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Photophysics of Ir(III) complexes with oligo(arylene ethynylene) ligands†

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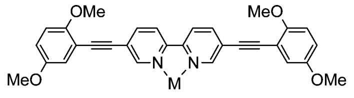
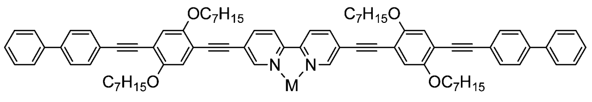
We report the photophysics of two complexes of the type $Ir(ppy)_2(OAE)^+$, where ppy = 2-phenylpyridine and OAE is a π-conjugated oligo(arylene ethynylene) ligand.

Luminescent transition metal complexes have been intensively studied during the last three decades.[1] While the excited state properties of Ru(II), Os(II), Re(I) and Pt(II) complexes have been thoroughly examined, until recently the properties of the isoelectronic Ir(III) complexes have attracted less attention.[2] This is primarily due to limits in the synthetic pathways to heteroleptic, tris-chelated Ir(III) complexes. Thompson and co-workers[3] recently reported a synthetic method for preparation of heteroleptic $Ir(III)(L)_3$ complexes that contain cyclometallated ligands such as 2-phenylpyridine (ppy), diketonates and/or diimine ligands such as 2,2′-bipyridine (bpy). These authors demonstrated the generality of the new synthetic approach by synthesizing a wide range of complexes that photoluminesce efficiently from triplet metal-to-ligand charge transfer (^{3}MLCT) and intraligand $^3\pi,\pi^*$ manifolds. These new Ir(III) complexes have received considerable attention as the active materials in high efficiency organic light emitting diodes.[3,4]

We have an ongoing program that seeks to understand the excited state properties of oligo(arylene ethynylene) (OAE) π-conjugated electronic systems that contain metal complex chromophores.[5] As part of this program we have synthesized and characterized the excited state properties of Ir(III) complexes **1** and **2** in an effort to better understand the structure–property relationships for π-conjugated systems that contain an Ir(III) chromophore. In the present communication we demonstrate that the luminescent excited state undergoes a smooth crossover from ^{3}MLCT in **1** to $^3\pi,\pi^*$ in **2**. Remarkably, both complexes photoluminesce with comparable efficiency, in spite of the different nature of the lowest excited state. This striking result may have significant implications in the design of conjugated materials in electrophosphorescent devices.



1 : M = $Ir(ppy)_2^+ PF_6^-$ **1a** : M = -- (free ligand)



2 : M = $Ir(ppy)_2^+ PF_6^-$ **2a** : M = -- (free ligand)

Table 1 lists the photophysical parameters deduced from absorption, luminescence and electrochemical studies of **1**, **2** and the parent complex $Ir(ppy)_2(bpy)^+$ (**3**). First, the absorption spectra of the oligomer complexes are dominated by the π,π* transitions centered on the OAE segments (Table 1, and ESI†). This conclusion is based on the fact that the spectra of **1** and **2** are very similar to the spectra of $(L)Re(CO)_3Cl$ and $(L)Ru(bpy)_2^{2+}$, where L = **1a** and **2a**.[5a] The low energy transition in **1** and **2** arises from the long-axis polarized π,π* transition of the OAE. Although Ir → OAE MLCT transitions are expected to arise in the 400–450 nm region,[2,5] these transitions are obscured by the more intense π,π* bands. For comparision absorption data for **3** are included in Table 1, and it can be seen that the low energy transitions in **1** and **2** are approximately 10-fold more intense than the MLCT bands for **3** which are in the 375–415 nm region. Note that the lowest energy π,π* transition is red-shifted by approximately 40 nm (0.3 eV) in **2** compared to **1**. This shift reflects the increased conjugation length in **2**.

The Ir(III) complexes feature a moderately intense orange or red photoluminescence, both in solution at 298 K and in the glass at 80 K. Fig. 1 compares normalized emission spectra for **1**, **2** and **3** obtained at 298 K and at 80 K. Table 1 lists the emission quantum yields (ϕ), decay lifetimes (τ_{em}) and radiative and non-radiative decay rates (k_r and k_{nr}, respectively) that are computed from ϕ and τ_{em}. The emission from **3**, which has previously been assigned to an Ir → bpy ^{3}MLCT excited state,[2a] appears as a broad structureless band at both 80 and 298 K. Note that the 298 K emission is red-shifted significantly from that at 80 K. This effect has been termed rigidochromism and it is characteristic of MLCT states.[1] The emission from the MLCT state is at higher energy in the glass because the solvent dipoles are unable to relax around the excited state dipole, and the thermally-induced Stokes shift (ΔE_s, Table 1) provides a measure of the outer sphere reorganization energy (λ_s) for the MLCT state ($\Delta E_s = 2\lambda_s$).[6] The λ_s value observed for **3** (0.14 eV) is comparable to that observed for other MLCT states in moderately polar solvents.[6]

