Synthesis, Structure, and Photophysical and Electrochemical Properties of Cyclometallated Iridium(III) Complexes with Phenylated Bipyridine Ligands

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Dedicated to Professor David Carillo on the occasion of his 65th birthday

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A series of cationic diiminoiridium(III) complexes [Ir(ppy-*N*,*C*)$_2$(L-*N*,*N*)](PF$_6$) has been prepared [Hppy = 2-phenylpyridine; L = 4,4′-*t*Bu$_2$dpbpy (**1**), 4,4′-Me$_2$dpbpy (**2**), 4,4′-Me$_2$pbpy (**3**), 4,4′-Me$_2$bpy (**4**)] and their photophysical and electrochemical properties studied. X-ray diffraction studies of complex **1** reveal a dihedral angle of about 33° between the pyridine rings, and that the two phenyl groups are also tilted with respect to the adjacent pyridine rings. All the complexes exhibit moderately intense and long-lived emission. The origin of the emission is tentatively assigned to a triplet metal-to-ligand charge-transfer ^{3}MLCT [dπ(Ir) → π*(diimine)] excited state, although the possibility of a triplet σ-bond-to-ligand charge transfer ^{3}SBLCT [σ(Ir–C) → π*(diimine)] cannot be excluded. The luminescence properties of the complexes are dependent on the substituents on the diimine ligands. Selective *N*-methylation of the diimine ligands has been achieved and their *N*,*C*-coordination to the Ir centre has been attempted.

Introduction

Cyclometallated polypyridineiridium(III) complexes have attracted a great deal of interest due to their photophysical properties.[1−8] These systems exhibit luminescence emitted predominantly from triplet MLCT excited states with high quantum yields. Another interesting feature of these compounds is the possibility to tune the emission energy by simply modifying the cyclometallating and/or polypyridine ligands. One class of compounds that has been particularly well investigated for their photophysical properties and their use as dopants in organic light-emitting diode (OLED) devices are homoleptic neutral tris(cyclometallated) Ir^{III} complexes and related complexes.[2−4] The design of cationic cyclometalled Ir^{III} complexes [Ir(ppy-*N*,*C*)$_2$(bpy-*N*,*N*)]$^+$ (where bpy is 2,2′-bipyridine and Hppy is 2-phenylpyridine) has also been reported and their use as biological labelling reagents has been described recently.[5−8] A wide range of substituted 2,2′-bipyridines are now available, and, in particular, aromatic substituents can be introduced in the 6- and 6′-positions.[9,10] Such ligands are particularly attractive since they could adopt both *N*,*N* and *N*,*C* coordination. The latter coordination mode, involving orthometallation of the aryl group, requires prior *N*-protection of one pyridine ring in order to avoid the more facile *N*,*N*-coordination. It is anticipated that sequential *N*,*C*-coordination would allow access to polymetallic systems. We report herein the preparation, molecular structure, and photophysical and electrochemical properties of a series of cyclometallated diiminoiridium(III) complexes [Ir(ppy-*N*,*C*)$_2$(L-*N*,*N*)](PF$_6$) containing phenyl, methyl and/or *tert*-butyl substituents at various locations of the diimine ligands L. The effects of these different substituents on the luminescence properties of the complexes are discussed. We also describe here the selective *N*-methylation reactions of these ligands and attempts to coordinate them in an *N*,*C*-mode to the Ir centre.

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Results and Discussion

Synthesis and Characterization

The phenylated bipyridine ligands were prepared by classical procedures.[9,10] The phenylation reaction of 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy) affords a mixture of monophenylated (Me$_2$pbpy) and diphenylated (Me$_2$dpbpy)

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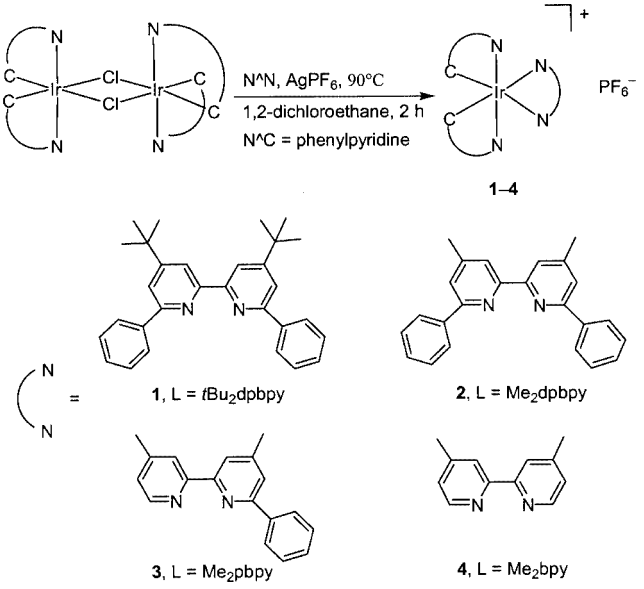
derivatives. They are readily separated by column chromatography and were isolated in 46% and 25% yield, respectively. Diphenylation of 4,4′-di-*tert*-butyl-2,2′-bipyridine (*t*Bu_2bpy) is similar to that of Me_2bpy.[10] The reaction is performed in refluxing THF, followed by hydrolysis and oxidation by manganese dioxide. After chromatographic purification, the diphenylated derivative *t*Bu_2dpbpy was isolated as a white solid in 84% yield; formation of the monophenylated product was not observed in this case.

The corresponding complexes [Ir(ppy-*N*,*C*)$_2$(L-*N*,*N*)](PF_6) [L = 4,4′-*t*Bu_2dpbpy (**1**), 4,4′-Me_2dpbpy (**2**), 4,4′-Me_2pbpy (**3**)] were then obtained from the reaction of the *ortho*-metallated dimer [Ir(ppy-*N*,*C*)$_2$(μ-Cl)]$_2$ and the appropriate diimine ligand L (Scheme 1). For comparison, the non-phenylated complex [Ir(ppy-*N*,*C*)$_2$(Me_2bpy-*N*,*N*)](PF_6) (**4**) was also prepared. The chloro-bridged dimer was synthesized following the procedure of Nonoyoma.[11] The coordination reactions of the diimine ligands to the Ir centre were performed in refluxing 1,2-dichloroethane; the use of methanol was avoided due to a protonation side-reaction of the diimine ligand. The presence of a silver salt is required, otherwise the starting material is recovered. All the complexes were crystallized from CH_2Cl_2/Et_2O and isolated as yellow crystals (yield: 70−80%). Complexes **1**−**4** were characterized by ^{1}H and ^{13}C NMR spectroscopy, and assignments were made on the basis of HMBC, HMQC, and COSY spectra. The heterocycles of the ppy ligands remain in a *trans* configuration as in the precursor dimer. Complexes **1**−**4** were formed as one isomer of low symmetry, as indicated by the NMR spectroscopic data. No *N*,*C*-chelation was thus observed under the reaction conditions used.



