

An Unprecedented Family of Luminescent Iridium(III) Complexes Bearing a Six-Membered Chelated Tridentate C^NAC Ligand

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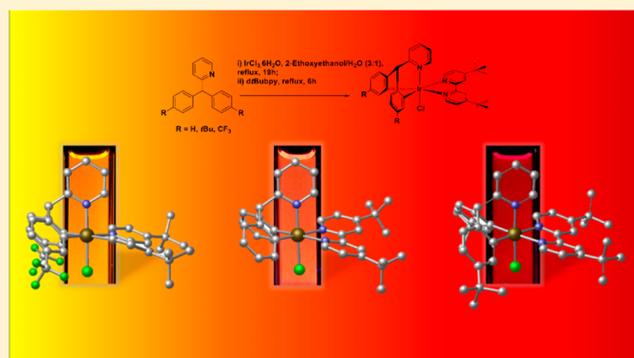
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Supporting Information

ABSTRACT: A new family consisting of three luminescent neutral Ir(III) complexes with the unprecedented [Ir(C^NAC)-(N^NN)Cl] architecture, where C^NAC is a bis(six-membered) chelating tridentate tripod ligand derived from 2-benzhydrylpyridine (bnpy) and N^NN is 4,4'-ditert-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 of 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(dfz-pz)₂(fptz)] (where (dfz-pz)H = 2,4-difluorobenzyl-N-pyrazole and fptz = 3-trifluoromethyl-5-(2-pyridyl) triazole) containing a nonconjugated N-benzylpyrazole ligand that forms a six-membered chelated framework. This complex is a blue emitter in dichloromethane with $\lambda_{em} = 437$ and 460 nm ($\Phi_{PL} = 10\%$ and $\tau_e = 0.10 \mu s$). The methylene spacer of the cyclometalated ligand effectively interrupts the conjugation to produce a significant blue shift, compared to [Ir(dFppy)₂(fptz)] (where (dFppy)H = 2-(2,4-difluorophenyl)pyridine and fptz = 3-trifluoromethyl-5-(2-pyridyl) triazole), which uses a five-membered ring chelate

C^N ligand and the same ancillary ligand ($\lambda_{em} = 460$ 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'}]picolate)] ([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 $\lambda_{em} = 538$ nm ($\Phi_{PL} = 5\%$).

