

Bright Blue Phosphorescence from Cationic Bis-Cyclometalated Iridium(III) Isocyanide Complexes

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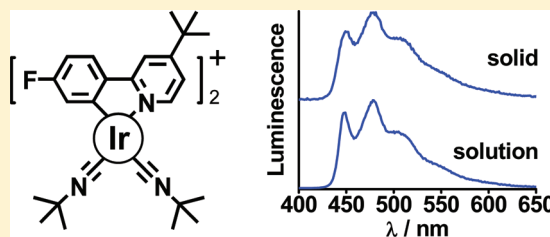
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S Supporting Information

ABSTRACT: We report new bis-cyclometalated cationic iridium(III) complexes $[(C^N)_2Ir(CN-tert-Bu)_2](CF_3SO_3)^+$ that have *tert*-butyl isocyanides as neutral auxiliary ligands and 2-phenylpyridine or 2-(4'-fluorophenyl)-*R*-pyridines (where *R* is 4-methoxy, 4-*tert*-butyl, or 5-trifluoromethyl) as C^N ligands. The complexes are white or pale yellow solids that show irreversible reduction and oxidation processes and have a large electrochemical gap of 3.58–3.83 V. They emit blue or blue-green phosphorescence in liquid/solid solutions from a cyclometalating-ligand-centered excited state. Their emission spectra show vibronic structure with the highest-energy luminescence peak at 440–459 nm. The corresponding quantum yields and observed excited-state lifetimes are up to 76% and 46 μ s, respectively, and the calculated radiative lifetimes are in the range of 46–82 μ s. In solution, the photophysical properties of the complexes are solvent-independent, and their emission color is tuned by variation of the substituents in the cyclometalating ligand. For most of the complexes, an emission color red shift occurs in going from solution to neat solids. However, the shift is minimal for the complexes with bulky *tert*-butyl or trifluoromethyl groups on the cyclometalating ligands that prevent aggregation. We report the first example of an iridium(III) isocyanide complex that emits blue phosphorescence not only in solution but also as a neat solid.



INTRODUCTION

Highly phosphorescent cationic iridium(III) complexes $[(C^N)_2Ir(L)_n]^+$, where C^N is a cyclometalating ligand and *L* is a neutral auxiliary ligand,^{1–3} are widely used as triplet emitters in luminescent sensors^{4–6} and switches,⁷ organic light-emitting diodes (OLED),^{8–11} and light-emitting electrochemical cells (LEC).^{12–32} They are also developed for application as nonlinear optical materials,³³ donor–acceptor chromophores with long-lived charge-separated states,³⁴ and sensitizer dyes for solar cells.³⁵ The photophysical properties of these complexes are determined by the strong spin–orbit coupling provided by the Ir(III) and by the triplet-emitting excited state of ligand-centered (LC) or charge-transfer (CT) nature.² Key advantages of these complexes are the ease of synthetic modification, the facile variation of emission colors from blue to near-infrared, the high phosphorescence quantum yields, and the relatively short excited-state lifetimes.^{1–3,36–39}

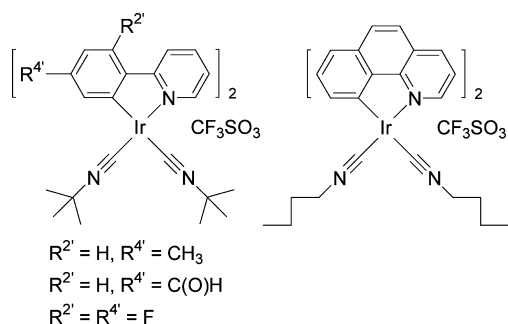
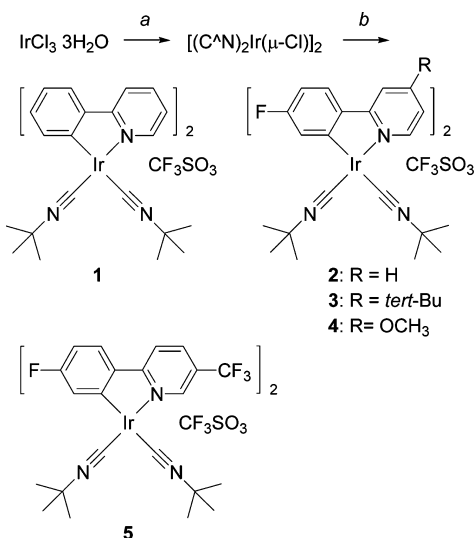
We are particularly interested in high-energy-emitting Ir(III) complexes because they are required for generation of blue^{9,23–28} and white^{9,29–31} light in electroluminescent devices. Blue-phosphorescent bis-cyclometalated cationic Ir(III) complexes with various neutral ligands such as diimines,^{22–27,40} carbenes,^{28,32} carbon monoxide,⁴¹ and phosphines^{41,42} are known. The common

problems encountered with these complexes are (a) low phosphorescence quantum yields that result from quenching of high-energy emissive excited states by d–d metal states and (b) red-shift and quenching of phosphorescence in going from solutions to neat solids caused by aggregation and triplet–triplet interaction.

Recently, it was reported that neutral and cationic Ir(III) complexes with alkyl isocyanides show blue to green phosphorescence in solution (Chart 1).^{6,10,43–46} However, their solid-state photophysical properties, which are of importance for practical applications, were only briefly mentioned.¹⁰ Here, we present new bis-cyclometalated, cationic Ir(III) complexes, $[(C^N)_2Ir(CN-tert-C_4H_9)_2](CF_3SO_3)^+$, with 2-phenylpyridines (C^N) and strong-field, nonchromophoric neutral *tert*-butyl isocyanides (1–5 in Scheme 1). To tune the photophysical properties of the complexes, we modified the cyclometalating 2-phenylpyridine ligands with electron-withdrawing (4'-F and 5-CF₃), electron-donating (4-OCH₃), and bulky (4-*tert*-butyl and 5-CF₃) substituents. As a result, we developed cationic iridium(III) isocyanide complexes that emit phosphorescence at higher

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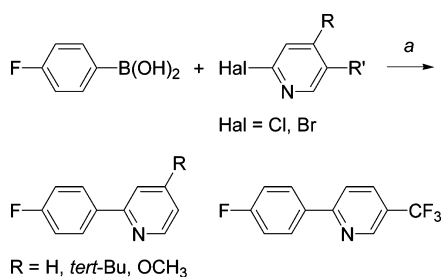
Chart 1. Previously Reported Cationic Iridium(III) Isocyanide Complexes^{6,10,43–45}**Scheme 1. Synthesis of New Ir(III) Complexes^a**

^aReaction conditions: (a) cyclometalating ligand, 2-ethoxyethanol/water (3/1), under Ar, 120 °C; (b) under Ar, RT (i) AgCF₃SO₃, CH₃OH/CH₂Cl₂; (ii) *tert*-butyl isocyanide, CH₂Cl₂.

energies and with higher efficiencies than do the known analogs (Chart 1),^{6,10,43–46} and we report the first example of an iridium(III) isocyanide complex that is blue-phosphorescent as a neat solid.

