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Highly Efficient Red-Emitting Bis-Cyclometalated Iridium Complexes

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Supporting Information

ABSTRACT: Bis-cyclometalated iridium complexes with enhanced phosphorescence quantum yields in the red region of the visible spectrum are described. Here, we demonstrate that incorporating strongly π -donating, nitrogen-containing β -ketoiminate (acNac), β diketiminate (NacNac), and N,N'-diisopropylbenzamidinate (dipba) ancillary ligands can demonstrably perturb the excited-state kinetics, leading to enhanced photoluminescence quantum yields (Φ_{PL}) for redemitting compounds. A comprehensive study of the quantum yields and lifetimes for these complexes reveals that for the compounds with the highest quantum yields, the radiative rate constant (k_r) is significantly higher than that of related complexes, and contributes substantially to



the increase in $\Phi_{\rm PI}$. Experimental and computational evidence is consistent with the notion that an increase in spin-orbit coupling, caused by an enhancement of the metal-to-ligand charge transfer (MLCT) character of the excited state via destabilization of the HOMO, is mainly responsible for the faster radiative rates. One of the compounds was shown to be effective as the emissive dopant in an organic light-emitting diode device.

INTRODUCTION

Organometallic compounds of 4d and 5d metals, which emit from triplet excited states with mixed ligand-centered (³LC or ${}^{3}\pi\pi^{*}$) and metal-to-ligand charge transfer (${}^{3}MLCT$ or ${}^{3}d\pi^{*}$) character, have become the leading class of emitters for a number of optoelectronic applications, most prominently organic light-emitting diode (OLED) displays.¹⁻⁸ The strong spin-orbit coupling brought on by the heavy transition metal increases the rates of formally spin-forbidden processes, namely, intersystem crossing, to populate the triplet state, and radiative decay, which generates emitted light. Both of these effects contribute to the high phosphorescence quantum efficiencies observed in many organometallic complexes of 4d and 5d metals and make them ideal emitters for OLEDs and other applications. Several classes of phosphorescent complexes have been tested in OLEDs, with octahedral cyclometalated iridium(III) complexes emerging as the most prominent.1,6-

Facile color tunability is a key feature of cyclometalated iridium complexes, and there are several examples that emit in the blue to yellow region of the spectrum with near unity quantum yields.^{7,9-13} However, related complexes that emit in the lower-energy regions of the visible spectrum (orange to red) often exhibit phosphorescence quantum yields that are significantly smaller. It is still possible to fabricate red iridiumbased OLEDs with sufficient performance for device applications,¹⁴⁻²¹ with the best-performing red emitters exhibiting photoluminescence quantum yields ≈ 0.5 .^{15,22,23} In reality, it is the lack of high-performing and stable iridiumbased blue OLEDs that is the biggest technological challenge for OLED display technologies.^{24,25} Nevertheless, there is certainly room for fundamental advances in the design of organometallic complexes that phosphoresce efficiently in the lower-energy regions of the visible spectrum, and phosphors with deep red and near-IR emission are important for applications outside of OLED displays, namely, night-vision technology, medical imaging, and biological probes and sensors.

There are a few reasons for the typically lower quantum yields in red-emitting phosphors. According to the energy gap law,^{26–29} the rate of nonradiative decay (k_{nr}) is inversely related to the energy difference between the ground and excited states. In addition, the radiative rate (k_r) has a cubic dependence on the transition energy and thus is expected to be smaller for lower-energy emitters.² Finally, k_r depends on the spin-orbit interactions of the triplet states with higher-lying singlets, which increases the allowedness of the spin-forbidden radiative transition by relaxing spin-selection rules. This spinorbit coupling is only significant for ^{1,3}MLCT states, but it can indirectly influence lower-lying ³LC states via configuration interaction between LC and MLCT states.^{1,3} The excited states of low-energy emitters with highly conjugated cyclometalating (C^N) ligands are often primarily ligand-centered.

Received: May 8, 2018 Published: July 21, 2018 There is a larger energy separation between the LC and MLCT states, which results in weaker configuration interaction between the two states, diminishing the spin-orbit coupling term in the emissive state and contributing to a smaller k_r . Thus, in order to have large spin-orbit coupling in the emissive T₁ state, there must be significant MLCT character.

The relationship between MLCT character, spin-orbit coupling, and k_r has long been recognized and has been demonstrated in several archetypal cyclometalated iridium complexes by direct measurement of zero-field splitting $(ZFS)^{30,31}$ or by measuring radiative rate constants (k_r) for a series of compounds with systematically varied MLCT character.³² Indirect evidence for enhanced MLCT character can come from rigidochromic shifts in low-temperature emission spectra,³³ solvatochromism, or from analysis of vibronic structure, which is less pronounced for MLCT emission. However, this dependence of k_r on spin-orbit coupling has not been intentionally exploited in the design of red and near-infrared emitters with faster radiative rates. In this work, we demonstrate the ability to increase k_r and the photoluminescence quantum yield (Φ_{PL}) by using systematic changes to ancillary ligands in heteroleptic complexes, engineering more MLCT character into the emissive excitedstate. There are several well-known studies on the effects of ancillary ligands on cyclometalated iridium emission, including chromophoric diimine ancillary ligands that can be used to tune emission color over a wide range^{8,34} and other accounts describing spectroscopically inert ancillary ligands and their effects on mostly blue or green-emitting complexes.^{7,11,12,32,35} Here, we show that by increasing the π -donating character of the ancillary ligand, red-emitting complexes with faster radiative rates and augmented quantum yields can be designed. Motivation for this approach comes from work from our group, where we demonstrated that β -ketoiminate (acNac) and β -diketiminate (NacNac) ancillary ligands, isoelectronic with the widely used β -diketonate $(acac)^{6,36}$ ancillary ligands, can have profound impacts on the electronic structures of biscyclometalated iridium complexes.^{37,38} Related to these studies, another recent account shows the influence of acNac ligands on phosphorescent platinum cyclometalates.³⁹ As part of our previous work, we observed impressive phosphorescence quantum yields for the yellow-emitting complex $Ir(bt)_2(acNac)$ (bt = 2-phenylbenzothiazole, $\Phi_{PL} = 0.82$), spurning our efforts to better understand this enhancement and pursue red and near-infrared-emitting compounds using similar design elements.

