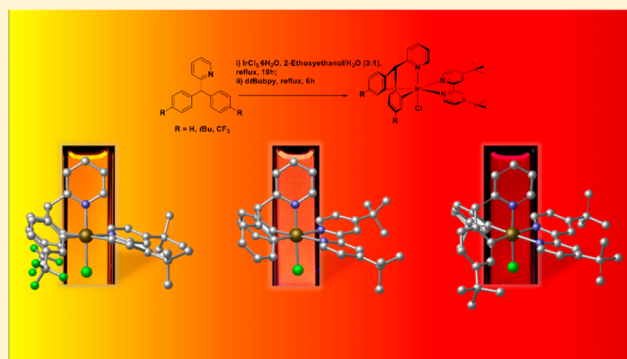


An Unprecedented Family of Luminescent Iridium(III) Complexes Bearing a Six-Membered Chelated Tridentate C^NC LigandClaus Hierlinger,^{†,‡} Thierry Roisnel,[†] David B. Cordes,[‡] Alexandra M. Z. Slawin,[‡] Denis Jacquemin,^{*,§,||} Véronique Guerschais,^{*,†} and Eli Zysman-Colman^{*,‡,||}[†]Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France[‡]Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, United Kingdom[§]UMR CNRS 6230, Université de Nantes, CEISAM, 2 rue de la Houssinière, 44322 Nantes Cedex 3, France^{||}Institut Universitaire de France, 1, Rue Descartes, 75005 Paris Cedex 5, France

S Supporting Information

ABSTRACT: A new family consisting of three luminescent neutral Ir(III) complexes with the unprecedented [Ir(C^NC)-(N^N)Cl] architecture, where C^NC is a bis(six-membered) chelating tridentate tripod ligand derived from 2-benzhydrylpyridine (bnpy) and N^N is 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtBubpy), is reported. X-ray crystallography reveals an unexpected and unusual double C–H bond activation of the two distal nonconjugated phenyl rings of the bnpy coupled with a very short Ir–Cl bond *trans* to the pyridine of the bnpy ligand. Depending on the substitution on the bnpy ligand, phosphorescence, ranging from yellow to red, is observed in dichloromethane solution. A combined study using density functional theory (DFT) and time-dependent DFT (TD-DFT) corroborates the mixed charge-transfer nature of the related excited states.



■ INTRODUCTION

Nearly all of the photoactive iridium(III) complexes that are used as emitters in electroluminescent devices,^{1–6} as dyes in solar cells,^{7–9} in nonlinear optics (NLO),^{10–12} as photoredox catalysts,^{13,14} as solar fuels,¹⁵ and in bioimaging^{16,17} contain conjugated five-membered chelated ligands, such as the commonly used 2-phenylpyridine (ppyH), 2,2'-bipyridine (bpy), acetylacetonate (acac), and picolinate (pic). Photoactive iridium complexes containing a six-membered cyclometalating chelate are very rare, and the few reported examples can be categorized into two families of complexes: those containing conjugated^{18–21} or nonconjugated^{22–24} bidentate cyclometalating ligands. For instance, in 2008, Song et al.²² obtained a phosphorescent Ir(III) complex [Ir(dfb-pz)₂(fptz)] (where (dfb-pz)H = 2,4-difluorobenzyl-N-pyrazole and fptz = 3-trifluoromethyl-5-(2-pyridyl)triazole) containing a nonconjugated *N*-benzylpyrazole ligand to form a six-membered chelated framework. This complex is a blue emitter in dichloromethane with $\lambda_{\text{em}} = 437$ and 460 nm ($\Phi_{\text{PL}} = 10\%$ and $\tau_e = 0.10 \mu\text{s}$). The methylene spacer of the cyclometalated ligand effectively interrupts the π -conjugation to produce a significant blue shift, compared to [Ir(dFppy)₂(fptz)] (where dFppyH = 2-(2,4-difluorophenyl)pyridine, which uses a five-membered ring chelate C^NN ligand and the same ancillary ligand ($\lambda_{\text{em}} = 460$

and 489 nm in dichloromethane).²⁵ By contrast, Zhu et al.¹⁸ reported in 2005 the iridium(III) complex [Ir(bis[2-(*N*-carbazolyl)pyridinato-*N*,C^{3'})]picolinate] ([Ir(cpy)₂(pic)]) containing a six-membered chelating framework where the ligand is fully conjugated, leading to yellow luminescence in the recrystallized solid state with $\lambda_{\text{em}} = 538$ nm ($\Phi_{\text{PL}} = 5\%$).