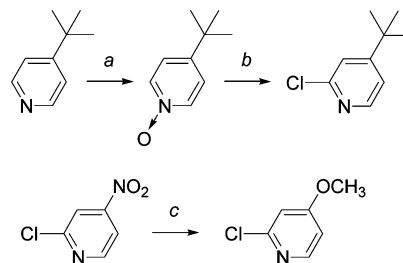
RESULTS AND DISCUSSION

Synthesis. The 2-phenylpyridine ligands were prepared by Suzuki–Miyaura coupling of 4-fluorophenylboronic acid with substituted 2-halopyridines (Scheme 2). Modified literature

Scheme 2. Synthesis of 2-Phenylpyridines^a

^aReaction conditions: (a) K₂CO₃, Pd(PPh₃)₄, THF/water (3/1), under Ar, 85 °C.

procedures gave access to the required 2-chloropyridines (Scheme 3).^{47,48} The cyclometalated precursors [(C^N)₂Ir(μ-Cl)]₂

Scheme 3. Synthesis of 2-Chloropyridines^a

^aReaction conditions: (a) H₂O₂, acetic acid, under air, 80 °C; (b) POCl₃, “dry finger”, under air, 130 °C; (c) NaOCH₃, dry DMF, under Ar, RT.

were made by reaction of IrCl₃·3H₂O with 2-phenylpyridines in 2-ethoxyethanol/water (Scheme 1).⁴⁹

Five new complexes, [(C^N)₂Ir(CN-*tert*-C₄H₉)₂]CF₃SO₃ (**1–5**), were prepared in higher than 60% yield by reaction of a cyclometalated Ir(III) precursor [(C^N)₂Ir(μ-Cl)]₂ with silver triflate (to remove the chloride anion)⁵⁰ and with an excess of *tert*-butyl isocyanide (Scheme 1).⁴³ The complexes were purified by column chromatography (on silica) and recrystallization; they were characterized by elemental analysis, ESI⁺ MS, and NMR spectroscopy. ¹H and ¹⁹F NMR spectra of **1–5** show a single set of signals for the constituent ligands; integration of ¹H peaks confirms the 1:1 ratio of the C^N to CN-*tert*-C₄H₉ ligands; ¹⁹F NMR confirms the presence of F group and of CF₃SO₃[−] counteranion; and ESI⁺ TOF mass spectra show the peak of [(C^N)₂Ir(CN-*tert*-C₄H₉)₂]⁺. The complexes are air- and moisture-stable solids that are soluble in polar organic solvents.

Structural Characterization. Figure 1 shows the X-ray molecular structure of **4**. Two independent molecules of the complex with similar structural features are present in the unit cell. The metal ion is in a distorted octahedral [(C^N)₂Ir(C₂)₂]⁺ coordination environment with the two pyridine nitrogen atoms in trans position. The Ir–C bonds with the *tert*-butyl isocyanides are shorter (on the average) and show a wider variation of length (Table 1) compared with the Ir–C bonds with the cyclometalating ligand. For the *tert*-butyl isocyanides, the Ir–C≡N angle is more linear and shows less variation than the C≡N–C angle (Table 1).

The cyclometalating ligands are nearly planar: the dihedral angle between their constituent rings is less than 10°, and the methoxy group is in-plane with the pyridyl ring. The complexes do not participate in face-to-face π–π stacking. Intermetallic communication is likely to be negligible because of the long Ir–Ir distance [8.8662(15) Å].

The main structural parameters of **4** (Table 1) are similar to those reported for two of the complexes shown in Chart 1 [R⁴ = CH₃⁴³ or C(O)H⁶]; of note is that all three structures have two independent molecules in the unit cell.

Electrochemistry. The electrochemical properties of **1–5** were studied by cyclic voltammetry in acetonitrile and DMF (Figure 2 and Figure S1 in the Supporting Information). All observed redox processes were irreversible, and their reduction potentials (relative to Fc⁺/Fc)⁵¹ were solvent-independent (Table 2).

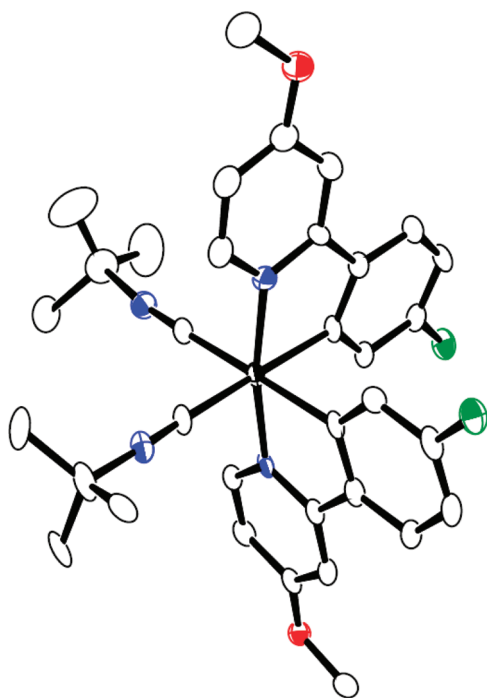


Figure 1. Structure of **4** (50% probability ellipsoids; only one of the two independent molecules shown; H atoms, triflate anion, and the disorder within the *tert*-butyl groups omitted; ORTEP). Heteroatom color codes: O, red; N, blue; F, green; Ir(1), black.

Table 1. X-ray Structural Parameters of **4^a**

	bond lengths (Å)			angles (deg)	
	C ^a N		isocyanide ^b	isocyanide ^b	
	Ir–C	Ir–N	Ir–C	Ir–C≡N	C≡N–C
Ir(1)	2.053(6)	2.060(5)	2.015(6)	175.7(6)	176.5(7)
	2.062(6)	2.049(5)	2.025(7)	178.2(6)	172.6(7)
Ir(2)	2.049(6)	2.077(6)	2.033(6)	173.4(6)	169.3(7)
	2.066(6)	2.052(6)	2.058(7)	176.4(6)	173.1(7)
avg ^c	2.058	2.060	2.033	175.9	172.9
Δ ^d	0.017	0.028	0.043	4.8	7.2

^aTwo independent molecules of the complex, labeled as Ir(1) and Ir(2), are present in the unit cell. Each row corresponds to one ligand.