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 70

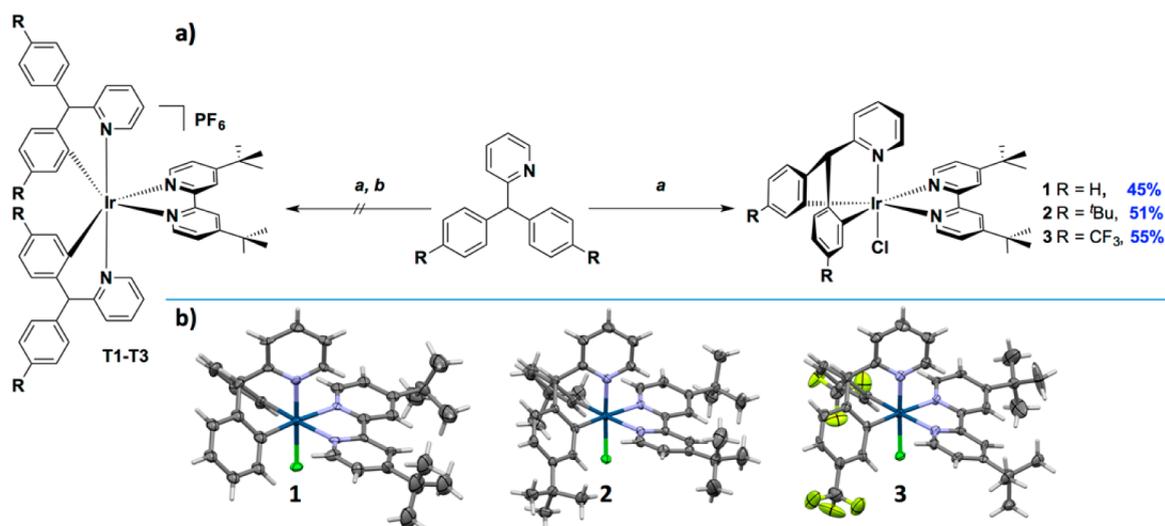


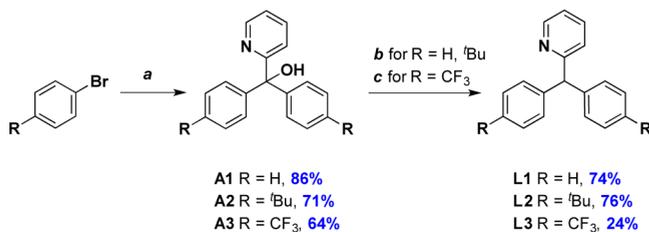
Figure 1. (a) Scheme for the proposed synthesis of the initial targets (T1–T3) and the synthesis of complexes 1–3. (a, i) IrCl₃·6H₂O, 2-ethoxyethanol/H₂O (3:1), reflux, 19 h; (ii) dtBubpy, reflux, 6 h. (b) aq. NH₄PF₆. (b) Solid-state structures of 1–3. Thermal ellipsoids correspond to a 50% probability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

71 either electron-donating *tert*-butyl or electron-withdrawing
 72 trifluoromethyl groups *meta* to the Ir–C bonds, were obtained.
 73 To the best of our knowledge, this is the first report of an
 74 iridium complex of the form [Ir(C[^]N[^]C)(N[^]N)Cl] and one in
 75 which the tridentate bis-cyclometalated ligand is a tripod
 76 featuring two six-membered metallacycles.²⁸ Indeed, the
 77 complex with the closest binding motif is [Ir(bppy)(N[^]N)Cl],²⁹
 78 where bppy is 2-([1,1'-biphenyl]-3-yl)pyridine. This previous
 79 complex possesses a related [Ir(C[^]A[^]N)(N[^]N)Cl] structure,
 80 but the bppy ligand coordinates to the iridium in the more
 81 commonly observed planar five-membered chelate fashion. It is
 82 a very poorly luminescent near-IR emitter in CH₂Cl₂ (λ_{em} =
 83 725 nm, Φ_{PL} = $8.4 \times 10^{-2\%}$). Ir(III) complexes bearing
 84 monocyclometalating planar tridentate bis(five-membered)
 85 chelate ligands (e.g., N[^]N[^]C[^]²⁹ or N[^]C[^]N[^]^{30–35}) and a
 86 cyclometalating bidentate ligand, C[^]N, have on the other
 87 hand been more widely explored, while Kozhevnikov has
 88 reported dinuclear Ir(III) complexes with a bridging ligand
 89 featuring two N[^]C[^]N motifs.^{36,37}

90 ■ RESULTS AND DISCUSSION

91 **Synthesis.** Compounds L1, L2, and L3 (Scheme 1) were
 92 synthesized in two steps via a Grignard reaction³⁸ followed by a
 93 reduction step³⁸ and obtained as solids in good yields. A

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.

mixture of the corresponding proligand and IrCl₃·6H₂O in 2-ethoxyethanol/H₂O (3:1) was refluxed. After 19 h, the ancillary ligand 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 2.360(2) Å for 3] is in the same range as that found for [Ir(tpy)(bpy)Cl]²⁺ (2.357 Å, where tpy = 2,2':6',2''-terpyridine and dmbpy = 4,4'-dimethyl-2,2'-bipyridine)⁴⁰ 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_{C[^]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) Å 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)°

133 for **2**, and 84.(3) for **3**) than the $N_{dtBubpy}-Ir-N_{dtBubpy}$ bond
134 angle.

135 **Electrochemical Properties.** The electrochemical behav-
136 ior for **1–3** was evaluated by cyclic voltammetry (CV) and
137 differential pulse voltammetry (DPV) in deaerated CH_2Cl_2
138 solution at 298 K at a scan rate of 50 mV s^{-1} using Fc/Fc^+
139 as the internal reference and referenced with respect to SCE.⁴⁸
140 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]	$\Phi_{PL}^{a,b}$ [%]	τ_e^c [ns]	$k_r^d \times 10^{-5}$ [s ⁻¹]	$k_{nr}^e \times 10^{-5}$ [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 $\lambda_{exc} = 420\text{ nm}$, recorded at 298 K in deaerated CH_2Cl_2 solution.
^b $[Ru(bpy)_3]PF_6$ in MeCN as reference ($\Phi_{PL} = 1.8\%$ in aerated MeCN
at 298 K).³¹ ^c $\lambda_{exc} = 378\text{ nm}$. ^d $k_r = \Phi_{PL}/\tau_e$. ^e $k_{nr} = [(1 - \Phi_{PL})/\tau_e]$.
^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 ($Fc/Fc^+ = 0.46\text{ V}$ in CH_2Cl_2).⁴⁸

