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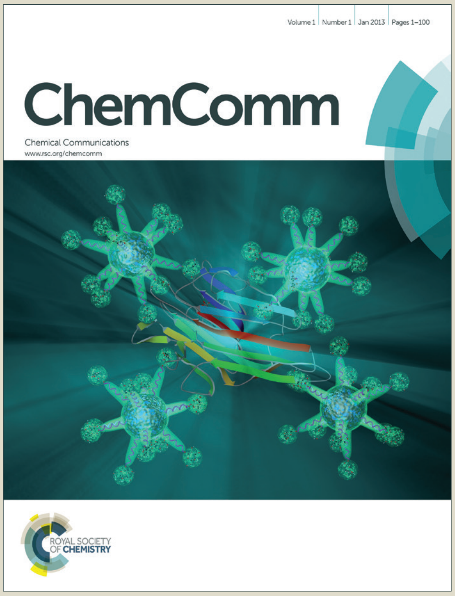

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ARTICLE TYPE

New Synthetic Pathways to the Preparation of Near-Blue Emitting Heteroleptic Ir(III)N$_6$ Coordinated Compounds with Microsecond Lifetimes

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A high yield synthetic route for the preparation of N6 coordinated heteroleptic Ir(III) complexes using bidentate polypyridyl type ligands is described. The complexes are near-blue emitters and show microsecond emission lifetimes, high emission quantum yields and have two quasi-reversible reduction processes between -1.0 and -1.3 V vs Ag/AgCl.

Since the early work of Thompson[1,2,3] and others[4,5,6] cyclometallated iridium(III) compounds have attracted widespread attention due to their application in OLED devices. This interest is as a consequence of the excited state properties of the Ir(III) complexes, which typically exhibit long-lived excited states and high emission quantum yields. Importantly, varying the nature of the ligands enables tuning of the emission spectrum, which is important in both colour tuning in devices and in optimising performance.[7] The potential of these complexes in solar energy applications has been investigated more recently also.[8] The cyclometallating ligands used to date not only include a wide range of phenyl pyridines and phenyl triazoles but also N-N coordinating ligands such as pyrazine-triazoles.[9] However, Ir(III) complexes of the types $[\mathrm{Ir(L\text{-}L)_2Cl_2}]^+$ and $[\mathrm{Ir(L\text{-}L)_2(L\text{-}L')}]^{n+}$ based on N-N bound bidentate ligands such as 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) and others have only seldom been investigated over the last 30 years,[10,11] presumably due to the lack of effective synthetic routes. Indeed, methods reported to date, have in general, provided complexes only in low yields and in combination with orthometallated side-products.[12,13,14,15,16]

Here, we report a new efficient method for the preparation of all-*N*-bound complexes of the type $[\mathrm{Ir^{III}(L\text{-}L)_2(L\text{-}L')}]^{n+}$ using $[\mathrm{Ir(L\text{-}L)_2Cl_2}]\mathrm{PF_6}$ complexes as precursors (where L-L is a bipy or phen type ligand). The method is illustrated through the synthesis of the complex $[\mathrm{Ir(dmbipy)_2(Hphpytr)}](\mathrm{CF_3SO_3})_3$, where dmbipy is 4,4'-dimethyl-2,2'-bipyridyl (dmbipy), and Hphpytr ((3-phenyl)-5-(pyridine-2-yl)-1,2,4-triazole).

N,N'-bound complexes of the type $[\mathrm{Ir(L\text{-}L)_2Cl_2}]\mathrm{Cl}$ were obtained in high yield, with isolation and purification facilitated by metathesis to their $\mathrm{PF_6}^-$ salts. It should be noted that $[\mathrm{Ir(bipy)_2Cl_2}]\mathrm{PF_6}$ can be prepared by this method in a 30% yield also, albeit with a side product where an additional orthometallated bipy ligand is bound, *i.e.* $[\mathrm{Ir(bipy\text{-}N,N)_2(bipy\text{-}C\text{-}N)}]^{2+}$.[17] Nevertheless in this case the complexes are readily separated. This side product is not observed for substituted bipyridines, presumably for steric reasons, and hence complexes of the ligand dmbipy were focused on in the present study.

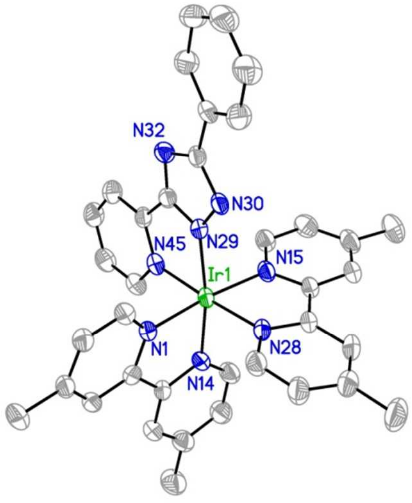

Fig. 1 Molecular structure (50% probability) of the cation of $[\mathrm{Ir(dmbipy)_2(phpytr)}][\mathrm{CF_3SO_3}]_2$.toluene. Hydrogen atoms, anions and solvent omitted for clarity.