^b*tert*-Butyl isocyanide in trans position to the carbon atom of the C^aN ligand in the same row. ^cAveraged value. ^dDifference between the minimum and the maximum values.

The first oxidation of the nonsubstituted complex **1** occurs at 1.23 V. The electron-withdrawing 4'-F substituent in the phenyl ring increases the oxidation potential to 1.42 V (**2**). Modification of the pyridyl ring in **2** with the electron-withdrawing 5-CF₃ group increases the oxidation potential by 200 mV (**5**), whereas electron donors facilitate the oxidation by 50 mV (4-*tert*-butyl, **3**; 4-OCH₃, **4**).

The first reduction of **1** occurs at −2.38 V. Fluorination of the phenyl ring facilitates the reduction by 40 mV (**2**). Modification of the pyridyl ring in **2** with an electron-withdrawing 5-CF₃ group shifts the reduction potential positively by 410/380 mV, whereas an electron donor shifts the reduction potential negatively by 50/90 mV (4-*tert*-butyl) and 100/120 mV (4-OCH₃) (the values stated for the potential shifts refer to DMF/CH₃CN solvents).

The trends observed in the redox potentials (Table 2) together with the results of theoretical calculations (see below)

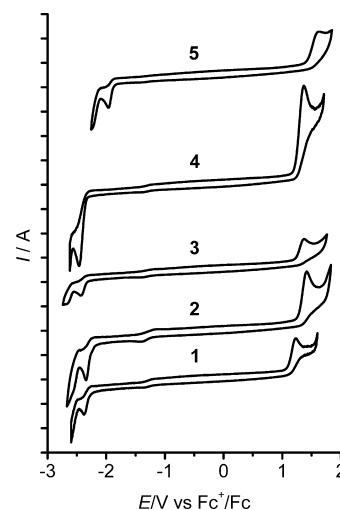


Figure 2. Cyclic voltammograms of **1–5** in CH₃CN (0.1 M NBu₄PF₆, 100 mV/s). The unit on the vertical axis is 20 μA. The cyclic voltammograms of **1–5** in DMF are shown in the Supporting Information.

indicate that the reduction of **1–5** is localized on the pyridyl ring, whereas oxidation takes place on the Ir–phenyl fragment.

Complexes **1–5** have a wide electrochemical gap of more than 3.58 V ($\Delta E = E^{\text{ox}} - E^{\text{red}}$, Table 2). The electrochemical gap increases when electron-donating and electron-withdrawing groups are attached to the pyridyl and phenyl rings of the cyclometalating ligand, respectively, and it reaches a maximum of 3.83 V for **4**. To our knowledge, this is the highest value reported for the electrochemical gap of a cationic, bis-cyclometalated Ir(III) complex;⁴³ it is slightly higher than the $\Delta E = 3.81$ V of the Ir(III) pyridine–carbene complex [(N,C⁴-(2-(2',6'-difluoro-3'-pyridyl)pyridyl)₂Ir(3-methyl-1-(4'-methyl-2'-pyridyl)-benzimidazol-2-ylidene)](PF₆)₂.³²

Infrared Spectroscopy. The infrared absorption spectra of **1–5** were measured in neat films obtained by evaporation of dichloromethane solutions. Complexes **1–5** show two infrared absorption peaks of equal intensity in the range of 2170–2201 cm^{−1} and separated by about 20 cm^{−1} that are characteristic of stretching vibrations of the *tert*-butyl isocyanide C≡N bond (Table 2 and Figure S2 in the Supporting Information).^{52,53} The increase in frequency of the C≡N stretching vibrations in going from the free ligand (2137 cm^{−1})⁵⁴ to **1–5** suggests a weak π backbonding from Ir(III) to the *tert*-butyl isocyanides (the alkyl isocyanide ligands are known to act as strong σ -donors and weak π -acceptors in the complexes with metals in high oxidation states).^{52,53}

We note that the frequencies of the infrared peaks are lower for complexes with lower oxidation potentials (Table 2 and Figure 3). This trend reflects either a stronger π backbonding from Ir(III) to the *tert*-butyl isocyanides or a weaker σ -donation from the *tert*-butyl isocyanides to Ir(III) in the easier-to-oxidize (more electron-rich) complexes.⁵²

Electronic Absorption Spectroscopy. The complexes are white (**3**, **4**) or pale yellow (**1**, **2**, **5**) solids and give nearly colorless solutions in dichloromethane and acetonitrile. Their electronic spectra in these solvents show intense bands below 300 nm with molar absorption coefficients $\epsilon = (10\text{--}50) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ originating from $\pi\text{--}\pi^*$ electronic transitions of the cyclometalating ligands (Figures S3–S7 and Table S2 in the Supporting Information). At lower energy, the spectra feature a

Table 2. Infrared Absorption, Electrochemical Properties, and DFT-Calculated HOMO and LUMO Energies of Ir(III) Complexes

complex	R ^a		IR, cm ^{-1b}	E ^{ox} , V ^{c,d}		E ^{red} , V ^{c,e}		ΔE , V ^f	calculated energy, eV ^g		
	Ph	Py		CH ₃ CN		CH ₃ CN	DMF		E _{HOMO}	E _{LUMO}	E _Δ ^h
1	H	H	2193, 2170	1.23		-2.38	-2.38	3.61	-6.06	-1.73	4.33
2	4'-F	H	2198, 2176	1.42		-2.34	-2.34	3.76	-6.18	-1.80	4.38
3	4'-F	4- <i>tert</i> -Bu	2196, 2174	1.37		-2.43	-2.39	3.80	-6.17	-1.72	4.45
4	4'-F	4-OCH ₃	2195, 2173	1.37		-2.46	-2.44	3.83	-6.19	-1.69	4.50
5	4'-F	5-CF ₃	2201, 2183	1.62		-1.96	-1.93	3.58	-6.41	-2.25	4.16

^aSubstituents on the phenyl (Ph) or pyridyl (Py) rings of the cyclometalating ligand. ^bInfrared absorption bands of solid films of the neat complex in the region of the C≡N stretching vibrations. ^cAll redox processes were irreversible. Relative to Fc⁺/Fc. Estimated errors: ±50 mV. On glassy carbon working electrode, in the presence of 0.1 M (NBu₄)PF₆, at scan rate 100 mV/s. ^dOxidation peak potentials. In DMF, the oxidation peak of 1–5 was outside of the electrochemical window of the solvent (>1.0 V relative to Fc⁺/Fc). ^eReduction peak potentials. ^f $\Delta E = E^{\text{ox}} - E^{\text{red}}$. ^gDFT calculations at the B3LYP/(6-31G**+LANL2DZ) level in CH₃CN. ^hE_Δ = E_{LUMO} - E_{HOMO}.