In an ongoing effort in our group to develop charged blue-emitting phosphors for solution-processed light-emitting electrochemical cells (LEECs) and organic light emitting diodes (OLEDs), we investigated the coordination of 2-benzhydrylpyridine (bnpyH₂) derivatives with Ir(III) in order to access six-membered chelate complexes **T1–T3** (Figure 1a). Surprisingly, given the prior art, upon sequential treatment of IrCl₃·6H₂O with bnpyH₂ and then 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtBubpy) in a one-pot reaction,²⁶ **T1** was not obtained. Instead, neutral complex [Ir(bnpy)(dtBubpy)Cl], **1**, was isolated. The formation of **1** arises from a highly unusual double C–H bond activation²⁷ of the bnpyH₂ ligand, which binds to the iridium in a tripodal fashion. Following a similar synthetic protocol, analogues **2** and **3**, functionalized with either electron-donating *tert*-butyl or electron-withdrawing

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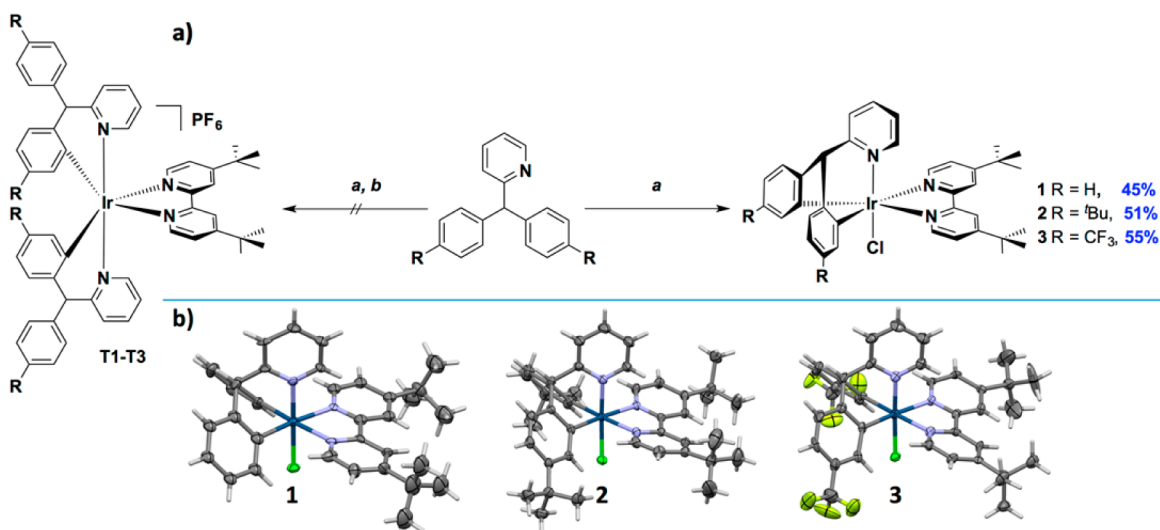


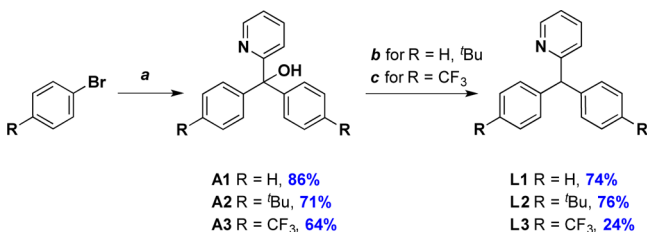
Figure 1. (a) Scheme for the proposed synthesis of the initial targets (T1–T3) and the synthesis of complexes 1–3. (a, i) IrCl₃·6H₂O, 2-ethoxyethanol/H₂O (3:1), reflux, 19 h; (ii) dtBubpy, reflux, 6 h. (b) aq. NH₄PF₆. (b) Solid-state structures of 1–3. Thermal ellipsoids correspond to a 50% probability level. Solvent molecules are omitted for clarity.

trifluoromethyl groups *meta* to the Ir–C bonds, were obtained. To the best of our knowledge, this is the first report of an iridium complex of the form [Ir(C[^]N[^]C)(N[^]N)Cl] and one in which the tridentate bis-cyclometalated ligand is a tripod featuring two six-membered metallacycles.²⁸ Indeed, the complex with the closest binding motif is [Ir(bppy)(bpy)Cl],²⁹ where bppy is 2-([1,1'-biphenyl]-3-yl)pyridine. This previous complex possesses a related [Ir(C[^]C[^]N)(N[^]N)Cl] structure, but the bppy ligand coordinates to the iridium in the more commonly observed planar five-membered chelate fashion. It is a very poorly luminescent near-IR emitter in CH₂Cl₂ ($\lambda_{\text{em}} = 725$ nm, $\Phi_{\text{PL}} = 8.4 \times 10^{-2}\%$). Ir(III) complexes bearing monocyclometalating planar tridentate bis(five-membered) chelate ligands (e.g., N[^]N[^]C[^]²⁹ or N[^]C[^]N[^]^{30–35}) and a cyclometalating bidentate ligand, C[^]N, have on the other hand been more widely explored, while Kozhevnikov has reported dinuclear Ir(III) complexes with a bridging ligand featuring two N[^]C[^]N motifs.^{36,37}

RESULTS AND DISCUSSION

Synthesis. Compounds L1, L2, and L3 (Scheme 1) were synthesized in two steps via a Grignard reaction³⁸ followed by a reduction step³⁸ and obtained as solids in good yields. A mixture of the corresponding proligand and IrCl₃·6H₂O in 2-

Scheme 1. Synthesis of Intermediates A1–A3 and Target Ligands L1–L3^a



^a(a, 1) Mg, 1,2-dibromoethane, THF, N₂, reflux, 4 h. (2) Methyl picolinate, THF, 0 °C to r.t., 90 min; (b, 1) HOAc, 57% HI. (2) NaOH_{aq}, 0 °C to r.t.; (c, 1) PBr₃, reflux, 2 h. (2) Zn, HOAc, (3) NaOH_{aq}, 0 °C to r.t.