Scheme 1

The ^{1}H NMR spectrum of complex **3** shows two different sets of signals for the phenylpyridine ligands. In addition, the two N-heterocycles of the unsymmetric Me_2pbpy ligand are clearly distinguishable.

X-ray Crystal Structure of Complex 1

Crystals were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of **1**. The ORTEP diagram is depicted in Figure 1. Selected bond lengths and angles are listed in Table 1. Complex **1** (containing 1.5 H_2O molecules) exhibits a pseudo-octahedral geometry around the iridium centre, the two Ir−C bonds being in a *cis* position as in the precursor dimer. The Ir−N distances of the diimine ligand are similar to those of related complexes, and they are in accordance with a *trans* influence of the *C*-cyclometallating ligands. The slight lengthening of the Ir−N bond is similar to that observed for related cationic complexes.[5d,5g,6,12] The bite angle of the *t*Bu_2dpbpy ligand is similar to that of [Ir(ppy-*N*,*C*)$_2$(4′-R-6′-phenyl-2,2′-bipyridine-*N*,*N*)](PF_6) (R = $OCOC_6H_4OCOC_6H_4OC_6H_{13}$) [75.2(4)°].[5g] The bipyridine rings are not coplanar (dihedral angle 32.97°) and the 6,6′-diphenyl groups are also tilted with respect to the adjacent pyridine rings (dihedral angles 45.27° and 93.85°). This is probably due to steric reasons. Moreover, the phenyl rings are almost coplanar with the phenyl groups of the ppy

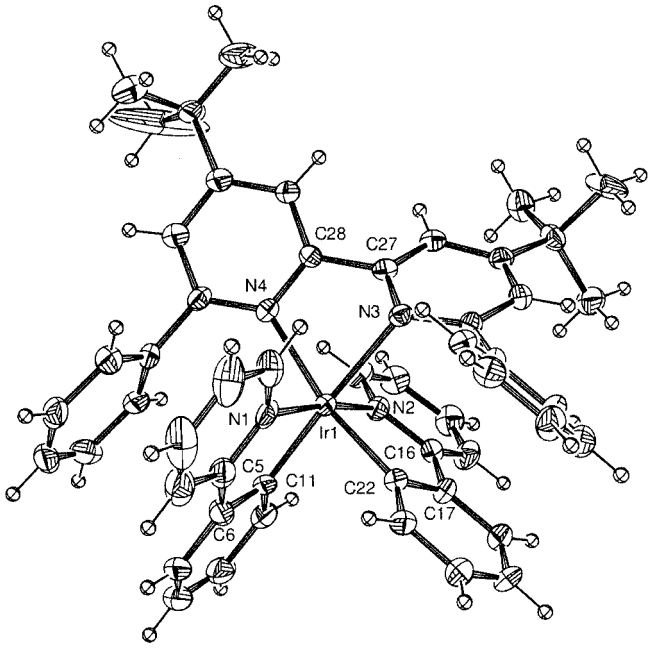


Figure 1. ORTEP representation of complex **1**; the unit cell contains 1.5 molecules of H_2O, which have been omitted for clarity, as has the PF_6^- counteranion

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**

Ir−N(1)	2.057(6)	Ir−C(11)	1.997(6)
Ir−N(2)	2.056(5)	Ir−C(22)	2.014(6)
Ir−N(3)	2.262(5)	C(22)−Ir−N(1)	95.5(2)
Ir−N(4)	2.217(5)	C(22)−Ir−N(2)	80.7(2)
N(1)−Ir−N(4)	90.53(19)	C(22)−Ir−N(3)	93.7(2)
N(1)−Ir−N(3)	104.3(2)	C(22)−Ir−N(4)	168.6(2)
N(3)−Ir−N(4)	75.44(18)	C(11)−Ir−N(1)	80.5(3)
N(2)−Ir−N(4)	94.22(19)	C(11)−Ir−N(2)	93.4(3)
N(2)−Ir−N(3)	81.69(19)	C(11)−Ir−N(3)	175.0(3)
C(11)−Ir−C(22)	84.6(2)	C(11)−Ir−N(4)	168.6(2)

ligands. This feature has been previously reported for the above-mentioned monophenylated derivative.[5g]

Electronic Absorption Spectroscopy

The electronic absorption spectral data for complexes **1**−**4** in CH_2Cl_2 are summarized in Table 2. All complexes display intense absorption bands in the ultraviolet region at about 250−300 nm, which are assigned to spin-allowed intraligand ^{1}IL [$\pi \rightarrow \pi^*$(ppy and diimine)] transitions. In the visible region, weak absorption bands at about 345−445 nm are observed; these bands are attributed to spin-allowed ^{1}MLCT [$d\pi(Ir) \rightarrow \pi^*$(ppy and diimine)] transitions. In addition, weaker absorption bands and tailing at lower energy, corresponding to spin-forbidden ^{3}MLCT [$d\pi(Ir) \rightarrow \pi^*$(ppy and diimine)] transitions, are also observed. The absorption characteristics of these complexes are similar to those of related cyclometallated polypyridineiridium complexes.[1,5−8]

Table 2. Electronic absorption spectral data for complexes **1**−**4** at 298 K[a]

Complex	λ_{abs} [nm] (ε [M^{-1} cm^{-1}])
1	260 (49000), 300 (32000), 345sh (12000), 385sh (5200), 445sh (1600), 480sh (1000)
2	260 (48000), 300sh (29000), 345sh (12000), 385sh (5600), 445sh (1600), 475sh (900)
3	260 (32000), 300sh (21000), 335sh (9400), 370sh (6300), 410sh (3700), 465sh (740)
4	260 (42000), 300sh (21000), 345sh (12000), 380 (6900), 420 (4100), 470 (1000)

[a] Data for deoxygenated CH_2Cl_2 solutions.