The emission from Ir(III)–OAE complexes **1** and **2** is more complicated. First, at 80 K, the emission from both complexes appears as a band with a resolved vibronic progression. At 298 K, the emission of **1** is broad, with only a hint of the 0–0 band resolved; however, the emission of **2** retains the vibronic structure. It is also noteworthy that the thermally-induced Stokes shift in **1** and **2** is considerably less than in **3**, and based on the observed ΔE_s values we estimate that λ_s is 0.07 and 0.04 for **1** and **2**, respectively. Although the λ_s for **1** is still in line with some MLCT excited states,[6] the value for **2** is unusually low,

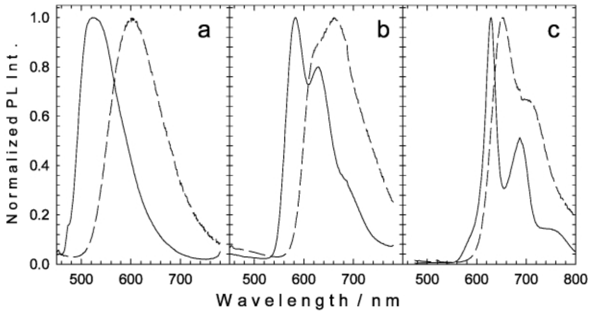


Fig. 1 Normalized photoluminescence spectra in 2-MeTHF solution. Solid lines: 80 K, dashed lines: 298 K. Note that absolute intensity of the 298 K emission is significantly lower than 80 K. (a) **3**, (b) **1**, (c) **2**.

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† Electronic supplementary information (ESI) available: synthesis and characterization of **1** and **2**; electrochemical data and absorption spectra of **1** and **2**; transient absorption spectrum of **3**. See http://www.rsc.org/suppdata/cc/b2/b206987c/

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Table 1 Photophysical parameters for Ir(III) complexes[a,b]

Complex	UV-Vis abs λ_{max} (log ε_{max})	λ_{max}^{em} (298 K)	$\lambda_{max}^{em\ c}$ (80 K)	ΔE_s/eV[d]	τ_{em}/μs[e] (298 K)	ϕ_{em}[f]	$k_r/10^5\ s^{-1}$	$k_{nr}/10^6\ s^{-1}$	E_{MLCT}[g]/eV	$E_{triplet}$[h]/eV
1	318 (4.60) 406 (4.50)	620[i]	580	0.14	0.44	0.036	0.82	2.2	2.0 ± 0.1	2.15[5a]
2	336 (4.84) 444 (4.72)	645	620	0.08	3.3	0.026	0.079	0.29	1.9 ± 0.1	1.95[5a]
3	376 (4.00) 416 (3.78)	590	520	0.28	0.18	0.018	1.0	5.4	2.25 ± 0.1	2.72[2a]

[a] All measurements in degassed THF. [b] Wavelength units: nm. [c] 2-methyltetrahydrofuran glass. [d] Thermally-induced emission Stokes shift. [e] Emission decay lifetime. [f] Photoluminescence quantum yield, determined relative to $Ru(bpy)_3^{2+}$ in aqueous solution (ϕ = 0.055). [g] Estimated energy of ^{3}MLCT state, see supporting information section. [h] Energy of $^3\pi,\pi^*$ state of OAE or bpy ligand. [i] Maximum of 0-0 transition.

and suggests that there is little charge transfer character in the emitting excited state for this complex.

Interestingly, the emission decay lifetimes follow the trend **3** < **1** < **2**. This trend in lifetimes arises because the non-radiative decay rates (k_{nr}, Table 1) vary as **3** > **1** > **2**. This trend is exactly opposite what is expected based on the energy gap law,[7] since the emission energies vary in the sequence **3** > **1** > **2**. Taken together, the structured emission at 298 K from complex **2**, the small λ_s values for **1** and **2**, along with the unusual trend in the non-radiative decay rates for the series, suggest the involvement of an intraligand, OAE-based $^3\pi,\pi^*$ excited state in the photophysics of the Ir–OAE complexes.

In order to probe the nature of the long-lived luminescent excited state in more detail, transient absorption (TA) spectroscopy was carried out on **1**–**3**. The TA spectra for **1** and **2** are shown in Fig. 2, and that of **3** is provided as ESI.† The TA spectrum of **3** is identical to that reported by Watts and co-workers,[2b] and it is dominated by a narrow band with λ_{max} = 370 nm. This feature arises from the bpy anion-radical that is present in the Ir → bpy ^{3}MLCT excited state, *i.e.*, $^*[(ppy)_2Ir^{IV}(bpy^{-\cdot})]^+$. The TA spectra for **1** and **2** are distinct from that of the parent complex. At first glance the spectra of **1** and **2** appear similar; both feature bleaching of the ground state absorption bands and transient absorption throughout the visible region. However, on closer inspection the TA spectra are clearly different. For complex **1**, the TA is dominated by a strong and relatively narrow band with $\lambda_{max} \approx$ 510 nm. Importantly, the transient absorption spectrum of **1** is essentially identical to that of $(L)Ru^{II}(bpy)_2^{2+}$ (L = 5,5′-bis(phenylethynyl)-2,2′-bipyridine), where it has been clearly established that the excited state is based on Ru → L ^{3}MLCT.[5d] This correspondence strongly suggests that the TA spectrum of **1** corresponds to the Ir → **1a** ^{3}MLCT excited state.