ethoxyethanol/H₂O (3:1) was refluxed. After 19 h, dtBubpy 4,4'-di-*tert*-butyl-2,2'-bipyridyl was added at once, and heating was continued for 6 h to give the neutral complexes 1–3 as solids in a one-pot synthesis²⁶ in 45%, 51%, and 55% yield, respectively (Figure 1a). Complexes 1–3 were characterized by ¹H, ¹³C, and, for 3, ¹⁹F NMR spectroscopy; ESI-HR mass spectra; elemental analysis; and melting point determination (see Figures S21–S30 in the Supporting Information (SI) for NMR and ESI-HR mass spectra).

Crystal Structures. Single crystals of sufficient quality of 1–3 were grown from CH₂Cl₂/Et₂O at –18 °C. The structures of 1–3 were determined by single-crystal X-ray diffraction (Figure 1b, Table S1).³⁹ All three complexes possess a distorted octahedral geometry with the tridentate tripod ligand coordinated to the iridium to form two six-membered chelated rings. Both cyclometalating carbon atoms are *trans* to the pyridine rings of the dtBubpy, and the pyridyl unit of the bnpy-type ligands is *trans* to the chloride. This contrasts with the configuration of the Ir–Cl bond in previously reported Ir(III) complexes,^{29,31,32,36,37,40,41} where an Ir–C bond is *trans* to the chloride ligand. For 1–3, the Ir–Cl bond [2.375(3) Å for 1, 2.3612(8) Å for 2, and 2.369(2) Å for 3] is in the same range as that found for [Ir(tpy)(dmbpy)Cl]²⁺ (2.357 Å, where tpy = 2,2':6',2''-terpyridine and dmbpy = 4,4'-dimethyl-2,2'-bipyridine)⁴² but is significantly shorter (by ca. 0.1 Å) than the Ir–Cl bond in other cyclometalated tridentate Ir(III) complexes.^{29,31,32,36,37,40,41} Given the short Ir–C_{N[^]N[^]C} bonds [2.048(13) and 2.064(6) Å for 1, 2.028(4) and 2.031(3) Å for 2, and 2.017(7) and 2.027 Å for 3], this leads also to a correspondingly shorter Ir–N_{C[^]N[^]C} bond [2.055(11) Å for 1, 2.044(3) for 2, and 2.032(7) Å for 3] compared to the Ir–N_{dtBubpy} bonds [2.158(10) and 2.159(11) Å for 1, 2.127(3) and 2.140(3) Å for 2, and 2.122(6) and 2.133(5) Å for 3]. The bite angle of the N[^]N ligand is unremarkable at 75.60(4)° for 1, 75.85(12)° for 2, and 76.1(2)° for 3 and in line with cationic Ir(III) complexes of the form [Ir(C[^]N)₂(N[^]N)]⁺.^{43–47} Owing to the presence of the six-membered chelates, the C–Ir–C bond angle is significantly larger (85.60(5)° for 1, 85.65(15)° for 2, and 84.3° for 3) than the N_{dtBubpy}–Ir–N_{dtBubpy} bond angle.

Electrochemical Properties. The electrochemical behavior for 1–3 was evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in deaerated CH_2Cl_2 solution at 298 K at a scan rate of 50 mV s^{-1} using Fc/Fc^+ as the internal reference and referenced with respect to SCE.⁴⁸ The electrochemistry data can be found in Table 1, and the

Table 1. Luminescent and Electrochemical Properties of Complexes 1–3

	λ_{em}^a [nm]	$\Phi_{\text{PL}}^{a,b}$ [%]	τ_e^c [ns]	$k_r^d \times 10^{-5}$ [s ⁻¹]	$k_{\text{nr}}^e \times 10^{-5}$ [s ⁻¹]	E_{pa}^f [V]	E_{pc}^f [V]
1	619	8	318	2.52	28.93	0.87	−1.82
2	630	6	239	2.51	39.33	0.80	−1.81
3	581	26	718	3.62	10.31	1.14	−1.62

^a $\lambda_{\text{exc}} = 420 \text{ nm}$, recorded at 298 K in deaerated CH_2Cl_2 solution.

^b $[\text{Ru}(\text{bpy})_3]\text{PF}_6$ in MeCN as reference ($\Phi_{\text{PL}} = 1.8\%$ in aerated MeCN at 298 K).³¹ ^c $\lambda_{\text{exc}} = 378 \text{ nm}$. ^d $k_r = \Phi_{\text{PL}}/\tau_e$. ^e $k_{\text{nr}} = [(1 - \Phi_{\text{PL}})/\tau_e]$.