Luminescence Properties

Upon photoexcitation, complexes **1**−**4** display moderately intense and long-lived orange-yellow to greenish-yellow emission under ambient conditions and in low-temperature glass. The emission spectra of complexes **1**−**4** in CH_3CN at 298 K and alcohol glass at 77 K are shown in Figures 2−5. The photophysical data are listed in Table 3. The observed emission lifetimes in the microsecond and sub-microsecond time scales indicate the phosphorescent nature of the emission. The emission maxima occur at higher energy in less-polar CH_2Cl_2 than in more-polar CH_3CN. This observation is commonly made in other luminescent cyclometallated diiminoiridium systems.[1,5−8] In view of the low-lying π^*-orbitals of the diimine ligands, the emission is assigned to an emissive state of predominately ^{3}MLCT [$d\pi(Ir) \rightarrow \pi^*$(diimine)] character. However, the low reversibility of the oxidation waves of the complexes (see below) suggests the involvement of covalent Ir−C bond character in the HOMOs of the complexes. The possibility of a triplet σ-bond-to-ligand ^{3}SBLCT [$\sigma(Ir-C) \rightarrow \pi^*$(diimine)] emissive state thus cannot be totally ignored.[5a,7b,7c]

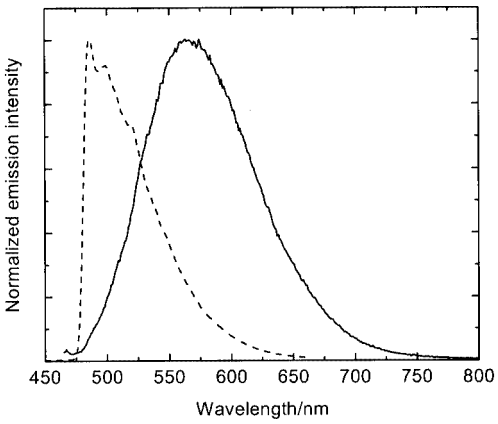


Figure 2. Emission spectra of complex **1** in CH_3CN at 298 K (− − −) and EtOH/MeOH (4:1, v/v) at 77 K (------)

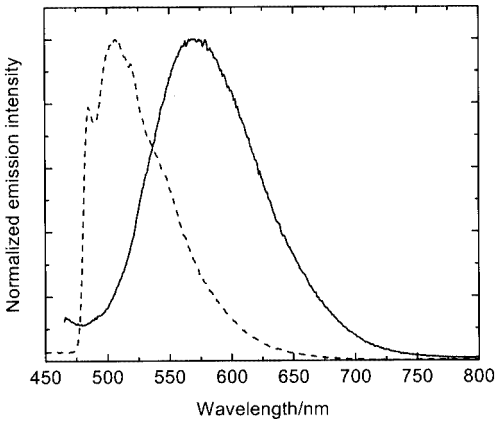


Figure 3. Emission spectra of complex **2** in CH_3CN at 298 K (− − −) and EtOH/MeOH (4:1, v/v) at 77 K (------)

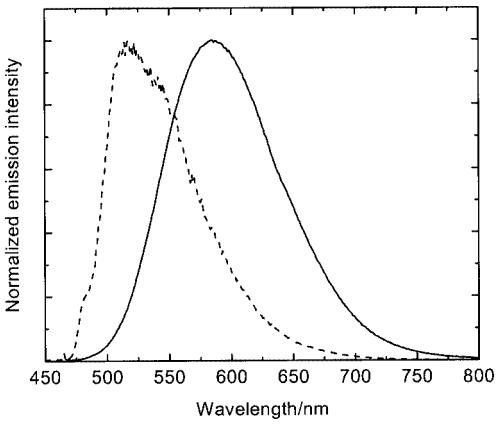


Figure 4. Emission spectra of complex **3** in CH_3CN at 298 K (− − −) and EtOH/MeOH (4:1, v/v) at 77 K (------)

Nevertheless, more detailed studies such as MO calculations are required to obtain a clearer picture of the electronic structures and excited-state nature of the complexes.

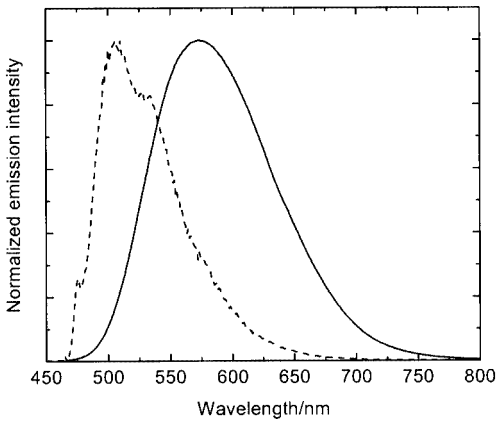


Figure 5. Emission spectra of complex **4** in CH_3CN at 298 K (– – –) and EtOH/MeOH (4:1, v/v) at 77 K (------)

The assignment of a ^{3}MLCT/^{3}SBLCT excited state is supported by the observation that the dimethyl complex **4** (λ_{em} = 573 nm in CH_3CN at 298 K) emits at noticeably higher energy than the non-substituted bipyridine analogue $[Ir(ppy\text{-}N,C)_2(bpy\text{-}N,N)]^+$ (λ_{em} = 606 nm).[1d] It is likely that the dimethyl substituents of complex **4** destablize the π*-orbitals of the Me_2bpy ligand, and thereby increase the ^{3}MLCT emission energy. The observation that the dimethylphenyl complex **3** (λ_{em} = 585 nm in CH_3CN at 298 K) emits at lower energy than complex **4** suggests that the phenyl ring at the 6-position of the bipyridine ligand of complex **3** lowers the energy level of the π*-orbitals due to electronic effects. Interestingly, the emission of the dimethyldiphenyl complex **2** occurs at almost the same energy as the dimethyl complex **4**, even though the former has two additional phenyl rings. The presence of two phenyl substituents in the 6- and 6′-positions does not lead to a bathochromic shift as would be expected for a more extended π-conjugated diimine ligand. A possible explanation is that in complex **2**, due to steric reasons, the two phenyl rings are not coplanar with the bpy moiety, and the degree of coplanarity of the bipyridine rings is also substantially reduced, as observed in the solid-state structure of complex **1** (see above). Thus, the lack of extensive π-conjugation raises the π*-level, and the ^{3}MLCT/^{3}SBLCT emission occurs at higher energy than expected. On the other hand, the di-*tert*-butyldiphenyl complex **1** (λ_{em} = 566 nm) emits at slightly higher energy than complex **2** (λ_{em} = 571 nm), probably due to the stronger electron-donating properties of the two *tert*-butyl substituents on the bipyridine ligand.

It is noteworthy that complex **1** (λ_{em} = 566 nm) emits at significantly higher energy than its phenyl-free counterpart $[Ir(ppy\text{-}C,N)_2(t\text{Bu}_2bpy\text{-}N,N)]^+$ (581 nm in CH_3CN).[8] This observation is in line with the crystal structure of complex **1**, which reveals that the two additional phenyl rings lower the π-conjugation between the two pyridine rings, and thereby destabilize the π*-orbitals of the diimine ligand, and increase the ^{3}MLCT/^{3}SBLCT emissive energy.