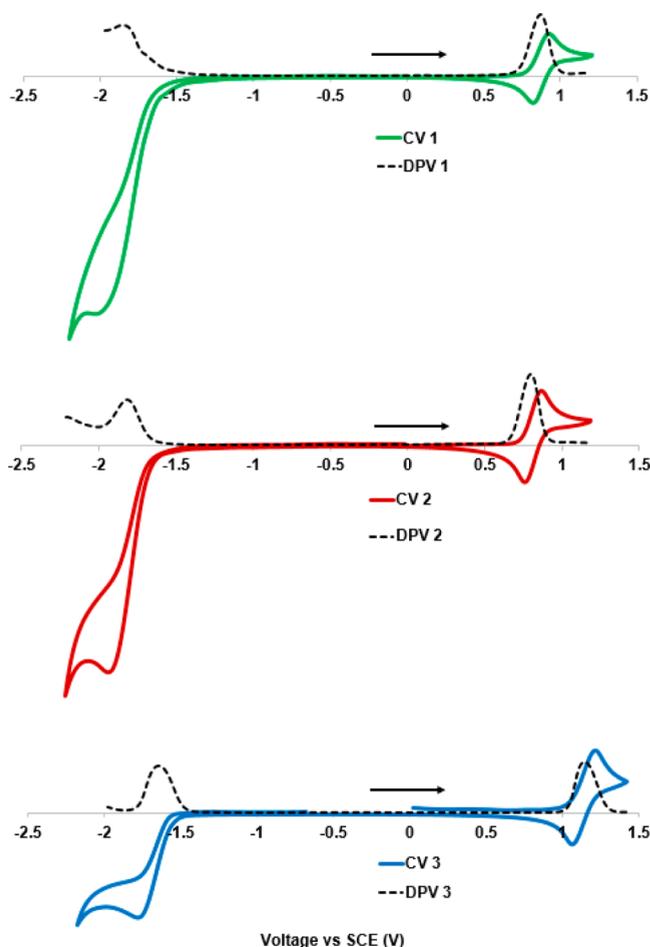


Figure 2. Cyclic voltammograms (in solid lines) and differential pulse voltammetry (in dotted lines) carried out in degassed CH_2Cl_2 at a scan rate of 50 mV s^{-1} , with Fc/Fc^+ as the internal reference, referenced to SCE (0.46 V vs SCE).⁴⁸

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
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 $[Ir(mesppy)_2(dtBubpy)]PF_6$ ($E_{1/2,ox.} = 1.17$
V in deaerated CH_2Cl_2 , where mesppy is 2-phenyl-4-mesityl-
pyridinato).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)

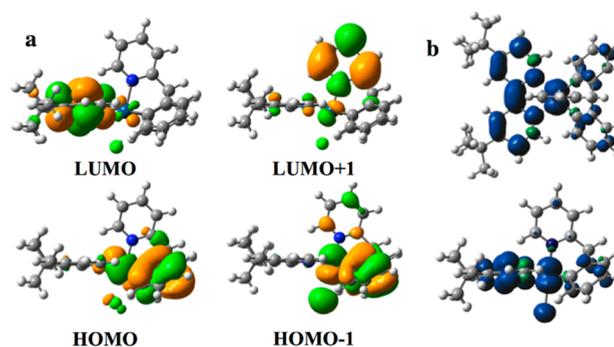


Figure 3. (a) Representation of the four frontier MOs of **1**. (b) Side and top views of the spin density distribution for the lowest triplet state (T_1) of **1**.