^fMeasurements were carried out in degassed CH_2Cl_2 at a scan rate of 50 mV s^{-1} with Fc/Fc^+ used as the internal reference, and referenced with respect to SCE ($\text{Fc}/\text{Fc}^+ = 0.46 \text{ V}$ in CH_2Cl_2).⁴⁸

voltammograms are shown in Figure 2. All complexes exhibit a quasi-reversible single electron oxidation peak, which is attributed to the Ir(III)/Ir(IV) redox couple with contributions

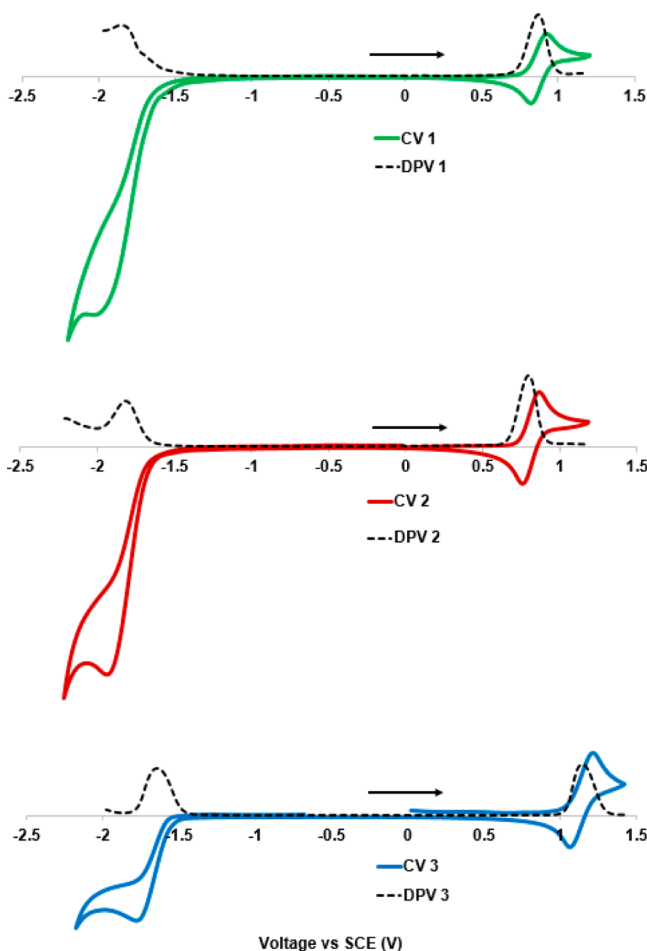


Figure 2. Cyclic voltammograms (in solid lines) and differential pulse voltammetry (in dotted lines) carried out in degassed CH_2Cl_2 at a scan rate of 50 mV s^{-1} , with Fc/Fc^+ as the internal reference, referenced to SCE (0.46 V vs SCE).⁴⁸

from the bnpy-type ligand. Complex 2 displays a lower oxidation potential (0.80 V) than 1 (0.87 V), both of which are notably lower than $[\text{Ir}(\text{mesppy})_2(\text{dtBubpy})]\text{PF}_6$ ($E_{1/2,\text{ox}} = 1.17 \text{ V}$ in deaerated CH_2Cl_2 , where mesppy is 2-phenyl-4-mesitylpyridinato).⁴⁹ Conversely, 3 shows a significantly anodically shifted oxidation potential at 1.14 V . The CVs of 1–3 show irreversible reduction waves that are monoelectronic as inferred from the respective DPVs. DFT calculations (Figure 3a)

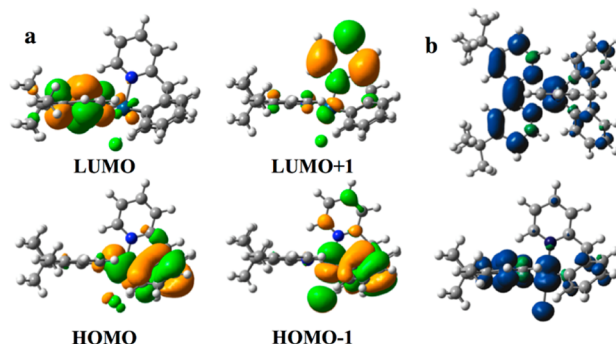


Figure 3. (a) Representation of the four frontier MOs of 1. (b) Side and top views of the spin density distribution for the lowest triplet state (T_1) of 1.

indicate that both the HOMO and HOMO−1, which are close in energy (see Figure S34 in the SI), involve the iridium and chloride atoms and the two phenyl rings of the bnpy ligand. The LUMO is almost exclusively localized on the dtBubpy ligand, while the LUMO+1 is primarily on the pyridyl ring of the bnpy ligand. Therefore, we conclude that the reduction is based on the ancillary ligand. The reduction potentials of 1 and 2 are each found at -1.82 V , while the reduction wave of 3 at -1.62 V is anodically shifted by 200 mV compared to 1 and 2. All three complexes are significantly more difficult to reduce than $[\text{Ir}(\text{mesppy})_2(\text{dtBubpy})]\text{PF}_6$ ($E_{1/2,\text{red}} = -1.15 \text{ V}$), which also shows an irreversible reduction in CH_2Cl_2 .⁴⁹

Photophysical Properties. The normalized UV–vis absorption spectra of 1–3 recorded in CH_2Cl_2 at 298 K are depicted in Figure 4 and the data summarized in Table S2 in the SI. All complexes show similar absorption profiles. The invariance of the intense high-energy (ϵ on the order of $(1-1.5) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) absorption bands below 300 nm are ascribed to $^1\pi-\pi^*$ ligand-centered (^1LC) transitions localized