Upon cooling to 77 K, all four complexes display structural spectra and hypsochromic shifts in their emission maxima. These findings are commonly observed in other related luminescent cyclometallated polypyridineiridium complexes.[1,5–8] The emission decay is strictly single-exponential, with a lifetime of about 4–5 μs. In general, the emission is tentatively assigned to an excited state of predominantly ^{3}MLCT/^{3}SBLCT character.

Electrochemical Properties

The electrochemical data for complexes **1**–**4** are reported in Table 4. The cyclic voltammograms of the complexes in CH_3CN solution exhibit a reversible reduction at about −1.90 V vs. Fc/Fc^+. These waves can be assigned to the reduction of the bipyridine ligand as the cyclometallating ppy ligand is known to be reduced at much lower potential.[5d,6d] The cyclic voltammograms also exhibit an irreversible oxidation wave at a potential between 0.82 and 0.87 V vs. Fc/Fc^+. According to previous electrochemical studies on related complexes, these waves are attributed to metal-centered Ir^{III}/Ir^{IV} oxidation processes.[5a,7b,7c] The irreversible nature of this process suggests that the HOMOs may involve some covalent σ(Ir–C) character.[5a,7b,7c] By contrast, a quasi-reversible oxidation is observed for complex **4** containing the non-phenylated 4,4′-dimethyl-2,2′-bipyridine ligand. It is noteworthy that the same reversible oxi-

Table 3. Photophysical data for complexes **1**–**4**

Complex[a]	Medium (T [K])	λ_{em} [nm]	τ_o [μs]	Φ_{em}	k_r [s^{-1}]	k_{nr} [s^{-1}]
1	CH_3CN (298)	566	0.69	0.0038	3.9×10^4	7.9×10^5
	CH_2Cl_2 (298)	555	0.52	0.0070	9.0×10^4	1.1×10^6
	glass (77)[b]	485, 499, 520 sh, 537 sh	4.44			
2	CH_3CN (298)	571	0.12	0.0076	6.3×10^4	8.3×10^6
	CH_2Cl_2 (298)	564	0.15	0.012	8.0×10^4	6.6×10^6
	glass (77)[b]	485, 507, 520 sh 547 sh	4.48			
3	CH_3CN (298)	585	0.18	0.039	2.2×10^5	5.3×10^6
	CH_2Cl_2 (298)	576	0.32	0.12	3.8×10^5	2.8×10^6
	glass (77)[b]	482 sh, 517, 547 sh	3.95	–	–	–
4	CH_3CN (298)	573	0.49	0.16	3.3×10^5	1.7×10^6
	CH_2Cl_2 (298)	563	0.78	0.31	4.0×10^5	8.8×10^5
	glass (77)[b]	476 sh, 506, 534 sh, 580 sh	4.83			

[a] Data for deoxygenated solutions. [b] EtOH/MeOH (4:1, v/v).

Table 4. Electrochemical data for complexes **1**−**4** in CH_3CN (0.1 M nBu_4NPF_6, Pt electrode, scan rate 100 mV·s^{-1})

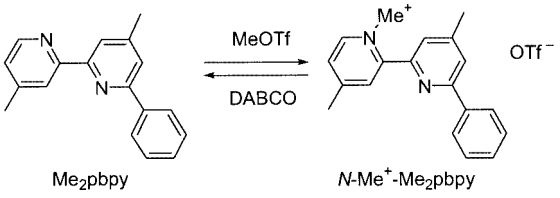
Complex	E_p [V] vs. Fc/Fc^+	$E_{1/2}$ [V] vs. Fc/Fc^+
1	0.83[a]	−1.91[b]
2	0.82[a]	−1.8[b]
3	0.87[a]	−1.89[b]
4	0.86[c]	−1.90[b]

[a] Irreversible process. [b] Quasi-reversible wave. [c] Reversible wave.

dation process has recently been reported for the related complex $[Ir(ppy\text{-}N,C)_2(t\text{Bu}_2\text{bpy-}N,N)]^+$.[8]

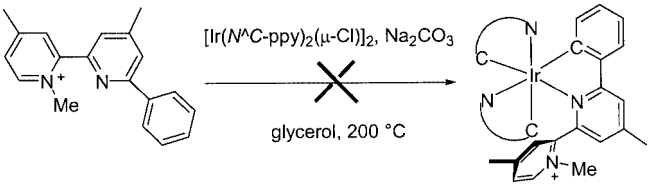
N-Alkylation Reactions and Attempts to Enforce N,C-Coordination of the Diimine Ligands

N-Protection by methylation of one pyridine ring of the above diimine ligands was performed in order to avoid *N*,*N*-coordination. The methylation reactions were performed with either MeOTf or $(Me_3O)(BF_4)$ as alkylating reagents in a chlorinated solvent. In the case of $t\text{Bu}_2$dpbpy, the reaction gives the dialkylated product. The desired monoprotected cations were obtained in a pure form after recrystallisation from a CH_2Cl_2/diethyl ether mixture as a white powder in moderate to good yield (36−56%). It is noteworthy that the monophenylated derivative Me_2pbpy undergoes selective methylation at the non-phenylated pyridine ring, probably due to steric reasons (Scheme 2). Thus, the phenylpyridine fragment of this compound is accessible for *N*,*C*-coordination. In addition, the *N*-methyl group can be readily removed in the presence of DABCO. A second *N*,*C*-coordination could be subsequently envisaged in the case of the diphenylated derivatives.



Scheme 2

It is noteworthy that the coordination of pyridinium ligands has not been reported for Ir so far, whereas examples are known for Ru, Rh, Pt and Pd complexes.[13,14] The classical procedures reported for the preparation of *fac*-tris-(cyclometallated) complexes have been applied for the cationic ligands.[2] The dimer $[Ir(ppy\text{-}N,C)_2(\mu\text{-Cl})]_2$ and [*N*-Me^+-Me_2pbpy](OTf) were refluxed at 200°C in glycerol in the presence of Na_2CO_3 (Scheme 3). However, this route



Scheme 3

was found to be inefficient, and the precursor dimer was partially recovered. Moreover, syntheses starting directly from $IrCl_3{\cdot}nH_2O$ to prepare the homoleptic complexes were also unsuccessful whatever the nature of the ligand. The fact that the bipyridine ligand may adopt a *transoid* conformation could induce a steric hindrance due to the presence of a substituent in the 4-position, especially in the case of the *t*Bu-substituted derivative.