In the present work, a suite of six new red-emitting complexes featuring two different cyclometalating ligands are described. The quantum yields of two of these complexes are ~80%, significantly higher than those of related fac-Ir(C^N)₃ and $Ir(C^N)_2(acac)$ complexes. The work described here also leads to a mechanistic proposal for the substantial increase in quantum yield in some of these complexes. A thorough investigation of time-resolved emission reveals that the increase in quantum yield correlates with an increase in $k_{..}$ Several pieces of experimental evidence, namely, rigidochromism, solvatochromism, vibronic structure, and electrochemical data, suggest that this augmentation of the radiative rate is brought on by the higher MLCT character and larger spinorbit coupling term in these complexes. This work demonstrates that acNac, NacNac, and other strongly donating, isoelectronic ancillary ligands are attractive targets

for the design of efficient red phosphors that can be incorporated into OLED devices or used in other applications.

RESULTS

Synthesis and Structural Characterization. Six new complexes of the type $Ir(C^N)_2(LX)$ ($C^N = 1$ -phenyl-isoquinoline (piq) and 2-(2-pyridyl)benzothiophene (btp)) were prepared as described in Scheme 1. These cyclo-



metalating ligands were chosen to engender the target complexes with emission in the red region of the spectrum.^{14,15,36} The ancillary ligands (LX) that are paired with these cyclometalating ligands are N,O-chelating β ketoiminate (acNac), the analogous N,N-chelating β -diketiminate (NacNac), and the smaller bite-angle N_iN' -diisopropylbenzamidinate (dipba). This procedure was previously applied to the syntheses of acNac and NacNac complexes with other C^N ligands^{37,38} and has proven to be a general route to access complexes of this type. To prepare the complexes, the chloridebridged dimers $[Ir(C^N)_2(\mu-Cl)]_2$ are treated with the potassium salt of the respective (N)acNac ancillary ligand at room temperature in THF or with the in situ-generated lithium salt of dipba. Following purification, new complexes 1-6 were obtained in moderate to good isolated yields ranging between 58% and 93%. ¹H and ¹³C{¹H} NMR establishes the identity and purity of all complexes. The NMR spectra of the NacNac and dipba complexes all evince C2 symmetry, whereas for acNac complexes the point group is C_1 , and each carbon and proton nucleus gives rise to a distinct NMR resonance. The NMR spectra also show only one species present in each case, with no evidence for the existence of any isomeric products.

Three of the new complexes, 1, 4, and 6, were characterized by single-crystal X-ray diffraction. The structures of these complexes are depicted in Figure 1, and the crystallographic data is summarized in Table S1 in the Supporting Information. In all cases, an approximately octahedral geometry about the iridium(III) center is observed, and a *trans* disposition of the two nitrogen atoms of the cyclometalating ligands is revealed. Another feature of all of the crystal structures is a planar, delocalized core for the acNac (1 and 4) and dipba (6) ancillary ligands. In the structures of 1 and 4, the C–O, C–N, and C–C bond distances of the acNac chelate ring are



Figure 1. X-ray crystal structures of **1**, **4**, and **6**. Thermal ellipsoids are drawn at the 50% probability level with solvent molecules and hydrogen atoms eliminated. Unlabeled atoms are carbon.

independent of the C^N ligand and intermediate between typical single- and double-bond distances, consistent with a π -delocalized core. Similarly, complex **6** resides on a special position in the crystal, such that the C_2 symmetry and equal C–N bond distances in the dipba ligand are enforced by crystallographic symmetry. The disparate bite angles of the acNac and dipba ligands are evident as well. The acNac O–Ir–N angles are 88.53(8)° in 1 and 88.08(16)° in 4, and the N–Ir–N angle of the dipba ligand is much smaller in **6** (60.67(14)°).

Electrochemistry. CVs for the complexes described here are presented in Figure 2. The compounds display both oxidation and reduction features in their cyclic voltammo-



Figure 2. Cyclic voltammograms of complexes 1-6, recorded at 0.1 V/s in acetonitrile with 0.1 M TBAPF₆ supporting electrolyte, a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire pseudoreference. Potentials are referenced to an internal standard of ferrocene, and currents are normalized to bring all of the traces onto the same scale.

grams. The latter occur beyond -2.0 V vs the ferrocenium/ ferrocene (Fc⁺/Fc) couple and involve population of a π^* orbital on the C^N ligand. When C^N = btp, only one reduction wave can be clearly resolved, which is irreversible in 4 and 5 and reversible in complex 6 (E = -2.53 V). For the remaining complexes with C^N = piq, two reversible oneelectron reduction waves are observed, likely resulting from the subsequent reduction of each C^N ligand. These potentials are only slightly dependent on the identity of the ancillary ligand. As shown in Table 1, when the ancillary ligand in the reference

Table 1. Summary of the Reversible Reduction Potentials for Complexes $Ir(piq)_2(LX) (1-3)^a$

$E/V LX = acac^{40}$	E/V LX = acNac (1)	E/V LX = NacNac (2)	E/V LX = dipba (3)
-2.12	-2.20	-2.25	-2.21
-2.36	-2.46	-2.51	-2.49
^a Potentials are	e reported vs. Fc ⁺ /	Fc.	

complex $Ir(piq)_2(acac)$ (acac = acetylacetonate) is replaced with nitrogen-containing ancillary ligands acNac, NacNac, and dipba, the reduction potentials are shifted cathodically to a small extent, the largest perturbation being ~150 mV for LX = NacNac (2). All of this data is consistent with minimal perturbation of the C^N-centered LUMO energies when the ancillary ligand is altered.

