findings were as follows: the lifetimes of the luminescence are in the range of hundreds of nanoseconds to a few microseconds, becoming a bit longer at low temperature; the quantum yields of luminescence are low, topping out around 1% for the py-ligated complex; and the UV-vis absorption peaks of the corroles display a strong dependence on the polarizability of the solvent, suggesting that the initial excited states of the complexes are quite a bit more polar than their ground states. Interestingly, the non-radiative decay rates of these near-IR emitters are fairly slow considering the low energy of the excited state; indeed, the low quantum yields (compared with, say, cyclometalated red Ir emitters) appear to stem from exceptionally slow radiative rates as opposed to the rapid non-radiative decay that usually foreshortens the luminescence lifetimes of near-IR emitters. Experiments to determine the reasons for this apparently slow radiative decay (which could perhaps be an artifactual result of incomplete $S_1 \rightarrow T_0$ ISC) are underway. Additionally, a number of other Ir(III) corroles are being examined for their luminescence properties, and TD-DFT calculations, thus far unsuccessful at modeling the absorption spectra of the compounds, are also being run with an eye toward determining more exactly the nature of the initial excited states and the emitting triplet states. Our work up to mid-2010 is presented below in JACS communication format.

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

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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

Metalloporphyrins 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 metalloporphyrins,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 3-1.

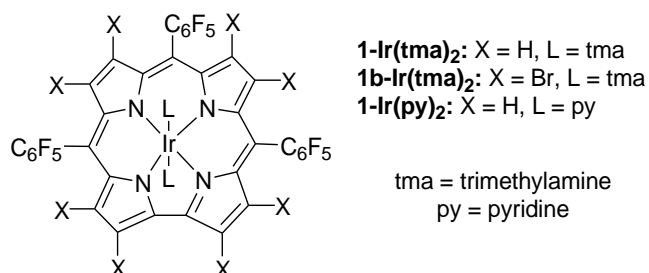


Figure 3-1: Details of synthesis and characterization (NMR, MS, XRD) of the three corroles are reported in Supporting Information

Emission spectra were recorded in toluene at 298 and 77 K (Figure 3-2). 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 3-2b). The narrow linewidth and $\sim 1400\text{ cm}^{-1}$ spacing suggest that the emission is from a $\pi \rightarrow \pi^*$ excited state. Electronic structure calculations place an occupied orbital with metal character close to the HOMO in related Ir(III) corroles,¹⁶ indicating that $^3\text{MLCT}$ states will be near those of the lowest corrole-localized excited states. Other investigators have reported that $^3\text{MLCT}$ is the emissive state in cyclometalated Ir(III) complexes.¹⁷

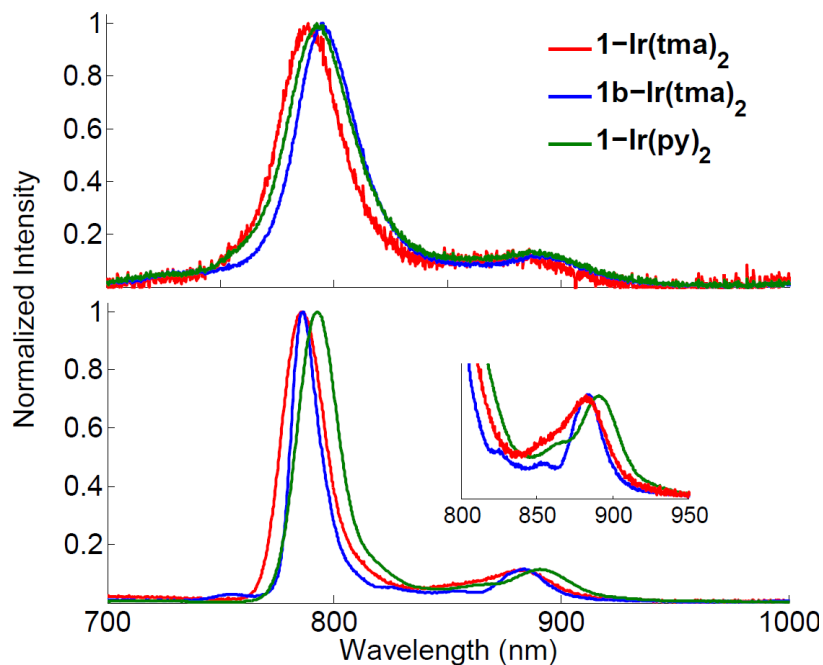


Figure 3-2: Emission spectra of Ir(III) corroles in degassed toluene solution at 298 K (top) and 77K (bottom)

Luminescence quantum yields and lifetimes in degassed and aerated toluene solutions at room temperature (and lifetimes at 77 K) are set out in Table 3-1. **1-Ir(tma)₂** and **1b-Ir(tma)₂** have relatively short lifetimes and low quantum yields. **1-Ir(py)₂** exhibits a much higher luminescence quantum yield (1.2%) and a longer lifetime.¹⁸ It is apparent even from these initial results that Ir(III)-corrole photophysical properties depend markedly on the nature of the axial ligand.