The visible absorption band in the TA spectrum of **2** is red-shifted ($\lambda_{max} \approx$ 550 nm), broader, and weaker than the visible band in the TA spectrum of **1**. The TA spectrum of **2** also features absorption that is rising in the 700–800 nm region, suggesting the presence of an excited state absorption band in the near-IR. Importantly, the TA spectrum of **2** is identical to that of (**2a**)$Re(CO)_3Cl$. This correspondence is significant because it has been established that in the latter complex the lowest excited state is $^3\pi,\pi^*$ of the OAE ligand (**2a**).[5b,c] We conclude that the TA spectrum in **2** also corresponds to the $^3\pi,\pi^*$ state of the OAE ligand. In summary, the TA experiments imply that at 298 K complex **1** has a lowest excited state based on Ir → **1a** ^{3}MLCT, while in complex **2** the lowest excited state is $^3\pi,\pi^*$ localized on **2a**.

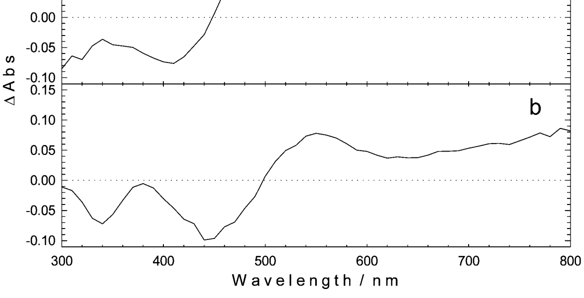

Fig. 2 Transient absorption difference spectra for THF solutions following 355 nm excitation pulse (355 nm, 5 mJ, 10 ns fwhm). (a) **1**, 80 ns delay; (b) **2**, 320 ns delay.

Several general conclusions can be drawn based on the results of this study. First, increased conjugation length in the OAE ligand lowers the energy of the OAE-based $^3\pi,\pi^*$ state by *ca.* 0.2 eV (Table 1, last column). Consequently, while the lowest excited state for **3** and **1** has mainly ^{3}MLCT character, the lowest excited state for **2** is predominantly of $^3\pi,\pi^*$ character. Second, a striking feature is that despite the difference in the lowest excited state in OAE complexes **1** and **2**, the two complexes have comparable emission quantum yields. This arises because the Ir(III) ion is strongly coupled to the OAE π-electron system in **2**. Therefore, spin–orbit coupling is strong and leads to enhanced radiative decay (phosphorescence) from the $^3\pi,\pi^*$ excited state of the OAE ligand. This observation implies that incorporation of Ir(III) complexes into the π-electron system of a conjugated polymer through chelation or *o*-metallation will afford materials that will produce efficient phosphorescence and electrophosphorescence from $^3\pi,\pi^*$ states on the polymer.

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Notes and references

1 A. J. Lees, *Chem. Rev.*, 1987, **87**, 711.
2 (*a*) Y. Ohsawa, S. Sprouse, K. A. King, M. K. DeArmond, K. Hanck and R. J. Watts, *J. Phys. Chem.*, 1987, **91**, 1047; (*b*) K. Ichimura, T. Kobayashi, K. A. King and R. J. Watts, *J. Phys. Chem.*, 1987, **91**, 6104; (*c*) K. Dedeian, P. I. Djurovich, F. O. Garces, G. Carlson and R. J. Watts, *Inorg. Chem.*, 1991, **30**, 1685.
3 (*a*) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. C. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2001, **40**, 1704; (*b*) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304.
4 (*a*) X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2002, **14**, 581; (*b*) J. C. Ostrowski, M. R. Robinson, A. J. Heeger and G. C. Bazan, *Chem. Commun.*, 2002, 784.
5 (*a*) K. D. Ley, Y. Li, J. V. Johnson, D. H. Powell and K. S. Schanze, *Chem. Commun.*, 1999, 1749; (*b*) K. A. Walters, K. D. Ley, C. S. P. Cavalaheiro, S. E. Miller, D. Gosztola, M. R. Wasielewski, A. P. Bussandri, H. van Willigen and K. S. Schanze, *J. Am. Chem. Soc.*, 2001, **123**, 8329; (*c*) K. A. Walters, D. M. Dattelbaum, K. D. Ley, J. R. Schoonover, T. J. Meyer and K. S. Schanze, *Chem. Commun.*, 2001, 1834; (*d*) Y. Wang, S. Liu, M. R. Pinto, D. M. Dattelbaum, J. R. Schoonover and K. S. Schanze, *J. Phys. Chem. A*, 2001, **105**, 11118.
6 P. Y. Chen and T. J. Meyer, *Chem. Rev.*, 1998, **98**, 1439.
7 E. M. Kober, J. V. Caspar, R. S. Lumpkin and T. J. Meyer, *J. Phys. Chem.*, 1986, **90**, 3722.