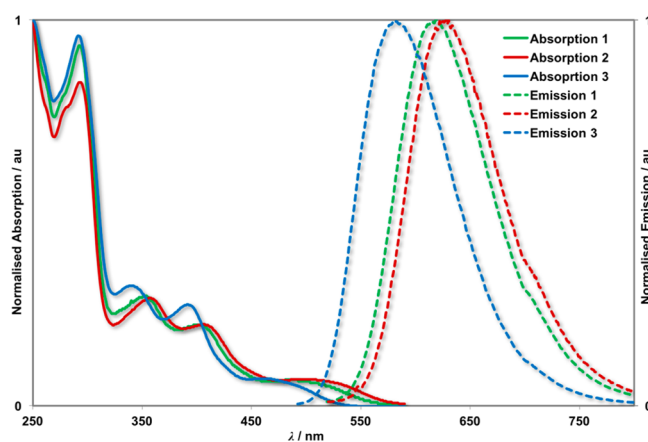


Figure 4. Normalized UV–vis absorption and photoluminescence spectra of 1–3 in CH_2Cl_2 at 298 K.

on the dtBubpy ligand. Two moderately intense bands (ϵ on the order of $(3-5) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) in the region of 340–360 nm and 390–405 nm are assigned to mixed charge-transfer transitions with the former consisting of more metal-to-ligand/ligand-to-ligand charge-transfer ($^1\text{MLCT}/^1\text{LLCT}$) character while the latter, according to TD-DFT calculations, implicate an intraligand CT ($^1\text{ILCT}$) from the phenyl rings to the pyridyl heterocycle of the bnpy-type ligand (see Figure S34 and Table S3 in the SI). Weak bands (ϵ on the order of $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) with onsets between 470 and 510 nm and tailing to 580 nm are attributed to a mixture of $^1\text{MLCT}/^1\text{LLCT}$ and spin-forbidden $^3\text{MLCT}/^3\text{LLCT}$ transitions involving the dtBubpy ligand. Introduction of the *tert*-butyl groups in **2** results in a small red-shift of the CT bands below 340 nm, whereas the trifluoromethyl groups in **3** produce a significant blue-shift of these bands, trends that are corroborated by TD-DFT calculations (Figure S35 in the SI).

The normalized photoluminescence (PL) spectra of **1–3** in degassed CH_2Cl_2 are shown in Figure 4, and the data are summarized in Table 1. Upon photoexcitation at 420 nm, all complexes show a broad and unstructured profile, indicative of an emission with mixed CT character. In line with the trends observed in the absorption spectra and the oxidation potentials in the CVs, the emission maxima are 581, 619, and 630 nm for **3**, **1**, and **2**, respectively. These emission maxima match very closely to the vertical phosphorescence energies calculated by spin-unrestricted DFT, which predicts emissions at 573, 613, and 622 nm, respectively. The calculations reveal that the emissive triplet state is localized on the iridium, chlorine, and dtBubpy but does not include significant contributions from the bnpy ligand (Figures 3b and S36 in the SI). The photoluminescence quantum yield (Φ_{PL}) of **1** is 8%, which is lower than that of the yellow-emitting $[\text{Ir}(\text{ppy})_2(\text{dtBubpy})]\text{PF}_6$ ($\Phi_{\text{PL}} = 64\%$ in CH_2Cl_2 , $\lambda_{\text{em}} = 570 \text{ nm}$, where ppyH is 2-phenylpyridine).⁵⁰ The Φ_{PL} of **2** is 6% while that of **3** is 26%. All three complexes show emission lifetimes, τ_{e} , in the submicrosecond regime. The radiative rate constants, k_{r} , for **1** and **2** are similar (2.52 vs $2.51 \times 10^5 \text{ s}^{-1}$, respectively). However, **2** exhibits a significantly larger nonradiative rate constant, k_{nr} ($39.33 \times 10^5 \text{ s}^{-1}$), compared to **1** ($28.93 \times 10^5 \text{ s}^{-1}$). Complex **3** possesses both the largest k_{r} ($3.62 \times 10^5 \text{ s}^{-1}$) and the smallest k_{nr} values ($10.31 \times 10^5 \text{ s}^{-1}$) in accordance with the energy gap law.

CONCLUSIONS

In conclusion, a new family of luminescent iridium(III) complexes bearing an unprecedented tripodal bis(six-membered) chelate tridentate ligand has been prepared through a highly unusual double cyclometalation reaction. The emission can be tuned through substitution on the cyclometalating aryl rings. DFT calculations support a mixed charge-transfer emission. Current efforts are focused on further modulating the electronics through a combination of modifications of the ancillary di-imine and the monodentate chloride ligands. This unprecedented tripodal ligand opens new perspectives for the design of tridentate Ir luminophores.