The formation of the tris-homo- and tris-hetereoleptic complexes was achieved by removal of the chlorido ligands. Meyer and co-workers have described a method to remove the chlorido ligands in $[\mathrm{Ir(L\text{-}L)_2Cl_2}]\mathrm{Cl}$ type compounds to form associated hydride complexes [18] using $\mathrm{CF_3SO_3H}$. We have taken this approach as a starting point and after some modifications were able to prepare a number of $[\mathrm{Ir(L\text{-}L)_2(L\text{-}L')}]^{n+}$ type compounds in a two-step process (see ESI). In the first step the chloride ligands were replaced by trifluoromethane sulfonic acid and the intermediate $[Ir(dmbpy)_2(CF_3SO_3)_2]$ CF_3SO_3 was isolated in good yield. In the last step this compound was reacted with the L-L' ligand, in this case Hphpytr, to obtain the target compound $[Ir(dmbipy)_2(Hphpytr)](CF_3SO_3)_3$. The compound $[Ir(bipy)_3](PF_6)_3$ was synthesised in the same manner. ^1H NMR spectra are shown in Figure S1. The structure of $[Ir(dmbipy)_2(phpytr)](CF_3SO_3)_2$.toluene (See Figure 1) was obtained by X-ray crystallographic analysis. The geometry of the Ir(III) centre is a distorted octahedron and is similar to that observed for analogous Ir(III) based complexes with orthometallated phenyl pyridine rather than bipy type ligands[19] and for similar complexes with isoelectronic Ru(II) metal centres.[20,21] There is little difference between the Ir-N bond lengths observed in the complex and all are within the range 2.033 to 2.069 Å. The longest Ir-N bond is to the pyridyl nitrogen on the triazole ligand and the angle between N28-Ir-N29 is the most distorted.

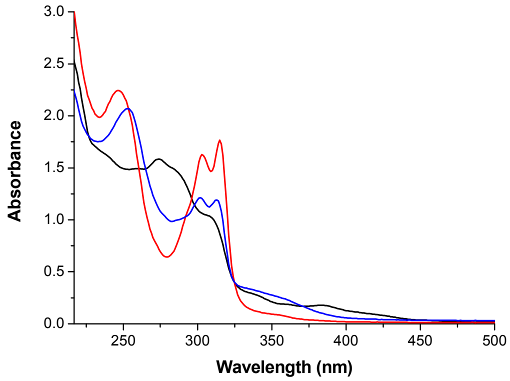

Fig. 2 UV/Vis absorption spectra of complexes $[Ir(dmbipy)_2Cl_2]PF_6$, (black), $[Ir(dmbipy)_2(OSO_2CF_3)_2]CF_3SO_3$ (red) and $Ir(dmbipy)_2(Hphpytr)](CF_3SO_3)_3$ (blue) (0.1 mM in CH_3CN).

Table 1 Absorption and molar absorptivities of at 298 K in CH_3CN.

Complex	**λ_{abs} (nm) (ε 10^3 $M^{-1}cm^{-1}$)**	**λ_{em} (nm)**	**Emission lifetime (μs) (quantum yield) [a]**
$[Ir(dmbipy)_2Cl_2]PF_6$	275 (13.67),311(8.73), 341(2.38),385(1.39)	470, 502	0.3 (0.02)
$[Ir(dmbipy)_2(OSO_2CF_3)_2]CF_3SO_3$	247 (24.25), 303 (7.73), 315 (8.64), 355 (0.62)	450, 477, 505	(N/A)
$[Ir(dmbipy)_2(Hphpytr)]^{3+}$	253 (29.43), 302 (5.01), 313 (4.92), sh 355 (1.03)	470, 495	8.43 (0.65)
[b]$[Ir(dmbipy)_2(phpytr)]^{2+}$	260, 300, 315, 370 sh	470, 490	2.7 (N/A)

[a] *deaerated* [*b] Protonation by addition of NaOH to $[Ir(dmbipy)_2(Hphpytr)]^{3+}$

It is important to note that while the elemental analysis indicates that the triazole is protonated, when the compound was isolated from the acidic reaction mixture, after recrystallisation from an acetonitrile/toluene mixture the triazole ring is deprotonated as confirmed by X-ray analysis. This difference indicates that the triazole moiety deprotonates easily when coordinated to a metal centre as observed before for analogous Ir(III)[19] and Ru(II) compounds.[22] The photophysical properties of both the protonated and deprotonated complexes are described in table 1 (See Fig. 2, 3, S2 and S3).