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 $[Ir(mesppy)_2(dtBubpy)]PF_6$ ($E_{1/2,red.} = -1.15\text{ V}$), 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 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
($^1MLCT/^1LLCT$) character while the latter, according to TD-DFT calculations,
implicate an intraligand CT (1ILCT) 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 $^1MLCT/^1LLCT$ and spin-forbidden
 $^3MLCT/^3LLCT$ transitions involving the dtBubpy ligand. Introduction of the
tert-butyl groups in **2** results in only a small red-shift of the CT bands below 340 nm,
whereas the trifluoromethyl groups in **3** produce a significant blue-shift of

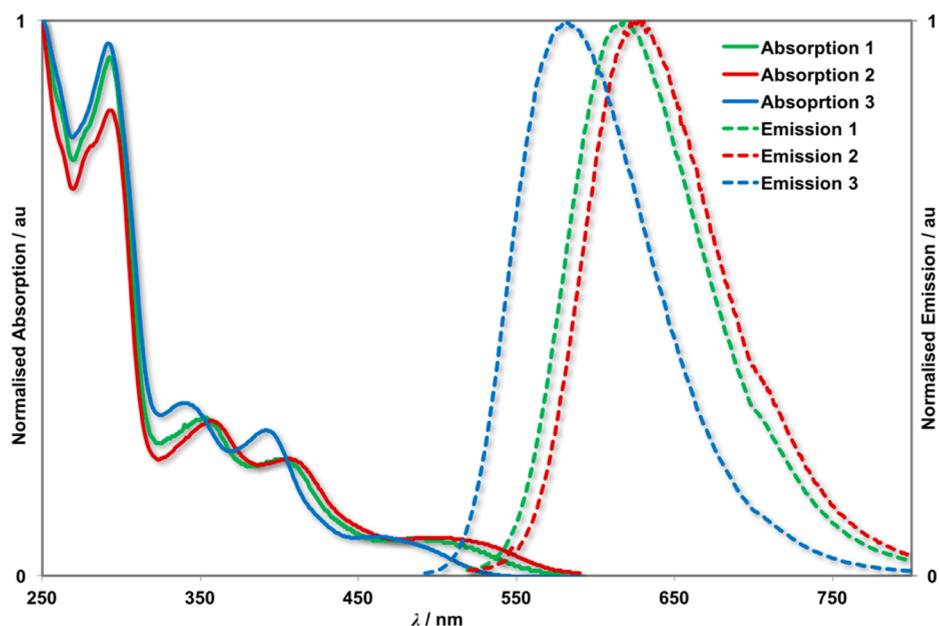


Figure 4. Normalized UV-vis absorption and photoluminescence spectra of 1–3 in CH_2Cl_2 at 298 K.

186 these bands, trends that are corroborated by TD-DFT
187 calculations (Figure S35 in the SI).

188 The normalized photoluminescence (PL) spectra of 1–3 in
189 degassed CH_2Cl_2 are shown in Figure 4, and the data are
190 summarized in Table 1. Upon photoexcitation at 420 nm, all
191 complexes show a broad and unstructured profile, indicative of
192 an emission with mixed CT character. In line with the trends
193 observed in the absorption spectra and the oxidation potentials
194 in the CVs, the emission maxima are 581, 619, and 630 nm for
195 3, 1, and 2, respectively. These emission maxima match very
196 closely to the vertical phosphorescence energies calculated by
197 spin-unrestricted DFT, which predicts emissions at 573, 613,
198 and 622 nm, respectively. The calculations reveal that the
199 emissive triplet state is localized on the iridium, chlorine, and
200 dtBubby but does not include significant contributions from the
201 bnpy ligand (Figures 3b and S36 in the SI). The photo-
202 luminescence quantum yield (Φ_{PL}) of 1 is 8%, which is lower
203 than that of the yellow-emitting $[\text{Ir}(\text{ppy})_2(\text{dtBubby})]\text{PF}_6$ (Φ_{PL}
204 = 64% in CH_2Cl_2 , $\lambda_{\text{em}} = 570$ nm, where ppyH is 2-
205 phenylpyridine).⁵⁰ The Φ_{PL} of 2 is 6% while that of 3 is
206 26%. All three complexes show emission lifetimes, τ_{e} , in the
207 submicrosecond regime. The radiative rate constants, k_{r} , for 1
208 and 2 are similar (2.52 vs $2.51 \times 10^5 \text{ s}^{-1}$, respectively).
209 However, 2 exhibits a significantly larger nonradiative rate
210 constant, k_{nr} ($39.33 \times 10^5 \text{ s}^{-1}$), compared to 1 (28.93×10^5
211 s^{-1}). Complex 3 possesses both the largest k_{r} ($3.62 \times 10^5 \text{ s}^{-1}$)
212 and the smallest k_{nr} values ($10.31 \times 10^5 \text{ s}^{-1}$) in accordance with
213 the energy gap law.