EXPERIMENTAL SECTION

General Procedure for Compound A1–A3. An oven-dried flask was charged under a nitrogen atmosphere with magnesium turnings (0.911 g, 37.50 mmol, 5 equiv) and THF (80 mL) followed by 2 mL of 1,2-dibromoethane. After the observation of gas evolution, the corresponding bromo derivative (22.50 mmol, 3 equiv) in THF (40

mL) was added dropwise. The reaction mixture was heated under stirring and kept at reflux for 4 h, resulting in a color change of the solution to gray. The reaction mixture was then cooled in an ice bath, and a solution of methyl picolinate (7.50 mmol, 1.00 equiv) in THF (40 mL) was added carefully. The mixture turned dark gray–black. The solution was allowed to warm to room temperature and was stirred for 90 min. The reaction mixture was quenched with aqueous NH_4Cl and extracted with Et_2O . The combined organic layers were dried over MgSO_4 , and the solvent was evaporated, leaving a residue, which was purified over silica (10% EtOAc in petroleum ether as the solvent). The desired fractions were combined, and the solvent was evaporated, leaving the title compound.

Diphenyl(pyridin-2-yl)methanol A1. Compound **A1** was prepared according to the general procedure and was obtained as a colorless solid (1.686 g, 6.45 mmol). Yield: 86%. R_{f} : 0.51 (10% EtOAc in petroleum ether on silica). Mp: 103 °C. Litt.⁵²: 102–103 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.60 (d, $J = 4.7 \text{ Hz}$, 1H), 7.64 (td, $J = 7.8, 1.8 \text{ Hz}$, 1H), 7.40–7.21 (m, 11H), 7.12 (d, $J = 7.9 \text{ Hz}$, 1H), 6.28 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.2, 147.7, 146.1, 136.4, 128.1, 127.9, 127.3, 122.9, 122.3, 80.8. HR-MS (FTMS⁺) $[\text{M} + \text{H}]^+$ Calculated ($\text{C}_{18}\text{H}_{15}\text{NOH}$): 262.1226. Found: 262.1226. CHN Calcd for $\text{C}_{18}\text{H}_{15}\text{NO}$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.68; H, 5.73; N, 5.41. The compound characterization is in agreement with that previously reported.⁵³

Bis(4-(*tert*-butyl)phenyl)(pyridin-2-yl)methanol A2. Compound **A2** was prepared according to the general procedure and was obtained as a colorless solid (1.994 g, 5.34 mmol). Yield: 71%. R_{f} : 0.39 (10% EtOAc in petroleum ether on silica). Mp: 156 °C. Litt.⁵⁴: 156 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.58 (d, $J = 3.2 \text{ Hz}$, 1H), 7.67–7.60 (m, 1H), 7.33–7.28 (m, 4H), 7.24–7.12 (m, 6H), 6.19 (s, 1H), 1.30 (s, 18H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.8, 150.1, 147.7, 143.3, 136.4, 127.9, 124.9, 123.1, 122.3, 80.6, 34.6, 31.5. HR-MS (FTMS⁺) $[\text{M} + \text{H}]^+$ Calculated ($\text{C}_{26}\text{H}_{31}\text{NOH}$): 374.2478. Found: 374.2476. CHN Calcd for $\text{C}_{26}\text{H}_{31}\text{NO}$: C, 83.60; H, 8.37; N, 3.75. Found: C, 83.45; H, 8.51; N, 3.88. The compound characterization is in agreement with that previously reported.⁵⁴

Pyridin-2-ylbis(4-(trifluoromethyl)phenyl)methanol A3. Compound **A3** was prepared according to the general procedure and was obtained as a beige solid (1.893 g, 4.76 mmol). Yield: 64%. R_{f} : 0.26 (10% EtOAc in petroleum ether on silica). Mp: 164 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.64 (d, $J = 7.4 \text{ Hz}$, 1H), 7.75–7.69 (m, 1H), 7.60 (s, 4H), 7.44 (s, 4H), 7.31 (d, $J = 8.5 \text{ Hz}$, 1H), 7.13 (d, $J = 9.7 \text{ Hz}$, 1H), 6.50 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 161.5, 149.4, 148.2, 136.9, 130.4, 130.1, 129.7, 129.4, 128.5, 125.2, 125.1, 125.1, 123.1, 122.7, 80.4, 77.4, 77.1, 76.7. ^{19}F NMR (376 MHz, CDCl_3): δ –62.59. HR-MS (FTMS⁺) $[\text{M} + \text{H}]^+$ Calculated ($\text{C}_{20}\text{H}_{13}\text{F}_6\text{NOH}$): 398.0974. Found: 398.0965. CHN Calcd for $\text{C}_{20}\text{H}_{13}\text{F}_6\text{NO}$: C, 60.46; H, 3.30; N, 3.53. Found: C, 60.51; H, 3.36; N, 3.59.

2-Benzhydrylpyridine L1. A mixture of **A1** (0.837 g, 3.21 mmol), aqueous 57% HI (2.5 mL), and HOAc (13 mL) was heated to 100 °C for 4 h. The resulting mixture was then cooled to 0 °C and basified to pH 9 with an aqueous NaOH solution (2 M). Ethyl acetate (100 mL) was added, and the mixture was washed successively with an aqueous NaHSO_3 solution and brine. The combined organic layers were dried over MgSO_4 , and the solvent was evaporated. The residue was purified over silica (10% EtOAc in petroleum ether as the solvent). The desired fractions were combined and the solvent evaporated leaving a beige solid (0.788 g, 3.21 mmol). Yield: 74%. R_{f} : 0.3 (10% EtOAc in petroleum ether on silica). Mp: 95 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.64 (d, $J = 4.1 \text{ Hz}$, 1H), 7.66–7.59 (m, 1H), 7.33 (t, $J = 7.3 \text{ Hz}$, 4H), 7.24 (dd, $J = 21.8, 7.2 \text{ Hz}$, 6H), 7.18–7.10 (m, 2H), 5.76 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.2, 149.5, 142.7, 136.4, 129.4, 128.4, 126.5, 123.8, 121.4, 59.4. HR-MS (FTMS⁺) $[\text{M} + \text{H}]^+$ Calculated ($\text{C}_{18}\text{H}_{15}\text{NH}$): 246.1277. Found: 246.1277. The compound characterization is in agreement with that previously reported.⁵⁵