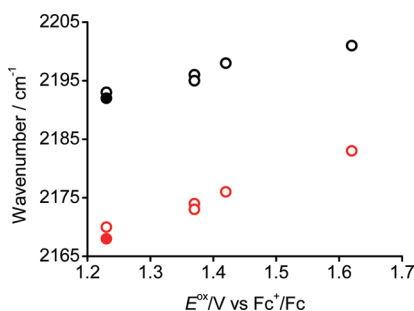


Figure 3. Correlation between the wavenumber of the two infrared transitions associated with the stretching vibrations of the C≡N bond (shown in black and red) and the oxidation potential (in CH₃CN; irreversible process) of 1–5. IR spectra were recorded for thin films of the neat complexes. Empty circles: data from this work (Table 2). Filled circles: literature data for [(N,C^{2'}-(2-*para*-tolylpyridyl))₂Ir(CN-*tert*-Bu)₂](CF₃SO₃)₂.⁴³

composite band with a main maximum at 318–354 nm and $\epsilon = (8\text{--}14) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ that we assign to the (Ir–phenyl)-to-pyridyl charge transfer (CT) transition (Figure 4 and Table 3).²

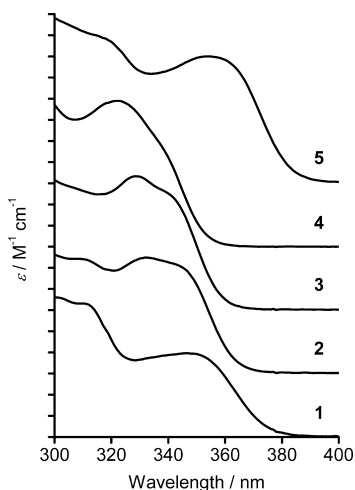


Figure 4. Absorption spectra of 1–5 in CH₂Cl₂. The unit on the vertical axis is $2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The spectra are shifted with respect to one another along the vertical axis by $6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Additional absorption spectra are shown in the Supporting Information.

The blue-shift of the CT band maximum by up to 6 nm in acetonitrile with respect to dichloromethane (Table 3) suggests that the ground state of 1–5 is more polar than the excited state.

Luminescence of Liquid Solutions. Upon excitation with near-UV light, the complexes exhibit blue (2–4) or blue-green (1, 5) luminescence in both dichloromethane and acetonitrile solutions. The luminescence spectra at room temperature show a vibronic structure with the highest-energy peak (λ_{em} , 0–0 transition) at 440–459 nm; the vibronic structure becomes better resolved at 77 K (Figures 5 and 6). The emission color of 1–5 (i.e., the position of the maxima and the relative intensities of the peaks in the spectrum) is solvent- and temperature-independent (Figure 6 and Table 3).

The luminescence of 1–5 is quenched by oxygen; therefore, photophysical measurements in 10^{-5} M liquid solutions were carried out under argon. Under these conditions, 1–5 display luminescence quantum yields (Φ) of 32–76% and observed excited-state lifetimes (τ) of 25–46 μs (Table 3). The luminescence decays are single-exponential functions suggesting the presence of one emissive center in liquid solution. The calculated radiative lifetimes of the excited states ($\tau_{\text{rad}} = \tau/\Phi$, which are the ideal lifetimes in the absence of radiationless processes) are in the range of 46–82 μs and are solvent-independent (Table 3).

The luminescence spectra of 1–5 show vibronic structure and are solvent-independent, whereas the radiative lifetimes are in the range of tens of microseconds. At the same time, the substituents in the cyclometalating ligands determine the emission color of 1–5: a blue shift is achieved by the 4'-F in the phenyl or the 4-OCH₃ in the pyridyl; a red shift is achieved by the 5-CF₃ in the pyridyl (Table 3). All of these findings suggest that 1–5 emit from a predominantly cyclometalating-ligand-centered triplet excited state of $\pi\text{--}\pi^*$ nature.^{2,43,44} In 1–5, the shorter wavelength of λ_{em} corresponds to the shorter wavelength of the CT absorption band maximum and to the larger electrochemical gap (Tables 2–4).

Luminescence of Solid Solutions. The photophysical properties of 1–5 were also studied in solid solutions in poly(methyl methacrylate) (PMMA) under air in the form of drop-cast films. In PMMA, 1–5 show blue or blue-green luminescence. The luminescence spectra, quantum yields (35–45%), and lifetimes (13–30 μs ; biexponential decays) of 1–5 in PMMA are similar to those measured in 10^{-5} M liquid solutions (Table 3 and Figure 6). It is a remarkable result, considering that the PMMA films had a relatively high concentration of the complex (1 wt %) and were exposed to air. We therefore conclude that 1–5 in PMMA do not form aggregates and are not quenched by oxygen.

Luminescence of Solid Complexes. In neat solids under air (spin-coated films), the complexes emit blue (3), green

Table 3. Photophysical Properties of Ir(III) Complexes

complex	medium ^a	λ_{abs} , nm (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) ^b	λ_{em} , nm ^c	Φ , % ^d	τ , μs ^{e,f}	τ_{rad} , μs ^g	T_1 , eV ^h
1	CH ₃ CN	341 (7.5)	453	52	32	62	3.15
	CH ₂ Cl ₂	347 (7.9)	455	45	25	56	
	CH ₂ Cl ₂ , 77 K		452		86 (20%), 28 (80%)		
	PMMA		455	35	14 (25%), 27 (75%)		
	solid		456	4.4	0.6 (44%), 2.0 (56%)		
2	CH ₃ CN	327 (10)	447	59	46	78	3.22
	CH ₂ Cl ₂	332 (11)	449	48	37	77	
	CH ₂ Cl ₂ , 77 K		447		80 (50%), 20 (50%)		
	PMMA		449	40	13 (38%), 30 (62%)		
	solid		456	2.6	0.8 (43%), 3.8 (57%)		
3	CH ₃ CN	326 (12)	447	55	40	73	3.27
	CH ₂ Cl ₂	328 (13)	449	50	33	66	
	CH ₂ Cl ₂ , 77 K		445		120 (42%), 35 (58%)		
	PMMA		448	39	14 (32%), 29 (68%)		
	solid		451	6.2	1.5 (70%), 4.1 (30%)		
4	CH ₃ CN	318 (13)	440	44	36	82	3.35
	CH ₂ Cl ₂	322 (14)	440	32	26	81	
	CH ₂ Cl ₂ , 77 K		436		50		
	PMMA		440	35	14 (37%), 30 (63%)		
	solid		444	4.1	1.3 (49%), 2.3 (51%)		
5	CH ₃ CN	348 (11)	458	76	35	46	3.10
	CH ₂ Cl ₂	354 (12)	459	69	33	48	
	CH ₂ Cl ₂ , 77 K		455		44 (24%), 23 (76%)		
	PMMA		458	45	13 (78%), 25 (22%)		
	solid		463	8.4	2.0 (92%), 4.5 (8%)		