214 CONCLUSIONS

215 In conclusion, a new family of luminescent iridium(III)
216 complexes bearing an unprecedented tripodal bis(six-mem-
217 bered) chelate tridentate ligand has been prepared through a
218 highly unusual double cyclometalation reaction. The emission
219 can be tuned through substitution on the cyclometalating aryl
220 rings. DFT calculations support a mixed charge-transfer
221 emission. Current efforts are focused on further modulating
222 the electronics through a combination of modifications of the
223 ancillary di-imine and the monodentate chloride ligands. This

unprecedented tripodal ligand will open new perspectives for
224 the design of tridentate Ir luminophores. 225

226 EXPERIMENTAL SECTION

General Procedure for Compound A1–A3. An oven-dried flask
227 was charged under a nitrogen atmosphere with magnesium turnings
228 (0.911 g, 37.50 mmol, 5 equiv) and THF (80 mL) followed by 2 mL
229 of 1,2-dibromoethane. After the observation of gas evolution, the
230 corresponding bromo derivative (22.50 mmol, 3 equiv) in THF (40
231 mL) was added dropwise. The reaction mixture was heated under
232 stirring and kept at reflux for 4 h, resulting in a color change of the
233 solution to gray. The reaction mixture was then cooled in an ice bath,
234 and a solution of methyl picolinate (7.50 mmol, 1.00 equiv) in THF
235 (40 mL) was added carefully. The mixture turned dark gray–black.
236 The solution was allowed to warm to room temperature and was
237 stirred for 90 min. The reaction mixture was quenched with aqueous
238 NH_4Cl and extracted with Et_2O . The combined organic layers were
239 dried over MgSO_4 , and the solvent was evaporated, leaving a residue,
240 which was purified over silica (10% EtOAc in petroleum ether as the
241 solvent). The desired fractions were combined, and the solvent was
242 evaporated, leaving the title compound. 243

Diphenyl(pyridin-2-yl)methanol A1. Compound A1 was prepared
244 according to the general procedure and was obtained as a colorless
245 solid (1.686 g, 6.45 mmol). Yield: 86%. R_{f} : 0.51 (10% EtOAc in
246 petroleum ether on silica). Mp: 103 °C. Litt.⁵²: 102–103 °C. ^1H NMR
247 (400 MHz, CDCl_3): δ 8.60 (d, $J = 4.7$ Hz, 1H), 7.64 (td, $J = 7.8, 1.8$
248 Hz, 1H), 7.40–7.21 (m, 11H), 7.12 (d, $J = 7.9$ Hz, 1H), 6.28 (s, 1H).
249 ^{13}C NMR (101 MHz, CDCl_3): δ 163.2, 147.7, 146.1, 136.4, 128.1,
250 127.9, 127.3, 122.9, 122.3, 80.8. HR-MS (FTMS⁺) [$\text{M} + \text{H}$]⁺
251 Calculated ($\text{C}_{18}\text{H}_{15}\text{NOH}$): 262.1226. Found: 262.1226. CHN Calcd
252 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;
253 N, 5.41. The compound characterization is in agreement with that
254 previously reported.⁵³ 255

Bis(4-(tert-butyl)phenyl)(pyridin-2-yl)methanol A2. Compound
256 A2 was prepared according to the general procedure and was obtained
257 as a colorless solid (1.994 g, 5.34 mmol). Yield: 71%. R_{f} : 0.39 (10%
258 EtOAc in petroleum ether on silica). Mp: 156 °C. Litt.⁵⁴: 156 °C. ^1H
259 NMR (400 MHz, CDCl_3): δ 8.58 (d, $J = 3.2$ Hz, 1H), 7.67–7.60 (m,
260 1H), 7.33–7.28 (m, 4H), 7.24–7.12 (m, 6H), 6.19 (s, 1H), 1.30 (s,
261 18H). ^{13}C NMR (101 MHz, CDCl_3): δ 163.8, 150.1, 147.7, 143.3,
262 136.4, 127.9, 124.9, 123.1, 122.3, 80.6, 34.6, 31.5. HR-MS (FTMS⁺)
263 [$\text{M} + \text{H}$]⁺ Calculated ($\text{C}_{26}\text{H}_{31}\text{NOH}$): 374.2478. Found: 374.2476.
264 CHN Calcd for $\text{C}_{26}\text{H}_{31}\text{NO}$: C, 83.60; H, 8.37; N, 3.75. Found: C, 265