Concluding Remarks

In conclusion, we have isolated a new series of luminescent cyclometallated diiminoiridium(III) complexes containing substituted bipyridine ligands. Upon photoexcitation, all the complexes are emissive in fluid solutions under ambient conditions and in low-temperature glass. The emission originates from an excited state of ^{3}MLCT [$d\pi(Ir) \rightarrow \pi^*$(diimine)] character, perhaps with some ^{3}SBLCT [$\sigma(Ir-C) \rightarrow \pi^*$(diimine)] character. Interestingly, instead of lowering the emission energy, addition of two phenyl substituents at the 6- and 6′-positions of the bipyridine ligand increases the emission energy of the complex. It is likely that the presence of the phenyl rings significantly lowers the degree of coplanarity of the bipyridine ligand, and thereby destabilizes the ^{3}MLCT emissive state. This is in line with the tilting of the two pyridine rings observed in the crystal structure of complex **1**. Our next target is to functionalize the 4,4′-dimethyl groups of the bipyridine ligand so that the complexes can be immobilized on a solid support. Related work is in progress.

Experimental Section

General Procedures: All manipulations were performed using Schlenk techniques under Ar. All solvents were dried and purified by standard procedures. All starting materials were used as received, MnO_2 was purchased from Merck. 6,6′-Diphenyl-2,2′-bipyridine (dpbpy), 6,6′-diphenyl-4,4′-dimethyl-2,2′-bipyridine (Me_2dpbpy) and 4,4′-di-*tert*-butyl-6,6′-diphenyl-2,2′-bipyridine ($t\text{Bu}_2$dpbpy) were prepared according to literature methods.[9,10] NMR spectra were recorded with Bruker DPX-200, AV 300 or AV 500 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are given versus $SiMe_4$ and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Attribution of carbon atoms was based on HMBC, HMQC and COSY experiments. UV/Vis absorption spectra were recorded using a UVIKON 9413 spectrophotometer, and emission spectra were measured with a PTI C 60 fluorescence spectrophotometer. High-resolution mass spectra (HRMS) were performed with an MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. Elemental analyses were performed by the Service central d'analyse du CNRS at Vernaison. Cyclic voltammograms were recorded using a PAR model 273 Autolab. The working electrode was polished Pt, the counter-electrode was a Pt wire, and a saturated calomel electrode (SCE) was used as the reference electrode. The Cp_2Fe/Cp_2Fe^+ redox couple was used as a secondary internal reference. Luminescence quantum yields were measured by the optically dilute method[15] using an aerated aqueous solution of $[Ru(bpy)_3]Cl_2$ (Φ_{em} = 0.028)[16] as the standard solution. Low-temperature (77 K) glass photophysical measurements were performed with the sample loaded in a quartz

tube inside a quartz-walled Dewar flask filled with liquid nitrogen. The excitation source for emission lifetime measurements was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser. Luminescence decay signals from a Hamamatsu R928 photomultiplier tube were converted into potential changes by a 50 Ω load resistor and then recorded with a Tektronix Model TDS 620A digital oscilloscope.

4,4′-Di-*tert*-butyl-6,6′-diphenyl-2,2′bipyridine (*t*Bu$_2$dpbpy): PhLi (11 mL, 20 mmol; 1.8 M, cyclohexane/diethyl ether) was added to a solution of 4,4′-di-*tert*-butyl-2,2′-bipyridine (1.34 g, 5 mmol) in 20 mL of THF. After stirring at room temperature for 30 min, the reaction medium was refluxed for 12 h. The reaction mixture was then hydrolysed at 0°C and the residue extracted with CH_2Cl_2 (3 × 150 mL). The organic phase was dried with $MgSO_4$ and MnO_2 (12.5 g, 144 mmol) was added. The reaction medium was stirred for 12 h and then filtered through Celite. Chromatography on silica gel (heptane/ethyl acetate, 95:5) afforded a white powder (1.34 g, 84%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.61 (d, ^4J = 1.8 Hz, 2 H, H$^{3/5}$-Py), 8.17 (m, 4 H, Ph *ortho*), 7.78 (d, ^4J = 1.8 Hz, 2 H, H$^{3/5}$-Py), 7.50 (m, 6 H, Ph *meta* and *para*), 1.47 (s, 18 H, *t*Bu) ppm. ^{13}C {^{1}H} NMR (75.4 MHz, $CDCl_3$): δ = 162.0 (C$^{2/6}$-Py), 156.9 (C$^{2/6}$-Py), 140.6 (C^4-Py), 129.2 (Ph), 128.8 (Ph), 127.6 (Ph), 127.0 (Ph), 118.0 (C$^{3/5}$-Py), 117.4 (C$^{3/5}$-Py), 35.7 (*t*Bu), 31.2 (*t*Bu). HRMS: *m*/*z* = 420.2563 [M]$^+$; calcd. for $C_{30}H_{32}N_2$ 420.25655. $C_{30}H_{32}N_2$ (420.6): calcd. C 85.67, H 7.67, N 6.66; found C 85.05, H 7.94, N 6.27.

4,4′-Dimethyl-6-phenyl-2,2′-bipyridine (Me$_2$pbpy): The monophenylated derivative 4,4′-dimethyl-6-phenyl-2,2′-bipyridine was obtained during the preparation of Me$_2$dpbpy.[9] Chromatography on silica gel using ethyl acetate as eluent gave pure Me$_2$pbpy as a white powder. Yield: 46%. ^{1}H NMR (200 MHz, CD_3COCD_3): δ = 8.51 (d, ^3J = 4.8 Hz, 1 H, H^6-Py), 8.49 (d, ^4J = 1.2 Hz, 1 H, H^3-Py), 8.22 (m, 3 H, H$^{3/5}$-Py* and Ph *ortho*), 7.79 (d, ^4J = 1.8 Hz, 1 H, H$^{3/5}$-Py*), 7.52 (m, 3 H, Ph), 7.22 (dd, ^3J = 4.8, ^4J = 1.2 Hz, 1 H, H^5-Py), 2.50 (s, 3 H, MePy*), 2.48 (s, 3 H, MePy) ppm; (Py* = Ph-Py). HRMS: *m*/*z* = 260.1328 [M]$^+$; calcd. for $C_{18}H_{16}N_2$ 260.13135. $C_{18}H_{16}N_2$ (260.3): calcd. C 83.04, H 6.19, N 10.76; found C 82.93, H 6.33, N 10.10.

Synthesis of [Ir(ppy-*N*,*C*)$_2$(L-*N*,*N*)](PF$_6$) (1−4): The chloride-bridged dimer [Ir(ppy-*N*,*C*)$_2$(μ-Cl)]$_2$ (0.1 mmol), the appropriate bipyridine derivative L (0.2 mmol), and $AgPF_6$ (0.2 mmol) were mixed in 1,2-dichloroethane (10 mL). The reaction mixture was refluxed under Ar for 2 h. The solution was then concentrated to dryness and the product was extracted with CH_2Cl_2 (3 × 5 mL). Crystallisation from a CH_2Cl_2/diethyl ether mixture gave a yellow-green powder.