2-(Bis(4-(*tert*-butyl)phenyl)methyl)pyridine L2. A mixture of the **A2** (0.900 g, 2.41 mmol), aqueous 57% HI (2.70 mL), and HOAc (13.20 mL) was heated to 100 °C for 4 h. The resulting mixture was then cooled to 0 °C and basified to pH 9 with an aqueous NaOH

solution (2 M). Ethyl acetate (100 mL) was added, and the mixture was washed successively with an aqueous NaHSO_3 solution and brine. The combined organic layers were dried over MgSO_4 , and the solvent was evaporated. The residue was purified over silica (10% EtOAc in petroleum ether as the solvent). The desired fractions were combined and the solvent evaporated, yielding the title compound as oil (0.655 g, 1.83 mmol). Yield: 76%. R_f : 0.33 (10% EtOAc in petroleum ether on silica). ^1H NMR (400 MHz, CDCl_3): δ 8.62–8.56 (m, 1H), 7.62–7.56 (m, 1H), 7.31 (s, 4H), 7.10 (s, 6H), 5.62 (s, 1H), 1.29 (s, 18H). ^{13}C NMR (126 MHz, CDCl_3): δ 163.8, 149.6, 149.2, 139.9, 136.5, 129.0, 125.4, 123.9, 121.4, 58.7, 34.5, 31.5. HR-MS (ASAP⁺) $[\text{M} + \text{H}]^+$ Calculated ($\text{C}_{26}\text{H}_{31}\text{N}$): 358.2535. Found: 358.2534.

2-(Bis(4-(trifluoromethyl)phenyl)methyl)pyridine L3. A mixture of A3 (0.500 g, 1.26 mmol, 1 equiv) and PBr_3 (25 mL) was vigorously stirred and heated and kept at 110 °C for 2 h. The mixture was then cooled to r.t. and was carefully poured onto ice, and aqueous NaOH (2 M) was added until the pH was neutral. The organic layer was dried over MgSO_4 , and the solvent was evaporated, leaving a residue which was dissolved in acetic acid (50 mL). Then, zinc dust (0.799 g, 12.60 mmol, 10 equiv) was added. The mixture was stirred at r.t. After 1 h, 20 mL of water was carefully added, and aqueous NaOH (2 M) was added until the pH was neutral. The organic layer was dried over MgSO_4 , and the solvent was evaporated, leaving a residue which was purified over silica (10% EtOAc in petroleum ether as the solvent). The desired fractions were combined, and the solvent was evaporated, leaving colorless oil (0.117 mg, 0.31 mmol). Yield: 24%. R_f : 0.55 (20% EtOAc in petroleum ether on silica). ^1H NMR (400 MHz, CDCl_3): δ 8.63 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 1H), 7.66 (td, $J = 7.7, 1.9$ Hz, 1H), 7.57 (d, $J = 8.2$ Hz, 4H), 7.30 (d, $J = 8.1$ Hz, 4H), 7.20 (ddd, $J = 7.6, 4.8, 1.1$ Hz, 1H), 7.10 (dt, $J = 7.9, 1.1$ Hz, 1H), 5.75 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ 161.4, 150.1, 146.0, 137.0, 129.8, 129.3, 125.7, 125.3, 124.0, 122.2, 58.9. ^{19}F NMR (376 MHz, CDCl_3): δ -62.50. HR-MS (FTMS⁺) $[\text{M} + \text{H}]^+$ Calculated ($\text{C}_{20}\text{H}_{13}\text{F}_6\text{N}$): 382.1030. Found: 382.1023.

General Procedure for the One-Pot Protocol. A mixture of the corresponding ligand (1.2 equiv) and $\text{IrCl}_3 \cdot 6\text{H}_2\text{O}$ (1 equiv) in 2-ethoxyethanol (15 mL) and H_2O (5 mL) was heated under stirring to 125 °C. After 19 h, 4,4'-di-*tert*-butyl-2,2'-bipyridine (1.5 equiv) was added, and heating was continued. After 6 h, the solvent was evaporated, leaving a solid, which was filtered over silica (1% MeOH in CH_2Cl_2). The desired fractions were combined, and the solvent was evaporated, leaving a solid which was washed with diethyl ether. After filtration, the desired complex was obtained as a solid.