All of the complexes here also display a formal Ir^{IV}/Ir^{III} redox couple, which is in contrast highly sensitive to the identity of the ancillary ligand. In most cases, the oxidation wave is not completely reversible with a 0.1 V/s scan rate, the ratio $i_{p,c}/i_{p,a}$ being less than 1 for the acNac and NacNac complexes and indicating "EC" behavior, i.e., an electrochemical oxidation followed by a chemical step. Individual cathodic and anodic sweeps, isolating the reduction and oxidation waves in 4 and 5, confirm that both features are truly irreversible for these complexes. To visualize the effect of the ancillary ligands on the redox couples, Table 2 summarizes the

Table 2. Summary of Ir^{IV}/Ir^{III} Potentials for $Ir(C^N)_2(LX)$ Complexes^{*a*}

	E/V LX = acac	E/V LX = acNac	E/V LX = NacNac	E/V LX = dipba
$C^N = piq$	+0.47 ⁴⁰	+0.27	-0.06	+0.12
C^N = btp	+0.43 ⁴¹	+0.34 ^b	+0.07 ^b	+0.21

 a Potentials are reported in volts (V) vs Fc⁺/Fc. b Irreversible wave. $E_{\rm p,a}$ is reported.

Ir^{IV}/Ir^{III} potentials for complexes **1–6**, as well as the previously reported acac analogues. The reported oxidation potentials for Ir(piq)₂(acac) and Ir(btp)₂(acac) are quite similar, and replacing acac with acNac, i.e., replacing one oxygen with one *N*-phenyl group, results in a cathodic shift of ca. 0.1 to 0.2 V in $E(Ir^{IV}/Ir^{III})$. Substituting acNac for NacNac, i.e., replacing the second oxygen with a second *N*-phenyl, results in a further and slightly larger cathodic shift of ca. 0.3 V. Thus, the oxidation potentials for the NacNac-containing complexes are very near the Fc⁺/Fc potential and shifted by ca. 0.5 V relative to the analogous acac complex. The dipba ancillary ligand results in Ir^{IV}/Ir^{III} potentials that are intermediate between those of the respective acNac and NacNac complexes, and in

the case of $Ir(btp)_2(dipba)$ (6), the redox couple is now reversible, in contrast to the couples in 4 and 5.

DFT Calculations. Orbitals were computed for the reference compound $Ir(piq)_2(acac)$ as well as the new compounds Ir(piq)₂(acNac) (1), Ir(piq)₂(NacNac) (2), and $Ir(piq)_2(dipba)$ (3), to investigate the effects of the ancillary ligand on the frontier orbitals. DFT-optimized atomic coordinates are provided in Tables S2-S5. Figure 3 shows Kohn-Sham frontier orbital depictions for these compounds, with partial orbital energy-level diagrams shown in Figures S1-S4 of the Supporting Information. The DFT calculations reproduce the trends observed electrochemically, with calculated LUMO energies varying minimally across the series. In contrast, the HOMO energies are progressively destabilized as additional nitrogen atoms are incorporated into the ancillary ligand, resulting in a progressive decrease of the HOMO-LUMO gap across the series as observed electrochemically. Even more striking, the orbital parentage of the HOMO changes dramatically as the ancillary ligand is altered. In $Ir(piq)_2(acac)$, the HOMO was determined to involve nearly equal contributions of the Ir center and the C^N ligands, as is typical for cyclometalated iridium complexes.³² However, in $Ir(piq)_2(acNac)$ (1) the HOMO includes nearly equal contributions from Ir, the C^N ligands, and the acNac ancillary ligand, and in $Ir(piq)_2(NacNac)$ (2), the HOMO is almost entirely centered on the NacNac ancillary ligand (80% by electron density), with a small contribution from Ir and minimal involvement of the cyclometalating ligands. The HOMO composition of $Ir(piq)_2(dipba)$ (3) is intermediate between 1 and 2, with 62% contribution from dipba.

Photophysical Properties. UV-vis absorption spectra and steady-state and time-resolved emission spectra were recorded for all complexes described here. UV-vis absorption spectra for the complexes are overlaid in Figures S5 and S6 in the Supporting Information. The absorption spectra are reminiscent of other well-characterized bis-cyclometalated iridium complexes^{6,36} and are dominated by intense ligandcentered $\pi \rightarrow \pi^*$ transitions in the UV region ($\lambda < 350$ nm, $\varepsilon >$ 10⁴ M⁻¹ cm⁻¹) and weaker, overlapping ^{1,3}MLCT transitions that tail into the visible range, tailing out to ca. 550 nm when C^N = btp and extending beyond 600 nm when C^N = piq. In general, the absorption spectra depend little on the ancillary ligand, with acNac, NacNac, and dipba complexes giving similar spectra at parity of C^N ligand. One notable difference is that unlike the acNac complexes the NacNac complexes display an intense absorption shoulder near 400 nm, with ε > 10^4 M⁻¹ cm⁻¹, which is tentatively assigned to a NacNaccentered $\pi \to \pi^*$ transition.³⁸ Complexes with LX = dipba (3 and 6) show additional well-resolved bands near 500 nm, not seen in the other complexes.