266 83.45; H, 8.51; N, 3.88. The compound characterization is in
267 agreement with that previously reported.⁵⁴

268 **Pyridin-2-ylbis(4-(trifluoromethyl)phenyl)methanol A3.** Com-
269 pound **A3** was prepared according to the general procedure and was
270 obtained as a beige solid (1.893 g, 4.76 mmol). Yield: 64%. R_f: 0.26
271 (10% EtOAc in petroleum ether on silica). Mp: 164 °C. ¹H NMR
272 (400 MHz, CDCl₃): δ 8.64 (d, J = 7.4 Hz, 1H), 7.75–7.69 (m, 1H),
273 7.60 (s, 4H), 7.44 (s, 4H), 7.31 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 9.7
274 Hz, 1H), 6.50 (s, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 161.5, 149.4,
275 148.2, 136.9, 130.4, 130.1, 129.7, 129.4, 128.5, 125.2, 125.1, 125.1,
276 125.1, 123.1, 122.7, 80.4, 77.4, 77.1, 76.7. ¹⁹F NMR (376 MHz,
277 CDCl₃): δ –62.59. HR-MS (FTMS⁺) [M + H]⁺ Calculated
278 (C₂₀H₁₃F₆NOH): 398.0974. Found: 398.0965. CHN Calcd for
279 C₂₀H₁₃F₆NO: C, 60.46; H, 3.30; N, 3.53. Found: C, 60.51; H, 3.36;
280 N, 3.59.

281 **2-Benzhydrylpyridine L1.** A mixture of **A1** (0.837 g, 3.21 mmol),
282 aqueous 57% HI (2.5 mL), and HOAc (13 mL) was heated to 100 °C
283 for 4 h. The resulting mixture was then cooled to 0 °C and basified to
284 pH 9 with an aqueous NaOH solution (2 M). Ethyl acetate (100 mL)
285 was added, and the mixture was washed successively with an aqueous
286 NaHSO₃ solution and brine. The combined organic layers were dried
287 over MgSO₄, and the solvent was evaporated. The residue was purified
288 over silica (10% EtOAc in petroleum ether as the solvent). The
289 desired fractions were combined and the solvent evaporated leaving a
290 beige solid (0.788 g, 3.21 mmol). Yield: 74%. R_f: 0.3 (10% EtOAc in
291 petroleum ether on silica). Mp: 95 °C. ¹H NMR (400 MHz, CDCl₃):
292 δ 8.64 (d, J = 4.1 Hz, 1H), 7.66–7.59 (m, 1H), 7.33 (t, J = 7.3 Hz,
293 4H), 7.24 (dd, J = 21.8, 7.2 Hz, 6H), 7.18–7.10 (m, 2H), 5.76 (s, 1H).
294 ¹³C NMR (101 MHz, CDCl₃): δ 163.2, 149.5, 142.7, 136.4, 129.4,
295 128.4, 126.5, 123.8, 121.4, 59.4. HR-MS (FTMS⁺) [M + H]⁺
296 Calculated (C₁₈H₁₅NH): 246.1277. Found: 246.1277. The compound
297 characterization is in agreement with that previously reported.⁵⁵

298 **2-(Bis(4-(tert-butyl)phenyl)methyl)pyridine L2.** A mixture of the
299 **A2** (0.900 g, 2.41 mmol), aqueous 57% HI (2.70 mL), and HOAc
300 (13.20 mL) was heated to 100 °C for 4 h. The resulting mixture was
301 then cooled to 0 °C and basified to pH 9 with an aqueous NaOH
302 solution (2 M). Ethyl acetate (100 mL) was added, and the mixture
303 was washed successively with an aqueous NaHSO₃ solution and brine.
304 The combined organic layers were dried over MgSO₄, and the solvent
305 was evaporated. The residue was purified over silica (10% EtOAc in
306 petroleum ether as the solvent). The desired fractions were combined
307 and the solvent evaporated, yielding the title compound as oil (0.655 g,
308 1.83 mmol). Yield: 76%. R_f: 0.33 (10% EtOAc in petroleum ether on
309 silica). ¹H NMR (400 MHz, CDCl₃): δ 8.62–8.56 (m, 1H), 7.62–7.56
310 (m, 1H), 7.31 (s, 4H), 7.10 (s, 6H), 5.62 (s, 1H), 1.29 (s, 18H). ¹³C
311 NMR (126 MHz, CDCl₃): δ 163.8, 149.6, 149.2, 139.9, 136.5, 129.0,
312 125.4, 123.9, 121.4, 58.7, 34.5, 31.5. HR-MS (ASAP⁺) [M + H]⁺
313 Calculated (C₂₆H₃₁NH): 358.2535. Found: 358.2534.