Table 3-1: Photophysical data for Ir(III) corroles in toluene solutions^a

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

^aAt 298 K unless noted otherwise. ^bLuminescence quantum yields were standardized against free-base tetraphenylporphyrin ($\Phi_{\text{f}} = 0.13$ in toluene solution at 298 K). ^cMeasured under atmospheric conditions. UV-vis absorption spectra (Figure 3-3) of the three 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 1400–1700 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.

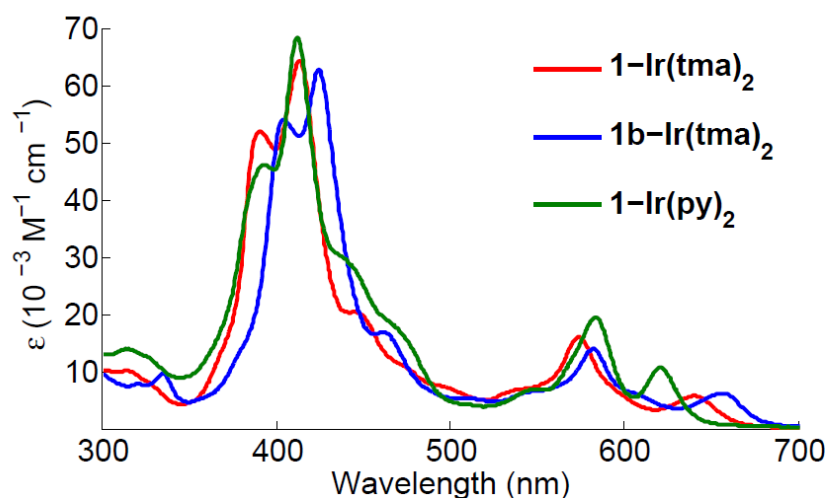


Figure 3-3: UV-vis spectra of Ir(III) corroles in toluene solution at 298 K. *1b*-Ir(*tma*)₂ is red-shifted and *1*-Ir(*py*)₂ has the tightened Q band system

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 3-4), defined as $f(n) = (n^2 - 1)/(2n^2 + 1)$,¹⁹ where n is the refractive index of the solvent. (The ground states are relatively 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.²⁰ 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.

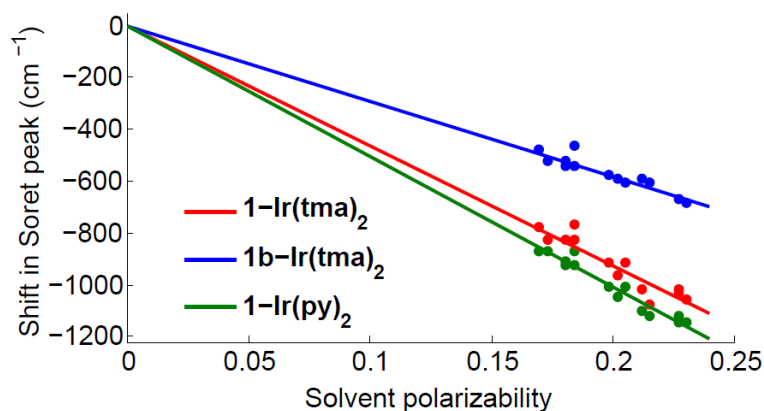


Figure 3-4: Shift in the lower energy Soret component as a function of solvent polarizability (n used is that of the sodium D line at 20 °C; **1b-Ir(tma)₂** is at the top, then **1-Ir(tma)₂** and **1-Ir(py)₂**)

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 “prepolarization” 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 temperatures with lifetimes and quantum yields that depend strongly on the nature of the axial ligands. We conclude from emission band shapes and vibronic splittings taken together with results from electronic structure calculations that the phosphorescence in each