All of the complexes described here are luminescent at room temperature when excited within their absorption manifold. Overlaid emission spectra of the complexes, grouped by cyclometalating ligand, are displayed in Figure 4. The steady-state and time-resolved emission data are summarized in Table 3, and as a point of comparison, the data for the corresponding $Ir(C^N)_2(acac)$ reference complexes are included. Excitation spectra were also collected for each of the new complexes and are shown in the Supporting Information, Figures S7–S12. In each case, the excitation spectrum and absorption spectrum are superimposed, indicating that the emission signal arises from the iridium complex and not from an impurity.



Figure 3. DFT-calculated frontier orbitals of $Ir(piq)_2(LX)$ complexes, with orbital plots shown at contour level 0.02 au. Orbital compositions and computed HOMO–LUMO energy gaps are shown, with percentages representing electron density. PBE0 hybrid and exchange functionals, TZVP (nonmetal atoms) and SDD (Ir) basis sets, and IEFPCM solvation (THF) were used in all computations.

As shown in Figure 4, changing the ancillary ligand can have different effects on the observed emission profile. The



Figure 4. Overlaid emission spectra of complexes 1-3 (top) and 4-6 (bottom), recorded in THF at room temperature. Samples were excited at $\lambda_{ex} = 420$ nm.

Table 3. Summary of Emission Data for All Complexes and Their acac Analogues^a

complex	$\lambda_{ m em} \ (m nm)$	$\Phi_{ ext{PL}}$	τ (μs)	$(k_{\rm r} \times 10^{-5} { m s}^{-1})/(k_{\rm nr} \times 10^{-5} { m s}^{-1})$
$Ir(piq)_2(acac)^{14}$	622	0.2	1.7	1.2/4.8
1	637	0.80	1.0	8.0/2.0
2	678	0.17	0.82	2.1/10
3	671	0.34	0.74	4.6/8.9
$Ir(btp)_2(acac)^6$	612	0.51 ^b	5.8	0.88/0.84
4	614	0.33	5.8	0.57/1.2
5	609	0.21	6.3	0.33/1.2
6	622	0.79	5.3	1.5/0.40

^{*a*}Data for **1–6** recorded at room temperature in THF solution. ^{*b*}Value corrected by a factor of 2.4 from the original reference, to account for a correction in the quantum yield of the *fac*-Ir(ppy)₃ standard that these values were referenced to.⁹

reference compound $Ir(piq)_2(acac)$ displays an emission maximum at 622 nm.¹⁴ Substitution of nitrogen-containing ancillary ligands has a pronounced effect on the emission maximum. Replacing one ancillary oxygen donor with *N*-Ph in the complex $Ir(piq)_2(acNac)$ (1) results in a 400 cm⁻¹ bathochromic shift in the emission maximum to 637 nm. The *N*,*N*-chelating NacNac and dipba ancillary ligands have a more profound effect on the observed emission maximum and result in similar emission maxima, 678 nm for NacNac complex 2, and 671 nm for dipba complex 3. These values represent a >1100 cm⁻¹ red shift in the spectral maximum relative to $Ir(piq)_2(acac)$, and a progressive loss of vibronic structure is noted as additional nitrogen donors are incorporated into the ancillary ligand. For btp complexes 4–

6, where the cyclometalating ligand includes a thiophene aryl donor, the behavior stands in contrast to the piq complexes, and there is almost no effect of the ancillary ligand on the emission spectrum. Comparing the spectra of these complexes with their acac analogues reveals a $<300 \text{ cm}^{-1}$ difference between the emission maxima, and in each case, well-resolved vibronic fine structure is evident. The spectrum of dipba complex **6** is significantly broadened when compared to **4** and **5**, with a poorer resolution of the vibronic structure.

Ouantum vields and emission lifetimes were also measured for all of the compounds at room temperature. The ancillary ligands can have a profound impact on the excited-state dynamics, and again the effect is dependent on the identity of the C^N ligand. For the $Ir(piq)_2(LX)$ series, replacing acac with acNac (complex 1) leads to a ca. 7-fold increase in k_r , from 1.2×10^5 s⁻¹ to 8.0×10^5 s⁻¹. This increase in k_r is accompanied by a small decrease in k_{nr} , resulting in a quantum yield (Φ_{PL}) of 0.80 for complex 1. In the NacNac and dipba complexes 2 and 3, the radiative rate constants are larger than the parent acac complex but smaller than acNac. The nonradiative rate constants in 2 and 3 are significantly larger than both the acac and acNac analogues. The resulting quantum yields are 0.17 for complex 2 and 0.34 for complex 3, albeit with a pronounced bathochromic shift as mentioned above. In the btp series (4-6) quite different trends in excitedstate dynamics are observed. Replacing acac with acNac and NacNac has a small but detrimental effect on the radiative and nonradiative rates, such that the quantum yields of 4 (Φ_{PL} = 0.33) and 5 ($\Phi_{PL} = 0.21$) are significantly smaller than that of Ir(btp)₂(acac) ($\Phi_{PL} = 0.51$).⁶ However, the dipba ancillary ligand does have a significant and beneficial effect on the excited-state dynamics of complex 6, and a ca. 2-fold increase in $k_{\rm r}$ and a 2-fold decrease in $k_{\rm nr}$ are both responsible for the much higher quantum yield ($\Phi_{PL} = 0.79$) for this complex relative to the parent acac analogue.

Steady-state spectra were recorded for all complexes at 77 K in toluene glass. One representative example, $Ir(piq)_2(acNac)$ (1), is shown in Figure 5, with the remaining spectra deposited in the Supporting Information (Figures S13–S17). As exemplified by the spectrum of 1 in Figure 5, the vibronic structure becomes sharper and better resolved at 77 K. Even for complexes 2 and 3, where the spectra are broad and featureless at room temperature, their vibronic structure is evident at 77 K, although it is poorly resolved in complex 2.