[Ir(ppy-*N*,*C*)$_2$(*t*Bu$_2$dpbpy-*N*,*N*)](PF$_6$) (1): Yield 76%. ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.65 (dd, ^3J = 5.8, ^4J = 1.4 Hz, 2 H, H^6-Py), 8.60 (d, ^4J = 2.0 Hz, 2 H, H^3-Py*), 7.96 (td, ^3J = 8.2, ^4J = 1.4 Hz, 2 H, H^4-Py), 7.86 (dd, ^3J = 8.2, ^4J = 1.5 Hz, 2 H, H^3-Py), 7.42 (d, ^4J = 2.0 Hz, 2 H, H^5-Py*), 7.26 (td, ^3J = 8.2, ^3J = 5.8, ^4J = 1.5 Hz, 2 H, H^5-Py), 7.21 (dd, ^3J = 7.7, ^4J = 1.2 Hz, 2 H, H^3-Ph), 6.99 (m, 2 H, Ph* *para*), 6.76 (m, 8 H, Ph* *meta* and *ortho*), 6.48 (td, ^3J = 7.7, ^4J = 0.8 Hz, 2 H, H^4-Ph), 6.13 (td, ^3J = 7.7, ^4J = 1.2 Hz, 2 H, H^5-Ph), 5.29 (dd, ^3J = 7.7, ^4J = 0.8 Hz, 2 H, H^6-Ph), 1.43 (s, 18 H, *t*Bu) ppm. ^{13}C {^{1}H} NMR (75.4 MHz, CD_3COCD_3): δ = 168.0 (C^2-Py), 163.9 (C^4-Py*, C^6-Py*), 160.1 (C^2-Py*), 150.8 (C^6-Py), 146.8 (C^1-Ph), 141.9 (C^2-Ph), 138.6 (Ph* *ipso*), 138.1 (C^4-Py), 130.8 (C^6-Ph), 129.1 (C^5-Ph), 128.0 (Ph* *para*), 127.4 (Ph* *ortho* and *meta*), 125.8 (C^5-Py*), 124.1 (C^3-Ph), 121.7 (C^5-Py, C^3-Py*), 120.5 (C^4-Ph), 119.1 (C^3-Py), 35.4 (*t*Bu), 29.4 (*t*Bu) ppm; Py* = Ph-Py. HRMS: *m*/*z* = 921.3510 [M]$^+$; calcd. for $C_{52}H_{48}N_4{}^{193}$Ir 921.3512.

[Ir(ppy-*N*,*C*)$_2$(Me$_2$dpbpy-*N*,*N*)](PF$_6$) (2): Yield 80%. ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.61 (dd, ^3J = 5.8, ^4J = 0.6 Hz, 2 H, H^6-Py), 8.57 (d, ^4J = 1 Hz, 2 H, H^3-Py*), 7.95 (td, ^3J = 8.3, ^3J = 7.6, ^4J = 0.6 Hz, 2 H, H^4-Py), 7.85 (dd, ^3J = 7.6, ^4J = 1.5 Hz, 2 H, H^3-Py), 7.28 (td, ^3J = 8.3, ^3J = 5.8, ^4J = 1.5 Hz, 2 H, H^5-Py), 7.25 (d, ^4J = 1 Hz, 2 H, H^5-Py*), 7.19 (dd, ^3J = 7.8, ^4J = 1.3 Hz, 2 H, H^3-Ph), 6.98 (m, 2 H, Ph* *para*), 6.71 (m, 4 H, Ph* *ortho* and *meta*), 6.45 (td, ^3J = 7.8, ^4J = 0.7 Hz, 2 H, H^4-Ph), 6.11 (td, ^3J = 7.8, ^4J = 1.3 Hz, 2 H, H^5-Ph), 5.25 (dd, ^3J = 7.8, ^4J = 0.7 Hz, 2 H, H^6-Ph), 2.57 (s, 6 H, Me) ppm. ^{13}C {^{1}H} NMR (75.4 MHz, CD_3COCD_3): 168.1 (C^2-Py), 164.4 (C^6-Py*), 159.1 (C^2-Py*), 151.5 (C^4-Py*), 150.9 (C^6-Py), 147.2 (C^1-Ph), 141.9 (C^2-Ph), 138.6 (Ph* *ipso*), 138.0 (C^4-Py), 130.7 (C^6-Ph), 130.1 (C^5-Py*), 129.1 (C^5-Ph), 127.9 (Ph *para*), 127.4 (Ph* *ortho*/*meta*), 127.3 (Ph* *ortho*/*meta*), 125.2 (C^3-Py*), 123.9 (C^3-Ph), 122.1 (C^5-Py), 120.4 (C^4-Ph), 119.3 (C^3-Py). 20.9 (Me) ppm; Py* = Ph-Py. HRMS: *m*/*z* = 837.2574 [M]$^+$; calcd. for $C_{46}H_{36}N_4{}^{193}$Ir 837.2572. $C_{46}H_{36}F_6IrN_4P$ (982.0): calcd. C 56.26, H 3.70, N 5.71; found C 56.32, H 4.06, N 5.62.