314 **2-(Bis(4-(trifluoromethyl)phenyl)methyl)pyridine L3.** A mixture of
315 **A3** (0.500 g, 1.26 mmol, 1 equiv) and PBr₃ (25 mL) was vigorously
316 stirred and heated and kept at 110 °C for 2 h. The mixture was then
317 cooled to r.t. and was carefully poured onto ice, and aqueous NaOH (2
318 M) was added until the pH was neutral. The organic layer was dried
319 over MgSO₄, and the solvent was evaporated, leaving a residue which
320 was dissolved in acetic acid (50 mL). Then, zinc dust (0.799 g, 12.60
321 mmol, 10 equiv) was added. The mixture was stirred at r.t. After 1 h,
322 20 mL of water was carefully added, and aqueous NaOH (2 M) was
323 added until the pH was neutral. The organic layer was dried over
324 MgSO₄, and the solvent was evaporated, leaving a residue which was
325 purified over silica (10% EtOAc in petroleum ether as the solvent).
326 The desired fractions were combined, and the solvent was evaporated,
327 leaving colorless oil (0.117 mg, 0.31 mmol). Yield: 24%. R_f: 0.55 (20%
328 EtOAc in petroleum ether on silica). ¹H NMR (400 MHz, CDCl₃): δ
329 8.63 (ddd, J = 4.9, 1.9, 0.9 Hz, 1H), 7.66 (td, J = 7.7, 1.9 Hz, 1H), 7.57
330 (d, J = 8.2 Hz, 4H), 7.30 (d, J = 8.1 Hz, 4H), 7.20 (ddd, J = 7.6, 4.8,
331 1.1 Hz, 1H), 7.10 (dt, J = 7.9, 1.1 Hz, 1H), 5.75 (s, 1H). ¹³C NMR
332 (126 MHz, CDCl₃): δ 161.4, 150.1, 146.0, 137.0, 129.8, 129.3, 125.7,
333 125.3, 124.0, 122.2, 58.9. ¹⁹F NMR (376 MHz, CDCl₃): δ –62.50.
334 HR-MS (FTMS⁺) [M + H]⁺ Calculated (C₂₀H₁₃F₆NH): 382.1030.
335 Found: 382.1023.

General Procedure for the One-Pot Protocol. A mixture of the 336
corresponding ligand (1.2 equiv) and IrCl₃·6H₂O (1 equiv) in 2- 337
ethoxyethanol (15 mL) and H₂O (5 mL) was heated under stirring to 338
125 °C. After 19 h, 4,4'-di-*tert*-butyl-2,2'-bipyridine (1.5 equiv) was 339
added, and heating was continued. After 6 h, the solvent was 340
evaporated, leaving a solid, which was filtered over silica (1% MeOH in 341
CH₂Cl₂). The desired fractions were combined, and the solvent was 342
evaporated, leaving a solid which was washed with diethyl ether. After 343
filtration, the desired complex was obtained as a solid. 344