^aAcetonitrile or dichloromethane solution at room temperature under air (absorption) or under argon (emission, 10^{-5} M); frozen dichloromethane solution at 77 K; PMMA film (1 wt % of the complex) or neat solid complex at room temperature under air. ^bLowest energy absorption band. ^cHighest-energy vibronic luminescence peak (0–0 transition). ^d $\lambda_{\text{exc}} = 330$ nm. ^e $\lambda_{\text{exc}} = 330$ or 373 nm. ^fThe luminescence decay is a biexponential function in solid samples; this observation may reflect the presence of different conformers of the complex in solid matrix (dichloromethane at 77 K; PMMA) or oxygen quenching/aggregate formation (neat complex). Biexponential luminescence decay was previously reported for neat films of $[(N,C^2-(2\text{-}para\text{-tolylpyridyl})_2)_2\text{Ir}(\text{CN-}tert\text{-Bu})_2](\text{CF}_3\text{SO}_3)$.¹⁰ ^gCalculated radiative lifetime: $\tau_{\text{rad}} = \tau/\Phi$. ^hEnergy of the first triplet state with respect to the ground singlet state S_0 (adiabatic energy difference) from DFT calculations in CH₃CN.

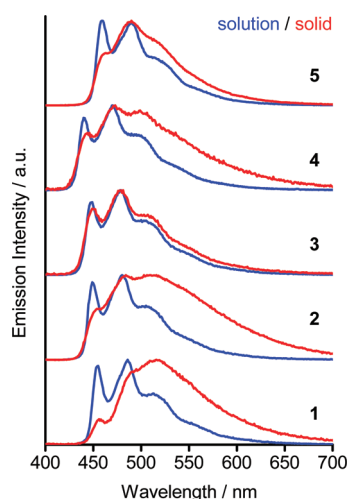


Figure 5. Corrected and normalized luminescence spectra of 1–5 at room temperature in dichloromethane solution (blue trace) and in neat solid film (red trace). The luminescence spectra in acetonitrile and PMMA are almost identical to the spectra in dichloromethane and are shown in Figure 6 and in the Supporting Information.

(1, 4, 5), or yellow (2) luminescence. For most of these complexes, a red shift of the emission color occurs in going from solutions to neat solids. It results from the red shift (by up to 9 nm), broadening, and change of the relative intensities of the

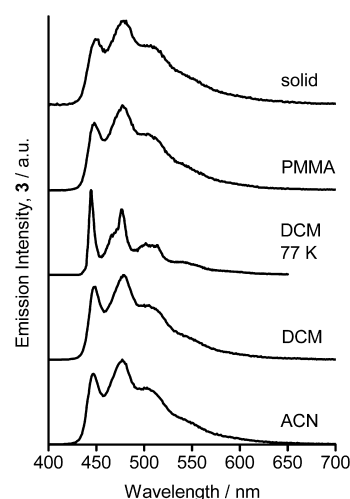


Figure 6. Corrected and normalized room-temperature luminescence spectra of 3 in acetonitrile (ACN), dichloromethane (DCM, also shown at 77 K), and PMMA and as a solid neat film. The luminescence spectra for the other complexes are shown in Figure 5 and in the Supporting Information.

luminescence peaks (Table 3 and Figure 5). In solutions, the 0–0 transition ($\lambda_{\text{em}} = 440\text{--}459$ nm) either dominates the emission spectrum or contributes significantly to it. In neat solids, however, the intensity of 0–0 transition is low (except for 3), and the

Table 4. Variation of Experimentally Measured and DFT-Calculated Parameters of Ir(III) Complexes with Respect to **1**^a

complex	$\Delta(P) = P(\text{complex}) - P(1)$, eV								
	$\Delta(E^{\text{ox}})$	$\Delta(E_{\text{HOMO}})$	$\Delta(E^{\text{red}})$	$\Delta(E_{\text{LUMO}})$	$\Delta(\Delta E)$	$\Delta(E_{\Delta})$	$\Delta(E_{\text{abs}})$	$\Delta(E_{\text{em}})$	$\Delta(T_1)$
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	+0.19	−0.12	+0.04	−0.07	+0.15	+0.05	+0.16	+0.04	+0.07
3	+0.14	−0.11	−0.05	+0.01	+0.19	+0.12	+0.17	+0.04	+0.12
4	+0.14	−0.13	−0.08	+0.04	+0.22	+0.17	+0.26	+0.08	+0.20
5	+0.39	−0.35	+0.42	−0.52	−0.03	−0.17	−0.07	−0.03	−0.05

^aThe nonsubstituted complex **1** was arbitrarily chosen as a benchmark. The data for calculations were taken from Tables 2 and 3. Spectroscopic parameters were converted from the wavelength (λ_{abs} , λ_{em} ; nm) to the energy (E_{abs} , E_{em} ; eV) scale. For all of the experimentally measured parameters, the values for CH₃CN solutions were used. The definitions of the parameters are the same as in Tables 2 and 3.

long-wavelength peaks ($\lambda > 475$ nm) are dominant. The quenching by oxygen and the self-quenching caused by aggregation and triplet–triplet interaction are responsible for the low quantum yields (<8.4%) and short lifetimes (<5 μ s; biexponential decays) of the neat complexes **1–5** under air.

In order to reduce aggregation, which red-shifts and quenches the emission of Ir(III) complexes in neat solids, the ligands are often modified with bulky spectator groups.^{15,18,31} In **1–5**, the bulky *tert*-butyl isocyanide ligands alone are not sufficient to prevent aggregation. For example, **4** is a blue emitter in solution, but a pale green emitter in neat solid (Figure 5). However, the complexes that have additional bulky groups in the cyclometalating ligands to further reduce aggregation (4-*tert*-butyl, **3**; 5-CF₃, **5**) show the smallest red shift of color and the highest luminescence quantum yields (6.2–8.4%) in neat solids (Table 3 and Figure 5). For example, the emission spectrum of **3** remains the same under all studied conditions (Figure 6), and **3** is the first iridium(III) isocyanide complex to show blue-phosphorescence in neat solid.