$[\text{Ir}(\text{bnpy})(\text{dtBubpy})\text{Cl}]$ (1). The general one-pot protocol using 0.114 g (0.38 mmol) of $\text{IrCl}_3 \cdot 6\text{H}_2\text{O}$ was followed, and 1 was obtained as a red solid (0.127 g, 0.013 mmol). Yield: 45%. Mp: 320 °C (decomp.). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.75 (d, $J = 5.8$ Hz, 2H), 8.42 (d, $J = 1.7$ Hz, 2H), 7.70 (dd, $J = 7.3, 1.4$ Hz, 2H), 7.53 (d, $J = 7.5$ Hz, 1H), 7.49 (dd, $J = 5.9, 1.9$ Hz, 3H), 7.24 (dd, $J = 7.1, 1.6$ Hz, 2H), 7.19 (d, $J = 5.9$ Hz, 1H), 6.90 (dtd, $J = 26.4, 7.3, 1.5$ Hz, 4H), 6.45–6.39 (m, 1H), 5.28 (s, 1H), 1.50 (s, 18H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 165.4, 162.6, 157.4, 151.8, 151.3, 143.9, 141.4, 138.7, 137.0, 125.8, 124.0, 123.8, 123.4, 122.7, 122.1, 120.8, 69.7, 35.9, 30.8. HR-MS (ASAP⁺) $[\text{M} - \text{Cl}]^+$ Calculated ($\text{C}_{36}\text{H}_{37}\text{IrN}_3$): 704.2618. Found: 704.2618. CHN Calcd for $\text{C}_{36}\text{H}_{37}\text{ClIrN}_3 \cdot 3/2 \text{H}_2\text{O}$: C, 56.42; H, 5.26; N, 5.48. Found: C, 56.45; H, 5.24; N, 5.28.

$[\text{Ir}(\text{dtBubnpy})(\text{dtBubpy})\text{Cl}]$ (2). The general one-pot protocol using 0.088 g (0.30 mmol) of $\text{IrCl}_3 \cdot 6\text{H}_2\text{O}$ was followed, and 2 was obtained as a red solid (0.129 g, 0.15 mmol). Yield: 51%. Mp: 331 °C (decomp.). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.79 (d, $J = 5.9$ Hz, 2H), 8.42 (d, $J = 2.0$ Hz, 2H), 7.80 (d, $J = 2.1$ Hz, 2H), 7.49–7.42 (m, 4H), 7.13 (d, $J = 7.7$ Hz, 3H), 6.89 (dd, $J = 7.7, 2.1$ Hz, 2H), 6.38 (ddd, $J = 7.0, 5.9, 2.0$ Hz, 1H), 5.22 (s, 1H), 1.51 (s, 18H), 1.32 (s, 18H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 166.0, 162.6, 157.5, 151.7, 151.3, 147.8, 141.1, 140.4, 136.8, 135.9, 123.6, 122.7, 122.4, 120.8, 118.8, 68.6, 35.9, 34.9, 32.1, 30.9. $[\text{M} - \text{Cl}]^+$ Calculated ($\text{C}_{44}\text{H}_{53}\text{IrN}_3$): 816.3869. Found: 816.3867. CHN Calcd for $\text{C}_{44}\text{H}_{53}\text{ClIrN}_3$: C, 62.06; H, 6.27; N, 4.93. Found: C, 61.96; H, 6.31; N, 5.02.

$[\text{Ir}(\text{dtfmbnpy})(\text{dtBubpy})\text{Cl}]$ (3). The general one-pot protocol using 0.060 g (0.20 mmol) of $\text{IrCl}_3 \cdot 6\text{H}_2\text{O}$ was followed, and 3 was obtained

as a yellow solid (0.096 g, 0.11 mmol). Yield: 55%. Mp: 324 °C (decomp.). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.59 (d, $J = 5.8$ Hz, 2H), 8.44 (d, $J = 2.0$ Hz, 2H), 7.98 (d, $J = 2.0$ Hz, 2H), 7.62–7.48 (m, 4H), 7.37 (d, $J = 7.7$ Hz, 2H), 7.20–7.15 (m, 3H), 6.50 (ddd, $J = 7.5, 5.9, 1.7$ Hz, 1H), 5.46 (s, 1H), 1.51 (s, 18H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 163.5, 163.3, 157.3, 151.9, 151.1, 147.4, 142.2, 137.6, 134.7, 127.6, 126.7, 124.5, 124.3, 123.5, 123.4, 121.2, 119.4, 69.2, 36.0, 30.8. ^{19}F NMR (376 MHz, CD_2Cl_2): δ -61.58. $[\text{M} - \text{Cl}]^+$ Calculated ($\text{C}_{38}\text{H}_{35}\text{F}_6\text{IrN}_3$): 840.2364. Found: 840.2379. CHN Calcd for $\text{C}_{38}\text{H}_{35}\text{F}_6\text{IrN}_3$: C, 52.14; H, 4.03; N, 4.80. Found: C, 52.10; H, 4.16; N, 4.74.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00328. The research data supporting this work can be accessed at: <http://dx.doi.org/10.17630/f6e8e203-82a9-406b-977e-308da1021de1>.

NMR and MS spectra for all precursors, C^NA^C ligands and complexes, supplementary crystallographic data, supplementary electrochemical and photophysical data, description of the DFT/TD-DFT protocol, and supplementary DFT and TD-DFT computational results (PDF)

X-ray crystallographic structures of 1–3, CCDC: 1519101–1519103 (CIF)

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Notes

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