Figure 5. Overlaid emission spectra of $Ir(piq)_2(acNac)$ (1) recorded in toluene at room temperature (blue, squares), 77 K (red, circles), and PMMA film (black, triangles) with $\lambda_{ex} = 420$ nm. The inset shows a photograph of the PMMA thin-film sample.

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Another consistent feature of the low-temperature spectra is a measurable hypsochromic shift in the emission maximum at the lower temperature. The magnitude of the hypsochromic shift depends somewhat on the ancillary ligand for the piq series (1-3). For the btp complexes, the rigidochromic shifts are modest (\sim 350 cm⁻¹) and independent of the ancillary ligand. In-depth solvatochromic studies were carried out for all complexes, recording room-temperature spectra in THF, toluene, acetonitrile, and butyronitrile (Figures S18-S23, Tables S6–S11). For the btp complexes, emission wavelengths are only mildly sensitive to solvent polarity, spanning small ranges of 609-615 nm (4), 605-609 nm (5), and 620-623 nm (6) in these solvents, a difference of no more than 160 cm^{-1} . The complex $Ir(piq)_2(acNac)$ likewise has weak solvatochromism, spanning a range of 633-642 nm (220 cm⁻¹) and systematically red-shifting as the solvent polarity increases. The remaining two piq complexes exhibit significantly larger solvatochromism. In Ir(piq)₂(NacNac) (2), a shorter wavelength maximum of 666 nm is seen in toluene (ε = 2.38), while in MeCN (ε = 37.5) the maximum shifts to 714 nm, a difference of 1000 cm⁻¹. Complex 3 is intermediate between 1 and 2 with respect to solvent dependence, with maxima falling between 667 nm (toluene) and 685 nm (MeCN), a range of 400 cm⁻¹. Quantum yields and lifetimes were also measured in three of the solvents, and they also depend somewhat on solvent polarity. In most cases, the Φ_{PI} values are very similar in THF and toluene, except complex 2 where the quantum yield increases significantly in toluene (0.42) compared to THF (0.17). One common feature is the quantum yield being significantly smaller in MeCN than in THF, even in the cases where the wavelength red-shifts very little in MeCN.

To study emission properties in media more relevant to OLEDs, the photoluminescence properties of the bestperforming compounds Ir(piq)₂(acNac) (1) and Ir- $(btp)_2(dipba)$ (6) were investigated when doped into PMMA (PMMA = poly(methyl methacrylate) thin films. The sample films were fabricated by drop-coating 2 wt % of the emitter in PMMA in dichloromethane solution inside the glovebox. Overlaid emission spectra in toluene solution and PMMA film are shown in Figure 5 (complex 1) and Figure S17 (complex 6) in the Supporting Information. In PMMA, a small but measurable hypsochromic shift is observed in the emission maximum of $Ir(piq)_2(acNac)$ (150 cm⁻¹) due to rigidochromism. For Ir(btp)₂(dipba), however, the spectral shift is minimal. Compared to the solution, both complexes display a decrease in $k_{\rm r}$ and an increase in $k_{\rm nr'}$ while the lifetimes are similar ($\tau = 1.1 \ \mu s$ for complex 1 and 5.1 μs for complex 6). As a result, the quantum yields for both complexes decrease relative to their solution values, to $\Phi_{PL} = 0.64$ (1) and $\Phi_{PL} =$ 0.47 (6).

Electroluminescence. To test the efficacy of complex 1 in an OLED device, identical OLEDs were fabricated using *fac*- $Ir(piq)_3^{15}$ and complex 1 as the emissive dopants. The inset of Figure 6 shows a schematic of the devices, which include an ITO anode (120 nm thickness) and aluminum cathode (200 nm thickness). The active layers are 4-4'-bis(*N*-1-naphthyl-*N*phenylamino)biphenyl (NPB, 40 nm) as the hole transport layer (HTL), 4,4'-bis(carbazole-9-yl)biphenyl (CBP, 20 nm) as the emissive layer (EML), 4,7-diphenyl-1-10-phenanthroline (BPhen, 50 nm) as the electron transport layer (ETL), and KF (~2 nm) as the electron injection layer (EIL). Devices were fabricated using layer-by-layer thermal evaporation, and the



Figure 6. Electroluminescence spectra for OLED devices fabricated from fac-Ir(piq)₃ and complex **1**. A schematic of the device is shown in the inset. Spectra were collected with an applied bias of 10 V.

emissive iridium complex was doped into the EML at a loading of 9 wt %. *I*–*V* curves for the devices are shown in Figures S24 and S25 of the Supporting Information. Electroluminescence spectra for the two devices are shown in Figure 6. Both were collected with an applied potential of 10 V, and under these conditions, both compounds generate deep red electroluminescence, with CIE chromaticity coordinates⁴² of (0.51, 0.42) for *fac*-Ir(piq)₃ and (0.46, 0.43) for complex 1. This data demonstrates that complex 1 is amenable to thermal deposition and can be incorporated into a functional OLED, although considerable future effort will be required to optimize the performance and color output of devices with 1 as the emissive dopant.