Overview of Photophysical Properties. Review of the literature shows that **1–5** emit phosphorescence at shorter wavelengths and with higher quantum yields than do the reported [(C[^]N)₂Ir(C₂)₂]⁺ and [(C[^]N)₂Ir(C[^]C)]⁺ analogs in all media.^{6,10,28,41,43–45} Up to now, the highest-energy [(C[^]N)₂Ir-(isocyanide)₂]⁺ emitters had $\lambda_{\text{em}} = 444$ nm/ $\Phi = 16\%^{43}$ or $\lambda_{\text{em}} = 458$ –461 nm/ $\Phi < 38\%^{6,43}$ in solution and $\lambda_{\text{em}} = 458$ nm/ $\Phi = 3.7\%$ in neat films.¹⁰ For dicarbene complexes [(C[^]N)₂Ir(C[^]C)]⁺, $\lambda_{\text{em}} = 452$ nm/ $\Phi < 35\%$ in solution and $\lambda_{\text{em}} = 458$ –460 nm/ $\Phi < 6\%$ in neat films.²⁸ For carbonyl complexes [(C[^]N)₂Ir(CO)₂]⁺, $\lambda_{\text{em}} = 441$ –451 nm/ $\Phi < 9.7\%$ in solution.⁴¹

The advantage of **1–5** is that they do not require polyfluorinated cyclometalating ligands to achieve blue phosphorescence, unlike the reported analogs^{28,41,43} or the extensively studied diimine [(C[^]N)₂Ir(N[^]N)]⁺ complexes^{22–27,40} [the problem with electron-deficient polyfluorinated ligands is that they have reactive C(sp²)–F bonds⁵⁵].

Therefore, bis-cyclometalated, cationic iridium(III) isocyanide complexes are promising blue-phosphorescent emitters in terms of color and quantum efficiency in solution (**2–4**) and in neat solid (**3**). However, their long radiative lifetimes may cause high sensitivity to triplet–triplet interaction and oxygen quenching and can limit their use in electroluminescent devices.

Theoretical Calculations. The molecular and electronic structures of **1–5** were investigated by performing density functional theory (DFT) calculations at the B3LYP/(6-31G**+LANL2DZ) level. The fully optimized ground-state geometries of **1–5** show a near-octahedral coordination of Ir(III) and are in good agreement with the X-ray structure of **4**.

Calculations show that the highest-occupied molecular orbital (HOMO) of **1–5** is composed of phenyl π -orbitals from the two

cyclometalating ligands together with a small contribution from d-orbitals of Ir(III) (Figure 7). The electron-withdrawing

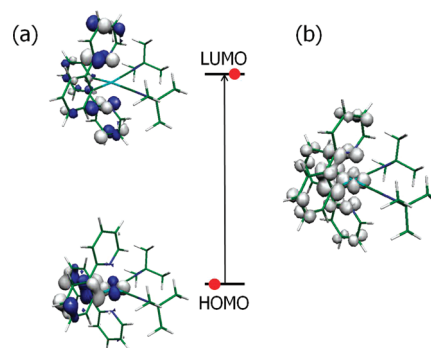


Figure 7. (a) Electron density contours (0.05 e bohr^{−3}) calculated for the HOMO and LUMO of **1**. (b) Spin density distribution (0.005 e bohr^{−3}) calculated for the triplet emitting excited state (*T*₁) of **1** resulting from the HOMO-to-LUMO monoexcitation.

groups (4'-F or 5-CF₃) in the cyclometalating ligands stabilize the HOMO of **1–5** (Table 2).

The lowest-unoccupied molecular orbital (LUMO) mainly resides on the pyridyl ring of the cyclometalating ligand (Figure 7). Therefore, modification of the pyridyl ring in **2** changes the LUMO energy: an electron-donor (4-*tert*-butyl or 4-OCH₃) destabilizes it by 0.08–0.11 eV; an electron-withdrawing 5-CF₃ group strongly stabilizes it by 0.45 eV (Table 2).

The trends in the calculated HOMO and LUMO energies of **1–5** are in agreement with the trends in the measured oxidation and reduction potentials: the lower (more negative) E_{HOMO} and E_{LUMO} energies correspond to the higher (more positive) E^{ox} and E^{red} potentials, respectively (Tables 2 and 4). At the same time, the larger calculated HOMO–LUMO energy gap corresponds to a larger electrochemical gap (Tables 2 and 4).

To gain insight into the photophysical properties of **1–5**, we optimized the geometry of the lowest-energy triplet excited state (*T*₁) by using the spin-unrestricted UB3LYP approach. The electron promotion associated with the excitation to *T*₁ shortens the Ir(III) bonds to the cyclometalating ligands by 0.01–0.05 Å and stretches the Ir(III) bonds to the *tert*-butyl isocyanide ligands by 0.05 Å. The unpaired-electron spin-density distribution calculated for *T*₁ perfectly matches the topology of the HOMO-to-LUMO monoexcitation. Therefore, excitation to *T*₁ involves an electron promotion from the HOMO (Ir–phenyl fragment) to the LUMO (pyridyl ring). All of the complexes have a similar spin-density distribution that is mainly localized on the C[^]N ligands together with a small contribution (about 0.13e) from Ir. Therefore, *T*₁ can be described as a cyclometalating-ligand-centered triplet state, with a small

contribution of $^3\text{MLCT}$ state, and with no participation of the *tert*-butyl isocyanides (Figure 7). The predominant ligand-centered nature of the emitting T_1 state explains the well-resolved vibronic structure of the luminescence spectra of **1–5** (Figures 5 and 6). The calculated changes in the adiabatic energy of T_1 with respect to the ground state are in agreement with the experimentally observed shifts in the emission energy of **1–5** (Tables 3 and 4).

Conclusions. We have developed bis-cyclometalated, cationic iridium(III) isocyanide complexes **1–5** that in solution show efficient blue or blue-green phosphorescence with the highest-energy luminescence peak at 440–459 nm and with quantum yields and excited-state lifetimes reaching 76% and 46 μs , respectively. Complexes **1–5** emit from a cyclometalating-ligand-centered triplet excited state, and their photophysical properties are solvent-independent. For most of the complexes, an emission color red shift occurs in going from solution to the neat solid. However, the shift is minimal for the complexes with bulky groups on the cyclometalating ligands that prevent aggregation, and complex **3** is the first in its class of compounds to show blue phosphorescence in neat solid. We expect that the easy-to-make cationic bis-cyclometalated Ir(III) isocyanide complexes will provide access to efficient phosphorescent emitters from deep-blue to near-infrared spectral range by simple variation of the cyclometalating and isocyanide⁵⁶ ligands.