[Ir(bnpy)(dtBubpy)Cl] (1). The general one-pot protocol using 345
0.114 g (0.38 mmol) of IrCl₃·6H₂O was followed, and **1** was obtained 346
as a red solid (0.127 g, 0.13 mmol). Yield: 45%. Mp: 320 °C 347
(decomp.). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.75 (d, J = 5.8 Hz, 2H), 348
8.42 (d, J = 1.7 Hz, 2H), 7.70 (dd, J = 7.3, 1.4 Hz, 2H), 7.53 (d, J = 7.5 349
Hz, 1H), 7.49 (dd, J = 5.9, 1.9 Hz, 3H), 7.24 (dd, J = 7.1, 1.6 Hz, 2H), 350
7.19 (d, J = 5.9 Hz, 1H), 6.90 (dtd, J = 26.4, 7.3, 1.5 Hz, 4H), 6.45– 351
6.39 (m, 1H), 5.28 (s, 1H), 1.50 (s, 18H). ¹³C NMR (126 MHz, 352
CD₂Cl₂): δ 165.4, 162.6, 157.4, 151.8, 151.3, 143.9, 141.4, 138.7, 353
137.0, 125.8, 124.0, 123.8, 123.4, 122.7, 122.1, 120.8, 69.7, 35.9, 30.8. 354
HR-MS (ASAP⁺) [M–Cl]⁺ Calculated (C₃₆H₃₇IrN₃): 704.2618. 355
Found: 704.2618. CHN Calcd for C₃₆H₃₇ClIrN₃·3/2 H₂O: C, 56.42; 356
H, 5.26; N, 5.48. Found: C, 56.45; H, 5.24; N, 5.28. 357

[Ir(dtBubnpy)(dtBubpy)Cl] (2). The general one-pot protocol using 358
0.088 g (0.30 mmol) of IrCl₃·6H₂O was followed, and **2** was obtained 359
as a red solid (0.129 g, 0.15 mmol). Yield: 51%. Mp: 331 °C 360
(decomp.). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.79 (d, J = 5.9 Hz, 2H), 361
8.42 (d, J = 2.0 Hz, 2H), 7.80 (d, J = 2.1 Hz, 2H), 7.49–7.42 (m, 4H), 362
7.13 (d, J = 7.7 Hz, 3H), 6.89 (dd, J = 7.7, 2.1 Hz, 2H), 6.38 (ddd, J = 363
7.0, 5.9, 2.0 Hz, 1H), 5.22 (s, 1H), 1.51 (s, 18H), 1.32 (s, 18H). ¹³C 364
NMR (126 MHz, CD₂Cl₂): δ 166.0, 162.6, 157.5, 151.7, 151.3, 147.8, 365
141.1, 140.4, 136.8, 135.9, 123.7, 123.6, 122.7, 122.4, 120.8, 118.8, 366
68.6, 35.9, 34.9, 32.1, 30.9. [M–Cl]⁺ Calculated (C₄₄H₅₃IrN₃) 367
816.3869. Found: 816.3867. CHN Calcd for C₄₄H₅₃ClIrN₃: C, 368
62.06; H, 6.27; N, 4.93. Found: C, 61.96; H, 6.31; N, 5.02. 369

[Ir(dtmbnpy)(dtBubpy)Cl] (3). The general one-pot protocol using 370
0.060 g (0.20 mmol) of IrCl₃·6H₂O was followed, and **3** was obtained 371
as a yellow solid (0.096 g, 0.11 mmol). Yield: 55%. Mp: 324 °C 372
(decomp.). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.59 (d, J = 5.8 Hz, 2H), 373
8.44 (d, J = 2.0 Hz, 2H), 7.98 (d, J = 2.0 Hz, 2H), 7.62–7.48 (m, 4H), 374
7.37 (d, J = 7.7 Hz, 2H), 7.20–7.15 (m, 3H), 6.50 (ddd, J = 7.5, 5.9, 375
1.7 Hz, 1H), 5.46 (s, 1H), 1.51 (s, 18H). ¹³C NMR (126 MHz, 376
CD₂Cl₂): δ 163.5, 163.3, 157.3, 151.9, 151.1, 147.4, 142.2, 137.6, 377
134.7, 127.6, 126.7, 124.5, 124.3, 123.5, 123.4, 121.2, 119.4, 69.2, 36.0, 378
30.8. ¹⁹F NMR (376 MHz, CD₂Cl₂): δ –61.58. [M–Cl]⁺ Calculated 379
(C₃₈H₃₅F₆IrN₃): 840.2364. Found: 840.2379. CHN Calcd for 380
C₃₈H₃₅F₆IrN₃: C, 52.14; H, 4.03; N, 4.80. Found: C, 52.10; H, 4.16; 381
N, 4.74. 382

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the 385
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NMR and MS spectra for all precursors, C¹³N¹⁵C ligands 388
and complexes, supplementary crystallographic data, 389
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