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

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References

- (1) Zenkevich, E.; Sagun, E.; Knyukshto, V.; Shulga, A.; Mironov, A.; Efremova, O.; Bonnett, R.; Phinda Songca, S.; Kassem, M. *J. Photochem. Photobiol. B: Bio.* **1996**, *33*, 171–180.
- (2) Papkovsky, D. B.; Ponomarev, G. V.; Trettnak, W.; O'Leary, P. *Anal. Chem.* **1995**, *67*, 4112–4117.
- (3) a) Kwong, R. C.; Sibley, S.; Baldo, M. A.; Forrest, S. R.; Thompson, M. E. *Chem. Mater.* **1999**, *11*, 3709–3713. b) Antipas, A.; Dolphin, D.; Gouterman, M.; Johnson, E. C. *J. Am. Chem. Soc.* **1978**, *100*, 7705–7709.
- (4) a) Sun, Y.; Borek, C.; Hanson, K.; Djurovich, P. I.; Thompson, M. E.; Brooks, J.; Brown, J. J.; Forrest, S. R. *App. Phys. Lett.* **2007**, *90*, 213503/1–213503/3. b) Wiehe, A.; Stollberg, H.; Runge, S.; Paul, A.; Senge, M. O.; Roder, B. *J. Porph. Phthal.* **2001**, *5*, 853–860.
- (5) Tait, C. D.; Holten, D.; Barley, M. H.; Dolphin, D.; James, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 1930–1934, and references therein.
- (6) a) Okun, Z.; Kupersmidt, L.; Amit, T.; Mandel, S.; Bar-Am, O.; Youdim, M. B. H.; Gross Z. *ACS Chem. Biol.* **2009**, *4*, 910–914. b) Agadjanian, H.; Ma, J.; Rentsendorj, A.; Valluripalli, V.; Hwang, J. Y.; Mahammed, A.; Farkas, D. L.; Gray, H. B.; Gross, Z.; Medina-Kauwe, L. K. *Proc. Nat. Acad. Sci.* **2009**, *106*, 6100–6105.
- (7) Agadjanian, H.; Weaver, J. J.; Mahammed, A.; Rentsendorj, A.; Bass, S.; Kim, J.; Domchowski, I. J.; Margalit, R.; Gray, H. B.; Gross, Z.; Medina-Kauwe, L. K. *Pharmaceutical Res.* **2006**, *23*, 367–377.
- (8) Weaver, J. J.; Sorasaene, K.; Sheikh, M.; Goldschmidt, R.; Tkachenko, E.; Gross, Z.; Gray, H. B. *J. Porph. Phthal.* **2004**, *8*, 76–81.
- (9) Hwang, J. Y.; Agadjanian, H.; Medina-Kauwe, L. K.; Gross, Z.; Gray, H. B.; Sorasaene, K.; Farkas, D. L. *SPIE* **2008**, *6859*, 68590G.
- (10) a) Palmer, J. H.; Day, M. W.; Wilson, A. D.; Henling, L. M.; Gross, Z.; Gray, H. B. *J. Am. Chem. Soc.* **2008**, *130*, 7786–7787. b) Palmer, J. H.; Mahammed, A.; Lancaster, K. M.; Gross, Z.; Gray, H. B. *Inorg. Chem.* **2009**, *48*, 9308–9315.
- (11) a) Dixon, I. M.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L.; Encinas, S.; Barigelletti, F. *Chem. Soc. Rev.* **2000**, *29*, 385–391. b) Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. *J. Am. Chem. Soc.* **2003**, *125*, 12971–12979. c) Hung, J.-Y.; Chi, Y.; Pai, I.-H.; Yu, Y.-C.; Lee, G.-H.; Chou, P.-T.; Wong, K.-T.; Chen, C.-C.; Wu, C.-C. *Dalton Trans.* **2009**, *33*, 6472–6475. d) Shin, C. H.; Huh, J. O.; Lee, M. H.; Do, Y. *Dalton Trans.* **2009**, *33*, 6476–6479.
- (12) a) Flamigni, L.; Gryko, D. T. *Chem. Soc. Rev.* **2009**, *38*, 1635–1646. b) Nardis, S.; Mandoj, F.; Paolesse, R.; Fronczek, F. R.; Smith, K. M.; Prodi, L.; Montalti, M.; Battistini, G. *Eur. J. Inorg. Chem.* **2007**, *16*, 2345–2352. c) Poulin, J.; Stern, C.; Guillard, R.; Harvey, P. D. *Photochem. Photobiol.* **2006**, *82*, 171–176. d) Liu, X.; Mahammed, A.; Tripathy, U.; Gross, Z.; Steer, R. P. *Chem. Phys. Lett.* **2008**, *459*, 113–118.
- (13) Ding, T.; Alemán, E. A.; Modarelli, D. A.; Ziegler, C. J. *J. Phys. Chem. A.* **2005**, *109*, 7411–7417.
- (14) Steene, E.; Wondimagegn, T.; Ghosh, A. *Inorg. Biochem.* **2002**, *88*, 113–118.
- (15) Chen, P.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439.
- (16) Dong, S. S.; Nielsen, R. J.; Palmer, J. H.; Gray, H. B.; Gross, Z.; Dasgupta, S.; Goddard, W. A. *submitted*.
- (17) Rausch, A. F.; Thompson, M. E.; Yersin, H. *J. Phys. Chem. A.* **2009**, *113*, 5927–5932.

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- (18) Ir(III) complexes with 3% quantum yields have been used successfully to stain living cells, see: Yu, M.; Zhao, Q.; Shi, L.; Li, F.; Zhou, Z.; Yang, H.; Yi, T.; Huang, C. *Chem. Commun.* **2008**, 2115–2117.
- (19) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd. Ed.; Kluwer Academic/Plenum Publishers: New York, **1999**.
- (20) a) Marcus, R.A. *J. Chem Phys.* **1965**, *43*, 1261–1274. b) Mody, V. V.; Fitzpatrick, M. B.; Zabaneh, S. S.; Czernuszewicz, R. S.; Galezowski, M.; Gryko, D. T. *J. Porph. Pthalo.* **2009**, *13*, 1040–1052.