[Ir(ppy-*N*,*C*)$_2$(Me$_2$pbpy-*N*,*N*)](PF$_6$) (3): Yield 80%. ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.78 (s, 1 H, H^3-Py*), 8.75 (s, 1 H, H^3-Py), 8.09 (m, 2 H, H^3-PyA, H^3-PyB), 8.00 (m, 2 H, H$^{4/6}$-PyB), 7.91 (m, 2 H, H$^{4/6}$-PyA), 7.76 (d, ^3J = 5.7 Hz, 1 H, H^6-Py), 7.68 (dd, ^3J = 7.8, ^4J = 1.2 Hz, 1 H, H^3-PhA), 7.41 (m, 2 H, H^5-Py, H^5-Py*), 7.37 (dd, ^4J = 1.3, ^3J = 7.8 Hz, 1 H, H^3-PhB), 7.26 (td, ^3J = 5.9, ^3J = 7.8, ^4J = 1.4 Hz, 1 H, H^5-PyA), 7.19 (td, ^4J = 1.6, ^3J = 5.9, ^3J = 7.8 Hz, 1 H, H^5-PyB), 6.92 (m, ^4J = 1.2, ^3J = 7.8 Hz, 2H, H^4-PhA, Ph *para*), 6.78 (m, 3 H, H^5-PhA, Ph *meta*), 6.66 (m, 2 H, Ph *ortho*), 6.54 (td, ^3J = 7.6, ^4J = 1.2 Hz, 2 H, H^4-PhB), 6.33 (td, ^3J = 7.6, ^4J = 1.3 Hz, 1 H, H^5-PhB), 6.00 (dd, ^4J = 1.2, ^3J = 7.6 Hz, 1 H, H^6-PhA), 5.63 (dd, ^3J = 7.7, ^4J = 1.2 Hz, 1 H, H^6-PhB), 2.67 (s, 3 H, Me-Py*), 2.57 (s, 3 H, Me-Py) ppm. ^{13}C {^{1}H} NMR (75.4 MHz, CD_3COCD_3): 169.0 (C^2-PyB), 167.2 (C^2-PyA), 164.9 (C^6-Py*), 156.9 (C^2-Py), 156.7 (C^2-Py*), 152.0 (C^4-Py*), 151.7 (C^4-Py, C^1-PhB), 149.8 (C^6-PyA), 149.3 (C^6-PyB, C^6-Py), 147.3 (C^1-PhA), 143.4 (C^2-PhA), 143.2 (C^2-PyB), 138.5 (C^4-PyA), 138.3 (Ph *ipso*), 138.2 (C^4-PyB), 131.4 (C^6-PhB), 130.5 (C^5-Py*), 130.3 (C^5-PhA), 130.2 (C^6-PhA), 129.0 (C^5-PyB), 128.6 (Ph *para*), 128.4 (C^5-Py), 127.6 (Ph *meta*), 127.4 (Ph *ortho*), 125.9 (C^3-Py), 124.6 (C^3-Py*), 124.5 (C^3-PhA), 124.4 (C^3-PhB), 123.6 (C^5-PyA), 122.5 (C^5-PyB), 120.2 (C^4-PhB), 119.9 (C^3-PyB), 119.7 (C^3-PyA), 20.4 (Me-Py), 20.1 (Me-Py*) ppm; Py* = Ph-Py. HRMS: *m*/*z* = 761.2268 [M]$^+$; calcd. for $C_{40}H_{32}N_4{}^{193}$Ir 761.2259.

[Ir(ppy-*N*,*C*)$_2$(Me$_2$bpy-*N*,*N*)](PF$_6$) (4): Yield 80%. ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.74 (s, 2 H, H^3-Py*), 8.27 (d, ^3J = 8.1 Hz, 2 H, H^3-Py*), 7.97 (m, 4 H, H^3-Ph, H^4-Py), 7.86 (m, 4 H, H^6-Py*, H^6-Py), 7.50 (d, ^3J = 6.2 Hz, 2 H, H^5-Py*), 7.19 (td, ^3J = 5.8, ^3J = 7.2, ^4J = 1.1 Hz, 2 H, H^5-Py), 7.05 (td, ^3J = 7.4, ^4J = 0.8 Hz, 2 H, H^4-Ph), 6.94 (td, ^3J = 7.4, ^4J = 1.2 Hz, 2 H, H^5-Ph), 6.38 (dd, ^3J = 7.4, ^4J = 0.8 Hz, 2 H, H^6-Ph), 2.59 (s, 6 H, Me) ppm. ^{13}C {^{1}H} NMR (75.4 MHz, CD_3COCD_3): δ = 167.6 (C^2-Py), 155.7 (C^2-Py*), 152.1 (C^4-Py*), 149.8 (C^1-Ph), 149.7 (C^6-Py*), 149.2 (C^6-Py), 144.3 (C^2-Ph), 138.7 (C^4-Py), 131.0 (C^6-Ph), 130.4 (C^5-Ph), 129.1 (C^5-Py*), 125.6 (C^3-Py*), 125.1 (C^3-Ph), 123.7 (C^5-Py), 122.6 (C^4-Ph),120.0 (C^3-Py), 20.4 (Me) ppm. HRMS: *m*/*z* = 685.1939 [M]$^+$; calcd. for $C_{34}H_{28}N_4{}^{193}$Ir 685.1945. $C_{34}H_{28}F_6IrN_4P$ (829.8): calcd. C 49.50, H 3.68, N 6.64; found C 49.21, H 3.40, N 6.75.

4,4′-Di-*tert*-butyl-1-methyl-6,6′-diphenyl-2,2′-bipyridinium Tetrafluoroborate: [Me$_3$O][BF$_4$] (97 mg, 0.66 mmol) was added to a solu-

tion of tBu$_2$dpbpy (250 mg, 0.60 mmol) in 10 mL of $ClCH_2CH_2Cl$. After refluxing for 15 h, the solution was concentrated to dryness. The residue was crystallized from a CH_2Cl_2/diethyl ether mixture in order to separate the *N,N*-dimethyl adduct and the diimine precursor. The product was isolated as a white powder by concentration of the resulting solution (112 mg, 36%). ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.40 (d, ^4J = 2.3 Hz, 1 H, H^3-Py*), 8.28−8.22 (m, 4 H, H^5-Py*, H^5-Py, Ph *ortho*), 8.05 (d, ^4J = 1.4 Hz, 1 H, H^3-Py), 7.90−7.85 (m, 2 H, Ph* *ortho*), 7.76−7.66 (m, 3 H, Ph* *meta* and *para*), 7.59−7.50 (m, 3 H, Ph *meta* and *para*), 4.13 (s, 3 H, *N*-Me), 1.57 (s, 9 H, *t*Bu*), 1.50 (s, 9 H, *t*Bu) ppm. ^{13}C {^{1}H} NMR (75.4 MHz, CD_3COCD_3): δ = 170.6 (C^4-Py*), 163.4 (C^4-Py), 157.4 (C^6-Py), 156.9 (C^6-Py*), 154.7 (C^2-Py*), 151.3 (C^2-Py), 138.4 (Ph *ipso*), 133.3 (Ph* *ipso*), 131.2 (Ph*), 129.8 (Ph), 129.6 (Ph*), 129.4 (Ph*), 128.9 (Ph), 127.3 (Ph), 126.8 (C^5-Py*), 126.1 (C^3-Py*), 121.8 (C^3-Py), 119.1 (C^5-Py), 45.0 (*N*-Me), 36.6 (*t*Bu*), 35.4 (*t*Bu), 29.8 (*t*Bu), 29.2 (*t*Bu*) ppm; Py* = *N*-MePy. HRMS: *m*/*z* = 435.2784 [M]$^+$; calcd. for $C_{31}H_{35}N_2$ 435.2800.