DISCUSSION

In this work, red-emitting cyclometalated iridium complexes with nitrogen-containing, strongly π -donating ancillary ligands were prepared. In doing so we uncovered two complementary designs that give rise to higher photoluminescence quantum yields than the compounds that have been used in some of the best-performing red OLEDs.^{15,23} Two compounds introduced here, $Ir(piq)_2(acNac)$ (1, $\lambda_{em} = 637$ nm) and $Ir(btp)_2(dipba)$ (6, λ_{em} = 622 nm), have photoluminescence quantum yields of ca. 80% in solution. Both of these exceed by a large margin the quantum yields of their respective acac complexes (see Table 3). In addition, Φ_{PL} values for 1 and 6 are also significantly higher than fac-Ir(piq)₃ ($\Phi_{PL} = 0.45$)²² and Ir(tmq)₂(acac) $(tmq = 4-methyl-2-(thiophen-2-yl)quinolone, \Phi_{PL} = 0.55)$ two compounds used in champion red OLEDs and a host of other top-performing red emitters, all of which have solution quantum yields ≤ 0.62 .⁴³⁻⁴⁶ The quantum yields do decrease somewhat when the compounds are immobilized in PMMA film, for reasons that are not entirely clear. Nevertheless, the quantum yields of 1 (Φ_{PL} = 0.64) and 6 (Φ_{PL} = 0.47) in PMMA exceed those of $fac-Ir(piq)_3$ ($\Phi_{PL} = 0.45$)²² and $Ir(tmq)_2(acac)$ ($\Phi_{PL} = 0.189$)⁴⁷ measured under nearly identical conditions.²² While the quantum yields of Ir- $(piq)_2(NacNac)$ (2) and $Ir(piq)_2(dipba)$ (3) are not nearly as high as those of 1 and 6, in these cases the emission maxima occur at >670 nm, and the observed solution quantum yields of 0.17 (2) and 0.34 (3) are still quite high for emission this deep in the red region and tailing into the near-infrared.

The increases in quantum efficiency that we observe are caused in large part by an increase in the radiative rate constant, k_r . The quantum mechanical expression for the triplet state k_r is shown in eq 1.²

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$$k_{\rm r} = {\rm const} \times \Delta E^3 \left[\sum_{S_n} \frac{\langle \phi_{\rm S_n} | \hat{H} | \phi_{\rm T_l} \rangle}{E_{\rm T_l} - E_{\rm S_n}} \times \langle \phi_{\rm S_0} | e \mathbf{r} | \phi_{\rm S_n} \rangle \right]^2$$
(1)

.2

The value of k_r depends on the cube of the energy gap between the excited-state and the ground state (ΔE^3), and a squared term that includes spin-orbit coupling (SOC) and the transition dipole. Substitution of nitrogen-containing ancillary ligands decreases the energy gap between the excited state and the ground state. However, in complexes 1-3 and 6, k_r increases relative to the respective acac complex in spite of this decrease in excited-state energy gap, indicating that one or both of the other two terms in eq 1 is being augmented. The transition dipole term in eq 1 is associated with the transition probability from the singlet ground state to the singlet excited state(s) that mix with the T_1 state through spin-orbit coupling. We have no direct evidence that the transition dipole is being favorably altered; UV-vis absorption spectra for acac^{6,36} complexes and the new compounds described here are markedly similar, with several overlapping singlet absorptions and a much weaker $S_0 \rightarrow T_1$ transition that overlaps the emission band. That said, we cannot rule out a subtle change in the transition dipole term.

Assuming similar transition dipoles, the photophysical data is consistent with a substantial increase in the spin-orbit coupling being an important contributor to the enhanced k_r values. A qualitative excited-state diagram is presented in Figure 7, focusing only on the states that mix into the emissive T_1 state and leaving out higher-lying states (e.g., ¹LC, $T_{n>1}$) ligand-field states). The emissive excited-states (T_1) of biscyclometalated iridium complexes have long been known to include contributions from ligand-centered (³LC, or ${}^{3}\pi\pi^{*}$) states on the C^N ligand and metal-to-ligand charge transfer (³MLCT, or ³d π^*) states, which mix through configuration interaction. This excited-state mixing requires that the interacting states be of the same symmetry, although in lowsymmetry complexes like those presented here (C_1 or C_2 point group) there are many states of the correct symmetry to mix.^{2,3} All of the spin-orbit coupling arises from the MLCT states, and a very simplified picture can be generated by considering only one ^{1,3}MLCT pair and one ³LC state, although in reality many states must be considered in order to quantitatively evaluate emission spectra.^{1,2} Note that even though ¹MLCT state is lower than the ¹LC, the ordering of the triplet states is inverted, on account of the much larger singlet-triplet gap in the LC states, originating from large electron exchange interactions. Also, spin-orbit coupling between ¹LC and ³LC is expected to be very small, both because of the larger singlettriplet energy gap and because the metal-centered orbitals do not participate to an appreciable extent in these states, which greatly diminishes the spin-orbit Hamiltonian. As the top diagram in Figure 7 shows, in $Ir(C^N)_2(acac)$ or fac- $Ir(C^N)_3$ complexes with highly conjugated C^N ligands, where the ³LC states are very low in energy, configuration interaction between the ³LC and ³MLCT states is weak, resulting in less spin-orbit coupling and a smaller k_r value. In contrast, when nitrogencontaining ancillary ligands like acNac, NacNac, or dipba are added, the MLCT states are stabilized, and they contribute more strongly to T1, which results in larger spin-orbit coupling and a larger k_r value, as shown in the bottom panel of Figure 7. For illustrative purposes the ³LC state is shown lower in energy than the ³MLCT state, which is typically the case for



Figure 7. Qualitative diagram showing a proposed mechanism for the increase in k_r caused by incorporating nitrogen-containing ancillary ligands.

cyclometalated iridium,^{2,3} and consistent with this supposition, all of the low-temperature emission spectra of 1-6 include vibronic structure. That said, the available experimental evidence does not rule out the possibility that in some cases the order is reversed.