EXPERIMENTAL SECTION

General Information. Elemental analyses were performed by Dr. E. Solari, Service for Elemental Analysis, Institute of Chemical Sciences and Engineering (ISIC EPFL). ^1H and ^{13}C NMR spectra were recorded with a Bruker AV400 (400 MHz) spectrometer; ^{19}F NMR spectra with a Bruker AV200 (200 MHz) or a Bruker AVIII-400 (400 MHz) spectrometers. ESI⁺ and GC-EI⁺ mass spectra were recorded with a Q-TOF Ultima (Waters) or TSQ7000 (Thermo Fisher) spectrometer (Mass-Spectroscopy Service, ISIC EPFL).

Purification, crystal growth, and handling of all compounds were carried out under air. All products were stored in the dark. Chemicals from commercial suppliers were used without purification. Chromatography was performed on a column with an i.d. of 30 mm on silica gel 60 (Fluka, Nr 60752). The progress of reactions and the elution of products were followed on TLC plates (silica gel 60 F₂₅₄ on aluminum sheets, Merck).

Synthesis of Ir(III) Isocyanide Complexes 1–5. The structures of **1–5** are shown in Scheme 1. The syntheses of 2-phenylpyridines and $[(\text{C}^{\text{N}})_2\text{Ir}(\mu\text{-Cl})_2]$ complexes are described in the Supporting Information. The reactions were performed under argon and in the absence of light. The solvents were deoxygenated by bubbling with Ar, but they were not dried. **CAUTION:** *tert*-butyl isocyanide is a foul-smelling volatile liquid—ensure adequate ventilation! The cyclometalated Ir(III) precursor $[(\text{C}^{\text{N}})_2\text{Ir}(\mu\text{-Cl})_2]$ was dissolved in CH_2Cl_2 (20 mL) at RT. A solution of AgCF_3SO_3 (excess, Aldrich) in CH_3OH (10 mL) was added dropwise. A precipitate of AgCl immediately formed. The reaction mixture was stirred (4 h) to give a yellow solution containing the white precipitate. It was filtered through a paper filter to remove AgCl , and evaporated to dryness (these operations were done under air). The resulting Ir(III) bis-solvato complex⁵⁰ was dissolved or suspended in degassed CH_2Cl_2 (20 mL), and *tert*-butyl isocyanide (large excess, Aldrich) was added. The reaction mixture became a solution, and its color changed from yellow to pale yellow or colorless. It was stirred at RT under argon for 96 h to give a pale yellow solution. It was directly loaded on the chromatography column (silica, 15 g) to avoid rotor-evaporating foul-smelling *tert*-butyl isocyanide. Elution with 0.5% CH_3OH in CH_2Cl_2 removed the impurities. Elution with 1.0–2.0% CH_3OH in CH_2Cl_2 recovered the product as pale yellow or colorless eluate. Purification by chromatography gave the pure product, unless

stated otherwise. The complexes were often isolated as oils that solidified on standing. Further details are provided below.

Complex 1. $[(\text{C}^{\text{N}})_2\text{Ir}(\mu\text{-Cl})_2]$ ($\text{C}^{\text{N}} = \text{N}, \text{C}^{2'}\text{-2-phenylpyridyl}$; 100 mg, 0.093 mmol), AgCF_3SO_3 (53 mg, 0.21 mmol), and *tert*-butyl isocyanide (0.25 mL, 183 mg, 2.2 mmol) gave pale yellow glass: 159 mg (0.19 mmol, 100%). Anal. Calcd for $\text{C}_{33}\text{H}_{34}\text{F}_3\text{IrN}_4\text{O}_3\text{S}\cdot\text{H}_2\text{O}$ (MW 833.94): C, 47.53; H, 4.35; N, 6.72. Found: C, 47.65; H, 4.34; N, 6.48. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.96\text{--}8.91$ (m, 2H), 8.11–8.04 (m, 4H), 7.73 (dd, $J = 7.6$, 1.2 Hz, 2H), 7.44–7.36 (m, 2H), 7.06 (td, $J = 7.2$, 1.2 Hz, 2H), 6.94 (td, $J = 7.6$, 1.2 Hz, 2H), 6.19 (ddd, $J = 7.6$, 1.2, 0.4 Hz, 2H), 1.36 (s, 18H, CN-*tert*-C₄H₉) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -78.9$ (3F, CF_3SO_3) ppm. ESI⁺ TOF MS: m/z 667.1 ($\{\text{M} - \text{CF}_3\text{SO}_3\}^+$, 100%). For the scaled-up procedure, $[(\text{C}^{\text{N}})_2\text{Ir}(\mu\text{-Cl})_2]$ (300 mg, 0.28 mmol, in 30 mL of CH_2Cl_2 and 10 mL of CH_3OH), AgCF_3SO_3 (170 mg, 0.66 mmol, in 5 mL of CH_3OH), and *tert*-butyl isocyanide (1.5 mL, 1.1 g, 0.013 mol, in 30 mL of CH_2Cl_2) gave 369 mg (0.44 mmol, 79%) of the product after chromatography (silica, 20 g). Complex **1** emits bluish-green and yellow-green phosphorescence in CH_2Cl_2 solution and as a powder, respectively.

Complex 2. $[(\text{C}^{\text{N}})_2\text{Ir}(\mu\text{-Cl})_2]$ ($\text{C}^{\text{N}} = \text{N}, \text{C}^{2'}\text{-2-(4'-fluorophenyl)-pyridyl}$; 100 mg, 0.087 mmol), AgCF_3SO_3 (50 mg, 0.195 mmol), and *tert*-butyl isocyanide (0.25 mL, 183 mg, 2.2 mmol) gave pale yellow solid: 137 mg (0.161 mmol, 92%). Anal. Calcd for $\text{C}_{33}\text{H}_{32}\text{F}_3\text{IrN}_4\text{O}_3\text{S}$ (MW 851.91): C, 46.53; H, 3.79; N, 6.58. Found: C, 46.34; H, 3.95; N, 6.22. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.89$ (d, $J = 6.0$ Hz, 2H), 8.13–8.05 (m, 2H), 8.01 (d, $J = 8.4$ Hz, 2H), 7.76 (dd, $J = 8.8$, 5.2 Hz, 2H), 7.45–7.38 (m, 2H), 6.78 (dt, $J = 8.8$, 2.4 Hz, 2H), 5.84 (dd, $J = 8.8$, 2.4 Hz, 2H), 1.39 (s, 18H, CN-*tert*-C₄H₉) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -78.8$ (3F, CF_3SO_3), -109.0 (2F, Ph-F) ppm. ESI⁺ TOF MS: m/z 703.1 ($\{\text{M} - \text{CF}_3\text{SO}_3\}^+$, 100%). Complex **2** emits pale blue and yellow phosphorescence in solution and as a powder, respectively.