1,4,4′-Trimethyl-6,6′-diphenyl-2,2′-bipyridinium Triflate: Me$_2$dpbpy (0.25 g, 0.74 mmol) was dissolved in 5 mL of $ClCH_2CH_2Cl$ in a Schlenk tube and MeOTf (83 μL, 0.74 mmol) was then added. The reaction mixture was stirred overnight and the solvent evaporated. The residue was extracted with 5 mL of CH_2Cl_2. Addition of diethyl ether precipitated the precursor compound; the monocation was then recovered as a white powder (176 mg, 48%) upon evaporation of the resulting solution. ^{1}H NMR (300 MHz, CD_3COCD_3): δ = 8.27 (d, ^4J = 1.9 Hz, 1 H, H^3-Py*), 8.22 (m, 2 H, Ph*), 8.13 (m, 2 H, H^5-Py, H^5-Py*), 7.88 (m, 3 H, Ph *ortho*, H^3-Py), 7.75 (m, 3 H, Ph *meta* and *para*), 7.55 (m, 3 H, Ph* *meta* and *para*), 4.22 (s, 3 H, *N*-Me), 2.85 (s, 3 H, Me*), 2.62 (s, 3 H, Me) ppm. ^{13}C {^{1}H} NMR (75.4 MHz, CD_3COCD_3): δ = 159.4 (C^4-Py*), 156.7 (C^6-Py*), 154.0 (C^2-Py*), 150.8 (C^2-Py, C^4-Py), 150.4 (C^6-Py), 138.9 (Ph* *ipso*), 133.0 (Ph *ipso*), 131.4 (Ph *para*), 130.3 (C^5-Py*), 129.8 (Ph*), 129.6 (C^3-Py*), 129.4 (Ph), 129.2 (Ph), 128.9 (Ph*), 127.1 (Ph*), 125.3 (C^3-Py), 122.8 (C^5-Py), 45.2 (*N*-Me), 20.9 (Me*), 20.4 (Me) ppm; Py* = *N*-MePy. HRMS: *m*/*z* = 351.1858 [M]$^+$; calcd. for $C_{25}H_{23}N_2$ 351.18612.

1,4,4′-Trimethyl-6′-phenyl-2,2′-bipyridinium Triflate: Me$_2$pbpy (0.10 g, 0.38 mmol) was dissolved in 5 mL of $CHCl_3$ in a Schlenk tube. The solution was cooled to −30°C and MeOTf (43 μL, 0.38 mmol) was then added. The reaction mixture was warmed up to room temperature and the solvent evaporated. The residue was washed with toluene (2 × 3 mL) and the residue extracted with 5 mL of $CHCl_3$. The solution was cooled to −20°C, filtered, and then concentrated to afford a white powder (90 mg, 56%). ^{1}H NMR (200 MHz, CD_3COCD_3): δ = 9.05 (d, ^3J = 6.6 Hz, 1 H, H^6-Py), 8.24 (d, ^4J = 1.8 Hz, 1 H, H^3-Py), 8.17 (d, ^4J = 1.6 Hz, 1 H, H$^{3/5}$-Py*), 8.16 (t, ^3J = 6.0 Hz, 2 H, Ph^3), 8.12 (dd, ^3J = 6.6, ^4J = 1.8 Hz, 1 H, H^5-Py), 7.78 (d, ^4J = 1.6 Hz, 1 H, H$^{3/5}$-Py*), 7.52 (td, ^3J = 6.0, ^4J = 1.8 Hz, 1 H, Ph^4), 7.49 (dd, ^3J = 6.0, ^4J = 1.8 Hz, 1 H, Ph^2), 4.52 (s, 3 H, *N*-Me), 2.80 (s, 3 H, MePy), 2.60 (s, 3 H, MePy*) ppm; Py* = *N*-MePy. HRMS: *m*/*z* = 275.1553 [M]$^+$; calcd. for $C_{19}H_{19}N_2$ 275.1548.

Deprotection of 1,4,4′-Trimethyl-6,6′-diphenyl-2,2′-bipyridinium Triflate: A solution of the salt (120 mg, 0.18 mmol) and DABCO (20 mg, 0.18 mmol) in 20 mL of DMF was refluxed for 2 h. After addition of 30 mL of water, the product was extracted with CH_2Cl_2 (2 × 20 mL). The organic phase was dried with $MgSO_4$. Evaporation of the solvent gave a white powder (50 mg, 82%) which was identified by ^{1}H NMR spectroscopy as Me$_2$dpbpy.

Attempts at *N,C*-Coordination: 1,4,4′-Trimethyl-6′-phenyl-2,2′-bipyridinium triflate (49 mg, 0.116 mmol) and Na_2CO_3 (49 mg, 0.46 mmol) were added to a solution of [Ir(ppy-*N,C*)$_2$(μ-Cl)]$_2$ (50 mg, 0.046 mmol) in 10 mL of glycerol. The reaction mixture was then heated to 200 °C for 24 h. Addition of water (10 mL) gave a brown precipitate, which was washed with diethyl ether (2 × 5 mL) and methanol (5 mL). ^{1}H NMR studies of the crude product showed the presence of the dimer precursor and an unidentified product.

Structural Determination of Complex 1: Single crystals for X-ray diffraction studies were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution of complex **1** at 20 °C. The samples were studied with a NONIUS Kappa CCD with graphite-monochromated Mo-K_α radiation. The data collection and refinement parameters are presented in Table 5. The structures were solved with SIR-97,[17a] which reveals the non-hydrogen atoms of the molecules. The whole structures were refined by full-matrix, least-squares techniques on F^2, with hydrogen atoms refined using the riding mode. Structures were solved by Patterson or direct methods. The structures were completed by subsequent difference Fourier techniques and refined by full-matrix least squares on F^2 (SHELXL-97) with initial isotropic parameters.[17] CCDC-225743 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [of from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ; Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 5. Crystallographic data and refinement for complex **1**

Empirical formula	$C_{52}H_{51}F_6N_4IrO_{1.5}P$
Formula mass	1093.14
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a [Å]	13.3214(2)
b [Å]	17.4083(3)
c [Å]	25.0454(3)
V [Å^3]	4936.1(1)
Z	4
$D_{calcd.}$ [g/cm^3]	1.471
F(000)	2196
λ(Mo-K_α) [Å]	0.71073
θ range [°]	2.48−27.50
No. of reflections collected	11257
No. of unique reflections	11257
No. of observed reflections [$I > 2\sigma(I)$]	9931
No. of parameters	596
Goodness of fit on F^2	1.023
Final R, Rw	0.044, 0.112
$\Delta\rho_{max,min}$ [e•Å^{-3}]	2.4, −1.126

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