Regardless of the absolute ordering of the states, several pieces of experimental evidence from our work are consistent with stabilization of the MLCT states and a larger contribution of the MLCT state to T_1 . First, the electrochemistry shows that the oxidation potentials, $E(Ir^{IV}/Ir^{III})$ (Table 2), are strongly perturbed to more negative potentials when nitrogencontaining ancillary ligands are incorporated, indicating a substantial destabilization of the iridium-centered $d\pi$ HOMO. The reduction potentials are minimally altered, consistent with LUMO energies that are nearly constant across the series. The net result of this would be a decrease in the energy of one or more MLCT states since the gap between the $d\pi$ HOMO and the C^N π^* LUMO is now smaller. We do point out that there is not a perfect correlation between electrochemical HOMO-LUMO gap and k_r , and some of the compounds with the most negative oxidation potentials (2 in particular) do not necessarily have the largest k_r values, showing the limited utility of electrochemistry in rationalizing photophysical trends. DFT studies (Figure 3) confirm that the energy and character of the HOMO are dramatically altered when the ancillary ligand is changed, whereas the LUMO is always C^N-centered and always at nearly the same energy. This change in the nature of the HOMO suggests the possibility that the excitedstates in compounds 1-6 also involve considerable ligand-toligand charge transfer (LL'CT) character, but more in-depth computational analysis, beyond the scope of this study, will be needed to determine the nature of the T₁ state, evaluate which frontier orbitals participate in the emissive state, and investigate the degree of spin-orbit coupling. Spin-orbit coupling between ¹MLCT and ³MLCT involves the participation of at least one other $d\pi$ orbital below the HOMO,^{2,3} and the calculations also show that these orbitals are destabilized in 1-3, which can influence the extent to which they mix into the T1 state. While the electrochemical and computational evidence do not directly speak to the ³MLCT energies and the character of the emissive state, they do suggest that in complexes 1-6 the metal-centered orbitals are much closer in energy to the C^N-centered π^* orbital, making it likely that there is greater mixing of the MLCT state into T_1 . Regardless of the finer details, the electrochemical and computational data show that HOMO destabilization is responsible for the bathochromic shifts that are observed in complexes 2 and 3 and that this perturbation of the HOMO most likely influences the character of the T₁ state and contributes to the increase in radiative rate.

Several aspects of the emission properties, particularly for the piq complexes, are also consistent with enhanced MLCT character in the excited state. One piece of supporting evidence comes from the rigidochromic shift in the emission spectra when cooled to 77 K as well as in rigid PMMA film. This shift is substantially larger than that observed for acac complexes, which have very little rigidochromism,³² and such behavior is attributed to the enhancement of charge-transfer character in the emissive excited state.³³ Furthermore, the complex $Ir(piq)_2(dipba)$ (3) exhibits pronounced solvatochromism for its room-temperature emission spectrum, further supporting the notion that charge-transfer character increases in complexes with nitrogen-containing ancillary ligands. One other piece of supporting evidence for the enhanced MLCT character is the vibronic structure, which becomes less pronounced in complexes 2 and 3 with N,N chelating ligands NacNac and dipba.

All of the foregoing evidence is consistent with increased MLCT character, which leads to larger spin-orbit coupling, being responsible for the increase in k_r that is observed for complex 1. For the related complex $Ir(piq)_2(NacNac)$ (2), the $k_{\rm r}$ value is significantly smaller than the acNac complex, even though the experimental evidence suggests that MLCT character increases. The decrease in k_r is partly caused by the decrease in excited-state energy when comparing acNac to NacNac, the latter exhibiting an emission band that is ~ 1000 cm⁻¹ lower in energy. In other words, for NacNac complexes the decrease in the ΔE^3 term of eq 1 counteracts any increase in SOC, although the energy-gap dependence of k_r cannot be the only cause based on the magnitude of the decrease in k_r . Regarding the nonradiative rate, k_{nr} , there is not an obvious trend that presents itself from the six compounds described in this Article. Compounds 2 and 3, which have the deepest red emission ($\lambda > 670$ nm), also have the largest k_{nr} values, which may be at least partially caused by the energy-gap law. We have previously shown that NacNac-centered ${}^{3}(\pi-\pi^{*})$ excited states, which are weakly luminescent, can be observed in some compounds with different C^N ligands and fluorinated NacNac ligands.³⁸ In addition, NacNac complexes 2 and 5 exhibit additional shoulders in their UV-vis absorption bands that we attribute to NacNac-centered states, so it is possible

that the higher $k_{\rm nr}$ in complex 2 is a result of a NacNaccentered "dark" state that deactivates the emissive triplet state. Finally, the disparate behavior between dipba complex 3, which has one of the highest nonradiative rate constants in the series, and its btp analogue 6, which has the smallest $k_{\rm nr}$, also cannot be explained purely by the energy-gap law, indicating there are additional details that must be uncovered to be able to fully understand and optimize nonradiative rates in these compounds.

The behavior of the btp complexes (4-6) run counter to the many of trends discussed above. For these complexes with a thiophene-containing aryl ligand, the excited state is much more ligand-localized, as evidenced by the sharper vibronic structure at room temperature (see Figure 4), the k_r values that are almost one order of magnitude smaller than the piq complexes (Table 3), the small rigidochromic shifts that are independent of ancillary ligand (Figures S21-S23), and the minimal solvatochromism. The effects of the ancillary ligand on redox potential are similar for the piq (1-3) and btp (4-6)series (Figure 2), but for the latter set of compounds, the influence of the ancillary ligand on the excited state is much different. In contrast to the pig series, replacing acac with acNac or NacNac has minimal effect on the emission wavelength, and the radiative rate constants diminish slightly to result in significantly lower quantum yields for these variants. In contrast, the ancillary ligand in $Ir(btp)_2(dipba)$ (6) causes a modest (260 cm⁻¹) red shift in the emission maximum and also results in a ca. 2-fold increase in k_r and a 1.5-fold increase in photoluminescence quantum yield. There is also a significant broadening of the spectrum of 6 when compared to 4 and 5, with less obvious vibronic structure, which supports the notion that the excited state of 6 has more MLCT character. Although the evidence for enhanced MLCT character and spin-orbit coupling is less decisive in this case, the larger k_r and the poorer resolution of the vibronic structure in complex 6 are both consistent with an augmentation of MLCT character. What remains unclear is why acNac and NacNac were ineffective partners for btp, whereas dipba produced such a dramatic effect on emission behavior. Nonetheless, these observations underscore the idea that the design of red and near-infrared emitters requires a judicious choice of both cyclometalating and ancillary ligands and motivates the continued pursuit of other structure types with different ancillary ligands that could result in further optimization of some of these key properties.