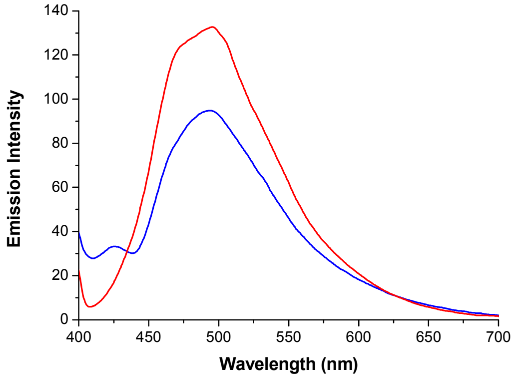

Fig. 3 Emission spectra of $[Ir(dmbipy)_2(phpytr)]^{2+}$ in CH_3CN with NaOH (blue line) and $[Ir(dmbipy)_2(Hphpytr)]^{3+}$ in CH_3CN with $HClO_4$ (red line). λ_{exc} 380 nm.

The emission spectrum of $[Ir(dmbipy)_2(Hphpytr)](CF_3SO_3)_3$ (Figure 3) has a maximum at 495 nm and a shoulder at 470 nm, similar to the analogous neutral complex $[Ir(ppy)_2(phpytr)]$ (489 and 517 nm, respectively).[24] The emission lifetime of $[Ir(III)(dmbipy)_2(Hphpytr)]^{3+}$ was 2.76 μs in aerated acetonitrile and increased to 8.43 μs (See Figure S4) after deaeration with N_2. Emission quantum yields for $[Ir(III)(dmbipy)_2(HphPytr)]^{3+}$ in CH_3CN in the presence of $HClO_4$ in aerated and deaerated solution were 0.54 and 0.65, respectively, which is comparable to that of $[Ir(ppy)_2(phpytr)]$ (0.45) in degassed CH_2Cl_2 where the triazole ring is deprotonated.[24]

Deprotonation with NaOH to form $[Ir(dmbipy)_2(phpytr)]^{2+}$ resulted in a decrease in emission lifetime (0.51 μs and 2.70 μs, in aerated and deaerated CH_3CN, respectively) which is comparable with that of the orthometallated analogue $[Ir(ppy)(phpytr)]$ (1.9 μs in deaerated solution).[24] These lifetimes are surprisingly long and another initially surprising finding is that the lifetime increases upon protonation of the triazole ring, which is opposite to that observed for the analogous Ru polypyridyl complexes.[22,23] However, this latter observation can be explained by taking into account that the decrease of the emitting lifetime in the case of the ruthenium compounds is related to a lowering on the deactivating ^3MC state, but this is not an important process in iridium compounds. Instead the increased emission lifetime may be associated with increased ligand localisation of the excited state triplet interligand transition. This is at present under further investigation using DFT techniques

Although the photophysical properties of N-N and C-N type Ir(III) compounds are similar, their electrochemical properties are considerably different. $[Ir(dmbipy)_2(Hphpytr)](CF_3SO_3)_3$ does not undergo oxidation within the potential window investigated, but does show four well-defined reductions in the range of 0 to -2.2 *vs.* Ag/AgCl with the least negative reversible process observed at -1.02 V. This compares with the analogous $[Ir(ppy)_2(phpytr)]$ complex, which undergoes oxidation at 1.06 V vs Ag/AgCl and is only reduced at -2.11 V *vs.* Ag/AgCl.[24] For many ppy based Ir(III) complexes the HOMO is located on the phenyl moiety of the ppy ligand with a substantial contribution coming from the atomic d-orbitals whereas the LUMO is assigned as being localised on the pyridine unit of the ppy ligand.[1,24] The data presented here demonstrate the large effect that changing from orthometallation to N-N coordination has on the redox chemistry with the first reduction ca. 1 V less negative for the dmbipy complex compared with the ppy cased analogue. Based on the electrochemical data, it is to be expected that the photophysical properties of Ir(III) compounds with N-N bound ligands would be quite different. The fact that they are so similar is at present under investigation using DFT techniques.

The data presented here clearly demonstrate that $[Ir(N\text{-}N)_2(L\text{-}L')]^{n+}$ type compounds have potentially attractive properties in the application of Ir(III) emitters in particular in electronic devices due to the large difference in redox properties compared with the orthometallated analogues but yet similar photophysical properties. Importantly, while the reduction potential are similar to some other cyclometallated OLEDS and therefore promise similar electron transfer rates, it is important to note that the oxidation potentials are very positive and therefore hole trapping is expected to be much less likely. In addition, the long emission lifetimes and high quantum yields are especially important in regard to applications such as OLEDS, solar cells and biosensors.

Notes and references

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