Complex 3. $[(\text{C}^{\text{N}})_2\text{Ir}(\mu\text{-Cl})_2]$ ($\text{C}^{\text{N}} = \text{N}, \text{C}^{2'}\text{-2-(4'-fluorophenyl)-4-(tert-butyl)pyridyl}$; 100 mg, 0.073 mmol), AgCF_3SO_3 (42 mg, 0.163 mmol), and *tert*-butyl isocyanide (0.3 mL, 220 mg, 2.6 mmol) gave white solid: 126 mg (0.131 mmol, 90%). During chromatography, brown and yellow impurities preceded and followed the product, respectively, but they were easily removed. Anal. Calcd for $\text{C}_{41}\text{H}_{48}\text{F}_3\text{IrN}_4\text{O}_3\text{S}$ (MW 964.12): C, 51.08; H, 5.02; N, 5.81. Found: C, 51.15; H, 5.06; N, 5.72. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.74$ (d, $J = 6.4$ Hz, 2H), 7.95 (d, $J = 2.4$ Hz, 2H), 7.77 (dd, $J = 8.8$, 5.2 Hz, 2H), 7.40 (dd, $J = 6.0$, 2.0 Hz, 2H), 6.77 (td, $J = 8.8$, 2.8 Hz, 2H), 5.84 (dd, $J = 8.8$, 2.4 Hz, 2H), 1.51 (s, 18H, Py-*tert*-C₄H₉), 1.39 (s, 18H, CN-*tert*-C₄H₉) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -78.9$ (3F, CF_3SO_3), -109.6 (2F, Ph-F) ppm. ESI⁺ TOF MS: m/z 815.2 ($\{\text{M} - \text{CF}_3\text{SO}_3\}^+$, 100%). Complex **3** emits pale blue phosphorescence in solution and as a powder.

Complex 4. The reaction was performed with $[(\text{C}^{\text{N}})_2\text{Ir}(\mu\text{-Cl})_2]$ ($\text{C}^{\text{N}} = \text{N}, \text{C}^{2'}\text{-2-(4'-fluorophenyl)-4-(methoxy)pyridyl}$; 94 mg, 0.074 mmol), AgCF_3SO_3 (42 mg, 0.163 mmol), and *tert*-butyl isocyanide (0.4 mL, 292 mg, 3.5 mmol). After chromatography, the product still contained impurities. It was dissolved in CH_2Cl_2 (1 mL) and poured into ether (15 mL) with vigorous stirring. The resulting white emulsion was diluted with hexane (10 mL) and sonicated to convert emulsion into suspension. It was allowed to settle. The product was filtered and washed with hexane. White solid: 85 mg (0.093 mmol; 63%). Anal. Calcd for $\text{C}_{35}\text{H}_{36}\text{F}_3\text{IrN}_4\text{O}_5\text{S}$ (MW 911.96): C, 46.10; H, 3.98; N, 6.14. Found: C, 46.04; H, 3.71; N, 6.24. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 8.63$ (d, $J = 6.8$ Hz, 2H), 7.69 (dd, $J = 8.8$, 5.2 Hz, 2H), 7.41 (d, $J = 2.8$ Hz, 2H), 6.98 (dd, $J = 6.8$, 3.2 Hz, 2H), 6.76 (td, $J = 8.4$, 2.4 Hz, 2H), 5.92 (dd, $J = 9.2$, 2.8 Hz, 2H), 4.11 (s, 6H, Py-OCH₃), 1.39 (s, 18H, CN-*tert*-C₄H₉) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): $\delta = -78.9$ (3F, CF_3SO_3), -109.6 (2F, Ph-F) ppm. ESI⁺ TOF MS: m/z 763.1 ($\{\text{M} - \text{CF}_3\text{SO}_3\}^+$, 100%). Complex **4** emits blue and pale-green phosphorescence in solution and as a powder, respectively.

Complex 5. $[(\text{C}^{\text{N}})_2\text{Ir}(\mu\text{-Cl})_2]$ ($\text{C}^{\text{N}} = \text{N}, \text{C}^{2'}\text{-2-(4'-fluorophenyl)-5-(trifluoromethyl)pyridyl}$; 100 mg, 0.071 mmol; its solution in CH_2Cl_2 may turn into suspension upon prolonged stirring), AgCF_3SO_3 (40 mg, 0.156 mmol), and *tert*-butyl isocyanide (0.3 mL, 220 mg, 2.6 mmol) gave pale yellow solid: 114 mg (0.115 mmol, 81%). Anal.

Calcd for $C_{35}H_{30}F_{11}IrN_4O_3S$ (MW 987.90): C, 42.55; H, 3.06; N, 5.67. Found: C, 42.66; H, 3.33; N, 5.57. 1H NMR (400 MHz, CD_2Cl_2): δ = 9.12 (s, 2H), 8.34 (dd, J = 8.4, 2.0 Hz, 2H), 8.21 (d, J = 8.8 Hz, 2H), 7.89 (dd, J = 8.8, 5.2 Hz, 2H), 6.87 (td, J = 8.4, 2.4 Hz, 2H), 5.80 (dd, J = 8.8, 2.4 Hz, 2H), 1.45 (s, 18H, CN-*tert*- C_4H_9) ppm. ^{19}F NMR (376 MHz, CD_2Cl_2): δ = -62.6 (6F, Py- CF_3), -78.9 (3F, CF_3SO_3), -105.3 (2F, Ph-F) ppm. ESI⁺ TOF MS: m/z 839.1 ($\{M - CF_3SO_3\}^+$, 100%). Complex **5** emits greenish-blue and bluish-green phosphorescence in solution and as a powder, respectively.

■ ASSOCIATED CONTENT

■ Supporting Information

General information; synthesis and characterization of 2-chloropyridines, 2-phenylpyridines, and $[(C^N)_2Ir(\mu-Cl)]_2$ complexes; 1H , ^{13}C , and ^{19}F NMR spectra; full experimental details for the X-ray, electrochemical, and spectroscopic measurements and DFT calculations; crystallographic data (Table S1); cyclic voltammograms in DMF (Figure S1); IR absorption spectra (Figure S2); electronic absorption spectra (Table S2 and Figures S3–S7); luminescence spectra (Table S3 and Figures S8–S11); HOMO and LUMO energies (Figure S12); Cartesian coordinates of the computed species; and CIF of the crystal structure of **4**, CCDC 857727. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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