Finally, in addition to the electronic contributions of the nitrogen-containing ancillary ligands to the excited state, discussed at length above, replacing acac with one of these nitrogen-containing ligands also introduces a sizable steric perturbation. In acNac and NacNac complexes, the crystal structures show a close approach of the N-phenyl ring with the cyclometalated aryl ring, and NMR spectra indicate a static conformation for the phenyl ring. This rigid conformation of the (N)acNac ancillary ligand may influence k_{nr} , although we do not have any direct evidence that this interaction is an important determinant of the excited-state dynamics. We have previously shown that a variant of $Ir(bt)_2(NacNac)$ with 3,5-(CF₃)₂ substitution on the N-phenyl rings exhibits almost identical emission spectra and lifetimes as the unsubstituted variant,38 but further studies will be needed to establish whether the steric properties of the N-phenyl substituent(s) play a role in any of the observations presented here.

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CONCLUSIONS

In this work, we demonstrate the principle that ancillary ligand modification in bis-cyclometalated iridium complexes can lead to larger radiative rates and higher phosphorescence quantum yields for red-emitting complexes. This strategy has produced some of the most efficient red phosphors known. A mechanism is proposed whereby destabilizing the metal-centered HOMO leads to lower MLCT energies, increasing the MLCT character of the emissive excited state. This larger MLCT contribution enhances spin-orbit coupling and leads to larger observed $k_{\rm r}$ values. In addition, we also present preliminary device data, showing that complex 1 is an effective emitter for OLEDs. Future work will include further optimization of OLED device performance and color using the compounds presented here. Furthermore, the principles outlined here should be applicable to the design of near-infrared emitters with high quantum yields, which will benefit applications beyond OLEDs. The work described here motivates future studies and applications of phosphors with ancillary ligands that are carefully tailored to control and optimize the excited-state dynamics for a particular application.

EXPERIMENTAL SECTION

Physical Methods. ¹H and ¹³C{¹H} NMR spectra (shown in Figures S26-S37) were recorded at room temperature using a JEOL ECA-400, ECA-500, or ECA-600 NMR spectrometer. UV-vis absorption spectra were recorded in THF, toluene, or acetonitrile solutions in screw-capped quartz cuvettes using an Agilent Carey 60 UV-vis spectrophotometer. Luminescence lifetimes were measured with a Horiba DeltaFlex Lifetime System, using 430 nm pulsed diode excitation. Steady-state emission spectra were recorded using a Horiba FluoroMax-4 spectrofluorometer with appropriate long-pass filters to exclude stray excitation light from detection. In order to exclude air, samples for emission spectra were prepared in a nitrogen-filled glovebox using anhydrous solvents. Samples for room-temperature emission were housed in 1 cm quartz cuvettes with septum-sealed screw caps, and samples for low-temperature emission were contained in a custom quartz EPR tube with high-vacuum valve and immersed in liquid nitrogen using a finger dewar. Solution quantum yields were determined relative to a standard of tetraphenylporphyrin in toluene, which has a reported fluorescence quantum yield $(\Phi_{\rm F})$ of 0.11.⁴⁸ Thin films were made by doping complexes into poly(methyl methacrylate) (PMMA), and their quantum yields were recorded using a Spectraloncoated integrating sphere (150 mm diameter, Labsphere). Cyclic voltammetry (CV) measurements were performed with a CH Instruments 602E potentiostat interfaced with a nitrogen glovebox via wire feedthroughs. Samples were dissolved in acetonitrile with 0.1 M TBAPF₆ as a supporting electrolyte. A 3 mm diameter glassycarbon working electrode, a platinum wire counter electrode, and a silver wire pseudoreference electrode were used. Potentials were referenced to an internal standard of ferrocene. OLED devices were fabricated by thermal evaporation; additional details are provided in the Supporting Information. Details of the DFT calculations are also included in the Supporting Information.

Preparation of Compounds. Complete details and characterization data are provided in the Supporting Information. Complexes with acNac and NacNac ancillary ligands were prepared using a method developed by our group to prepare related acNac and NacNac compounds with other cyclometalating ligands.³⁷ In short, the chloride-bridged dimers $[Ir(C^N)_2(\mu-Cl)]_2$ were treated with 2 equiv of the potassium salt of the ancillary ligand, (N)acNacK, in THF. The reaction mixtures were stirred for several hours at room temperature, during which time the starting chloride-bridged dimer was drawn into solution as it reacted. Complexes with dipba ancillary ligands were prepared by treating the chloro-bridged dimers with the in situ-generated lithium salt of dipba, in THF. After removing solvent *in vacuo*, the crude products were extracted into toluene and filtered to remove the alkali metal chloride byproduct. From there, the complexes were purified by silica gel column chromatography or by washing with Et_2O and/or pentane. ¹H and ¹³C{¹H} NMR spectra, shown in the Supporting Information (Figures S26–S37), confirm identity and purity for all new complexes.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b04841.

Experimental details, X-ray crystallographic data summary, partial Kohn–Sham orbital energy-level diagrams, tables of DFT-optimized atomic coordinates, UV–vis absorption spectra, excitation spectra, 77-K emission spectra, solvatochromism studies, I–V curves for OLEDs, NMR spectra of new compounds(PDF) Crystallographic data (CIF) DFT atomic coordinates of acac (XYZ), acNac (XYZ), and NacNac (XYZ)

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Notes

The authors declare no competing financial interest.

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